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# Gyroscope-Like Platinum and Palladium Complexes with Trans-Spanning Bis(pyridine) Ligands

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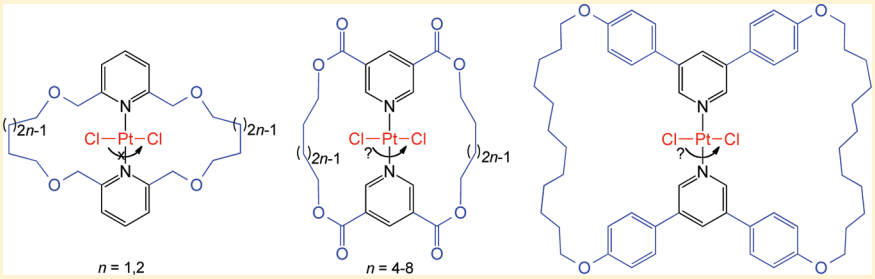
Supporting Information




**ABSTRACT:** Pyridines with one or two substituents terminating in vinyl groups are prepared. Intramolecular ring-closing metatheses of *trans*-$MCl_2$ adducts and hydrogenations supply the title compounds. Williamson ether syntheses using the alcohols $HO(CH_2)_nCH{=}CH_2$ ($n$ = 1 (**a**), 2 (**b**), 3 (**c**), 4 (**d**), 5 (**e**), 6 (**f**), 8 (**h**), 9 (**i**)) and appropriate halides give the pyridines 2-$NC_5H_4(CH_2O(CH_2)_nCH{=}CH_2)$ (**1a,b**), 3-$NC_5H_4(CH_2O(CH_2)_nCH{=}CH_2)$ (**2a−e,h,i**), and 2,6-$NC_5H_3(CH_2O(CH_2)_nCH{=}CH_2)_2$ (**4a−d**) in 92−45% yields. Reactions of 3,5-$NC_5H_3(COCl)_2$ and $HO(CH_2)_nCH{=}CH_2$ afford the diesters 3,5-$NC_5H_3(COO(CH_2)_nCH{=}CH_2)_2$ (**5a−f,h**, 90−41%). The reaction of 3,5-$NC_5H_3(4\text{-}C_6H_4OH)_2$, $Br(CH_2)_5CH{=}CH_2$, and $Cs_2CO_3$ yields 3,5-$NC_5H_3(4\text{-}C_6H_4O(CH_2)_5CH{=}CH_2)_2$ (**8**; 32%). Reactions of $PtCl_2$ with **1a,b**, **2a−e,h,i**, **4a,b** (but not **4c,d**), **5a,c−f,h**, and **8** afford the corresponding bis(pyridine) complexes *trans*-**10a,b** (40−12%), *trans*-**12a−e,h,i** (84−46%), *trans*-**17a,b** (88−22%), *trans*-**19a,c−f,h** (94−63%), and *trans*-**22** (96%). Selected adducts are treated with Grubbs' catalyst and then $H_2$ (Pd/C) to give *trans*-$PtCl_2[2,2'\text{-}(NC_5H_4(CH_2O(CH_2)_{2n+2}OCH_2)H_4C_5N)]$ (*trans*-**11a,b**; 79−63%), *trans*-$PtCl_2[3,3'\text{-}(NC_5H_4(CH_2O(CH_2)_{2n+2}OCH_2)H_4C_5N)]$ (*trans*-**13,d,h,i**; 93−80%), *trans*-$PtCl_2[2,6,2',6'\text{-}(NC_5H_3(CH_2O(CH_2)_{2n+2}OCH_2)_2H_3C_5N)]$ (*trans*-**18a,b**; 22−10%), *trans*-$PtCl_2[3,5,3',5'\text{-}(NC_5H_3(COO(CH_2)_{2n+2}OCO)_2H_3C_5N)]$ (*trans*-**20d−f,h**; 45−14%), and *trans*-$PtCl_2[3,5,3',5'\text{-}(NC_5H_3(4\text{-}C_6H_4O(CH_2)_{12}O\text{-}4\text{-}C_6H_4)_2H_3C_5N)]$ (40%). A previously reported ring-closing metathesis of *trans*-$PdCl_2[2,6\text{-}NC_5H_3(CH_2CH_2CH{=}CH_2)_2]_2$ is confirmed, and the new hydrogenation product *trans*-$PdCl_2[2,6,2',6'\text{-}(NC_5H_3((CH_2)_6)_2H_3C_5N)]$ (*trans*-**16**; 62%) is isolated. Additions of $CH_3MgBr$ to **12b,h** and **13d,h** afford the corresponding $PtClCH_3$ species (94−41%), but analogous reactions fail with 2-substituted pyridine adducts. The reaction of *trans*-**19c** with PhC≡CH and CuI/*i*-$Pr_2NH$ gives the corresponding PtCl(C≡CPh) adduct (18%). The crystal structures of *trans*-**17a**, *trans*-**11b**, *trans*-**13d**, *trans*-**13h**·$CH_2Cl_2$, *trans*-**16**, *trans*-**18a,b**, and *trans*-**20e**·$2CHCl_3$ are determined. Steric effects in the preceding data, especially involving 2-substituents and the $MCl_2$ or MCl(X) rotators, are analyzed in detail.

## INTRODUCTION

As summarized in a review, the term "gyroscope" has been applied to a variety of molecules.[1] The most intensive efforts to craft functional molecular analogues of macroscopic gyroscopes have been described by Garcia-Garibay.[2,3] In our research group, we have sought to develop transition-metal-based gyroscopes in which trans phosphorus donor atoms are bridged by three methylene chains or related linkers.[4−10] All of these have been prepared via 3-fold intramolecular ring-closing metatheses, as sketched in Scheme 1 (**I** → **II**). A variety of coordination geometries have proved accessible, as illustrated by **III**−**V**.

We have also sought systems based upon other types of trans donor atoms. Arsenic analogues of some of the species in Scheme 1 have been realized.[11] However, we were particularly interested in establishing new donor atom coordination

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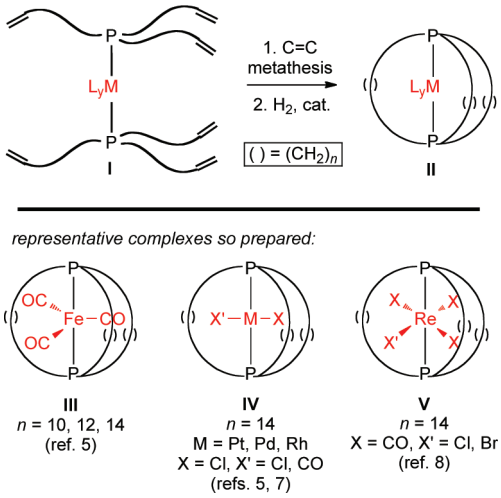
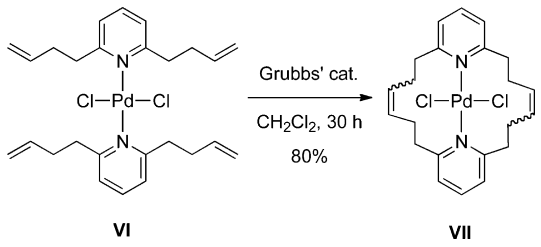
**Scheme 1. Syntheses of Gyroscope-Like Complexes with Trans Phosphorus Donor Atoms and $(CH_2)_n$ Linkers**




numbers. Toward this end, our attention was drawn to pyridine ligands. An additional motivation was the possibility of introducing functionality in the para or 4-position, which could allow for surface mounting, a subject of much interest within the broad field of molecular rotors.[12]

Further impetus derived from an intriguing preliminary communication by Lambert and Ng.[13] They reported the synthesis of the palladium bis(2,6-dihomoallylpyridine) complex, **VI** shown in Scheme 2, and its 2-fold intramolecular

**Scheme 2. Lambert's Initial Synthesis of a Complex with a Doubly Trans-Spanning Bis(pyridine) Ligand**



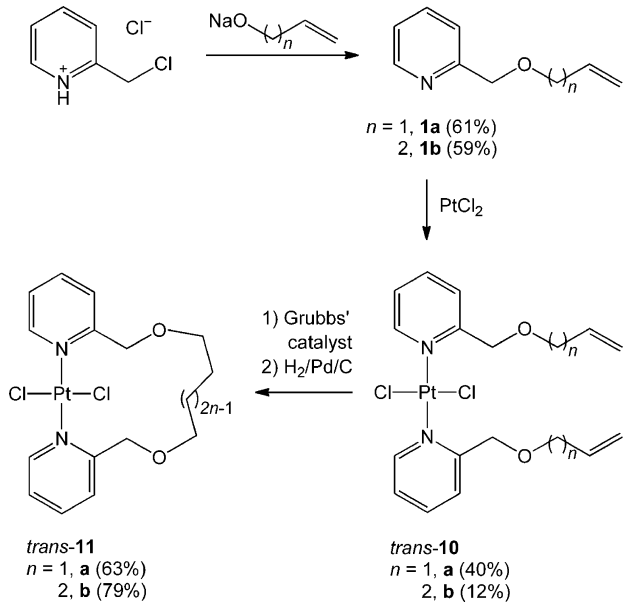

ring-closing metathesis with Grubbs' catalyst to give the doubly bridged trans-spanning bis(pyridine) complex **VII**. The crystal structure of **VII**, which can be viewed as an adduct of a diaza-*m*-cyclophane, was mentioned, but the data were not deposited with the Cambridge Crystallographic Data Centre. We sought to explore the generality of this type of process, including extensions to pyridines with other substitution patterns.

In this paper, we report (1) syntheses of a variety of 2-, 3-, 2,6-, and 3,5- mono- and disubstituted pyridine ligands in which the substituents terminate with vinyl groups, (2) the preparation of the corresponding *trans*-dichloroplatinum or *trans*-dichloropalladium bis(pyridine) complexes, (3) intramolecular ring-closing metatheses that lead to a variety of singly and doubly trans-spanning systems, (4) chloride ligand substitutions that lead to dipolar rotors, (5) crystal structures of representative species, and (6) analyses of numerous steric effects manifested in these data. Additional details can be found elsewhere.[14]

## RESULTS

**1. Syntheses of Alkene-Containing Pyridines.** For initial studies, monosubstituted pyridines were sought. Thus, commercial 2-(chloromethyl)pyridine hydrochloride was combined with excesses of the alcohols $HO(CH_2)_nCH{=}CH_2$ ($n$ = 1 (**a**), 2 (**b**)) and 3.0−2.3 equiv of sodium to generate the corresponding alkoxide bases. As shown in Scheme 3, workups

**Scheme 3. Syntheses of Complexes with 2-Substituted Trans-Spanning Bis(pyridine) Ligands**




gave the alkene-containing monoethers 2-$NC_5H_4(CH_2O(CH_2)_nCH{=}CH_2)$ (**1a,b**) as yellow or brown oils in 61−59% yields. Compounds **1a,b** have previously been prepared from 2-pyridinemethanol and the corresponding chlorides $Cl(CH_2)_nCH{=}CH_2$.[15,16] However, these building blocks are more costly.

Given the course of results below, 3-substituted pyridines were also desired. As shown in Scheme 4, analogous reactions of commercial 3-(chloromethyl)pyridine hydrochloride, alcohols $HO(CH_2)_nCH{=}CH_2$ ($n$ = 1 (**a**), 2 (**b**), 3 (**c**), 4 (**d**), 5 (**e**), 8 (**h**), 9 (**i**)), and sodium were conducted. Workups gave the new monoethers 3-$NC_5H_4(CH_2O(CH_2)_nCH{=}CH_2)$ (**2a−e,h,i**) as yellow-brown oils in 98−42% yields.

Disubstituted pyridines were sought next. As shown in Scheme 5, commercial 2,6-bis(bromomethyl)pyridine, 2,6-$NC_5H_3(CH_2Br)_2$, was combined with 2.5 equiv of the Grignard reagent $H_2C{=}CHCH_2MgBr$ in THF. A chromatographic workup gave the doubly butenylated pyridine 2,6-$NC_5H_3(CH_2CH_2CH{=}CH_2)_2$ (**3**) as a yellow oil in 60% yield. This compound was previously prepared by a similar route by Lambert, but no synthetic details or characterization were given.[13]

Ether-containing analogues were desired. Accordingly, 2,6-$NC_5H_3(CH_2Br)_2$ and the alcohols $HO(CH_2)_nCH{=}CH_2$ (**a−d**) were refluxed in the presence of the quaternary ammonium salt $C_6H_5CH_2N(CH_3)_3^+Cl^-$ (20 mol %), as shown in Scheme 6. A related procedure has been previously applied to benzyl halides.[17] Workups gave the dialkenylated diethers 2,6-$NC_5H_3(CH_2O(CH_2)_nCH{=}CH_2)_2$ (**4a−d**) as light yellow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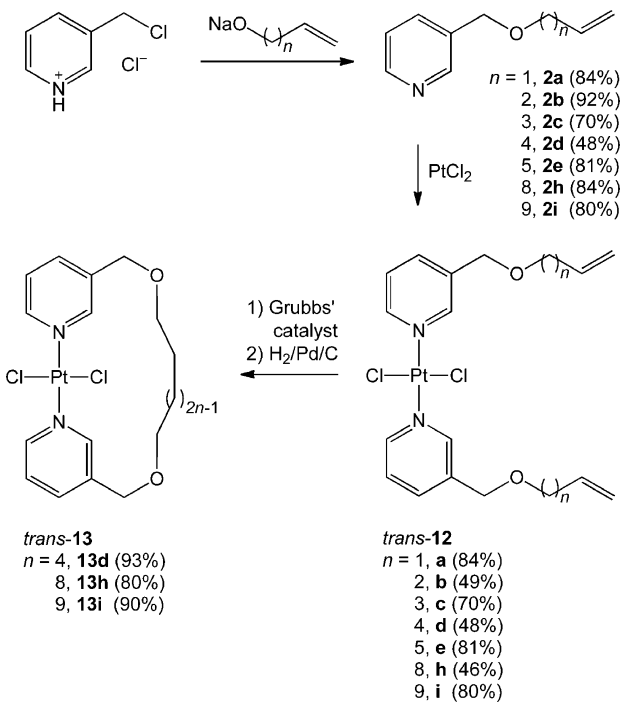
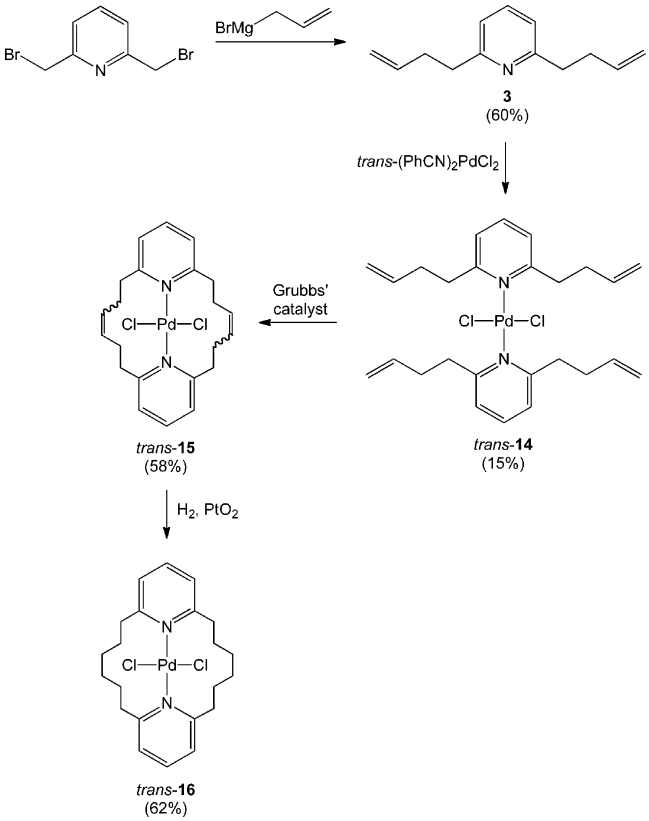
**Scheme 4. Syntheses of Complexes with 3-Substituted Trans-Spanning Bis(pyridine) Ligands**




**Scheme 5. Additional Chemistry Relating to Scheme 2**




oils in 55−45% yields. Compounds **4a,d** had been previously prepared by other Williamson ether syntheses.[18,19]

Next, 3,5-disubstituted systems were sought. Pyridine-3,5-dicarboxylic acid, 3,5-$NC_5H_3(COOH)_2$, was seen as an inexpensive building block, and the bis(acid chloride) 3,5-$NC_5H_3(COCl)_2$ was prepared in quantitative yield as previously described.[20] As shown in Scheme 7, this material was combined with a slight excess of $HO(CH_2)_nCH{=}CH_2$ (**a**−**f**,**h**) in dry $CH_2Cl_2$. After basic workups, the dialkenylated diesters 3,5-$NC_5H_3(COO(CH_2)_nCH{=}CH_2)_2$ (**5a**−**f**,**h**) were isolated as viscous yellow oils in 90−41% yields. Compounds **5d**,**h** have been previously synthesized by similar routes.[19,21]

Given certain results below, expanded 3,5-disubstituted pyridine frameworks were also desired. Two known reactions were conducted first. As shown in Scheme 8, the cross coupling of 3,5-dichloropyridine and (4-methoxyphenyl)magnesium bromide, 4-$CH_3OC_6H_4MgBr$, using the nickel catalyst (dppp)-$NiCl_2$ (dppp = $Ph_2P(CH_2)_3PPh_2$), afforded 3,5-bis(4-methoxyphenyl)pyridine (**6**) or 3,5-$NC_5H_3(4\text{-}C_6H_4OCH_3)_2$ in 73% yield.[22] Subsequent reaction with $BBr_3$ gave the bis(phenol) 3,5-$NC_5H_3(4\text{-}C_6H_4OH)_2$ (**7**)[23] in 66% yield. Treatment with $Br(CH_2)_5CH{=}CH_2$ and $Cs_2CO_3$ base (DMF, 100 °C) afforded the new dialkenylated diether 3,5-$NC_5H_3(4\text{-}C_6H_4O(CH_2)_5CH{=}CH_2)_2$ (**8**) as a white powder in 32% yield.

**2. Syntheses of *trans*-Bis(pyridine) Complexes.** *2.1. Singly Bridged Complexes.* As shown in Scheme 3, reactions of **1a**,**b** with $PtCl_2$ in refluxing benzene afforded the corresponding *trans*-dichloroplatinum bis(pyridine) complexes *trans*-**10a**,**b** as light yellow solids in 40−12% yields after workup. These and all other new complexes below were characterized by NMR and IR and (in most cases) microanalyses, as summarized in the Experimental Section. In particular, the $sp^2$ $^1H$ and $^{13}C$ NMR signals of the free and coordinated pyridines could be assigned on the basis of well-established chemical shift trends.[24,25] Coordination shifts have been tabulated elsewhere.[14a] Some DSC/TGA and mass spectral data are also reported.

Interestingly, $CDCl_3$ solutions of *trans*-**10a** exhibited two $NCCH_2O$ $^1H$ NMR signals (singlets, 1:1 ratio) at room temperature. These were presumed to arise from atropisomers (rotamers) with syn/anti dispositions of the two 2-pyridyl substituents, as shown in Scheme 9 (**VIII**, **VIII'**). The 2-methylpyridine analogue of *trans*-**10a** gives a 65:35 mixture of atropisomers, and similar phenomena have been found for closely related complexes.[24] The two signals coalesced between 35 and 40 °C. The coalescence temperature ($T_c$) was extrapolated as 311 K, giving a $\Delta G^{\ddagger}(T_c)$ value of 16.6 kcal/mol.

Next, $CH_2Cl_2$ solutions of *trans*-**10a**,**b** (0.0019−0.0021 M) and Grubbs' catalyst (4 and 8 mol %) were refluxed for 18−42 h as described in the Experimental Section. The crude metathesis products were treated with $H_2$ (balloon pressure) in the presence of Pd/C (5 mol %). Chromatography gave *trans*-**11a**,**b** as light yellow and off-white solids in 79−63% overall yields. These feature 8- and 10-atom linkers connecting the pyridine ligands, or 13- and 15-membered macrocycles. Single crystals of *trans*-**11b** were obtained as described in the Experimental Section. A crystal structure, described in the following section, confirmed the formulation.

Attention was turned to the analogous 3-substituted pyridines in Scheme 4. Under conditions comparable to those in Scheme 3, the corresponding platinum complexes *trans*-**12a**−**e**,**h**,**i** were obtained in higher yields (80−46%) as yellow solids. On the basis of additional data below, this was attributed to the absence of a 2-substituent, diminishing steric hindrance. In two cases (**12b**,**h**), comparable amounts of cis isomers formed, but these more polar adducts were readily separated by silica gel chromatography.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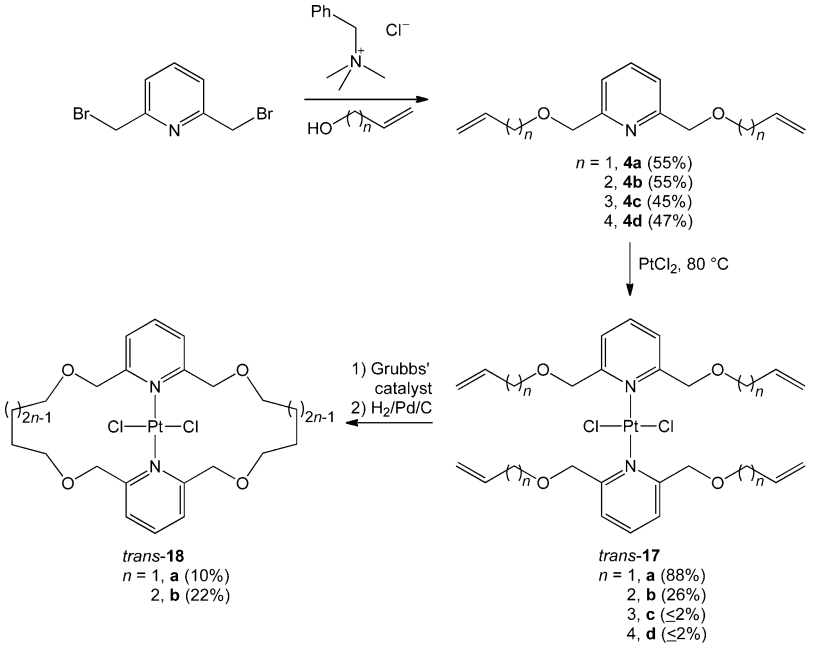
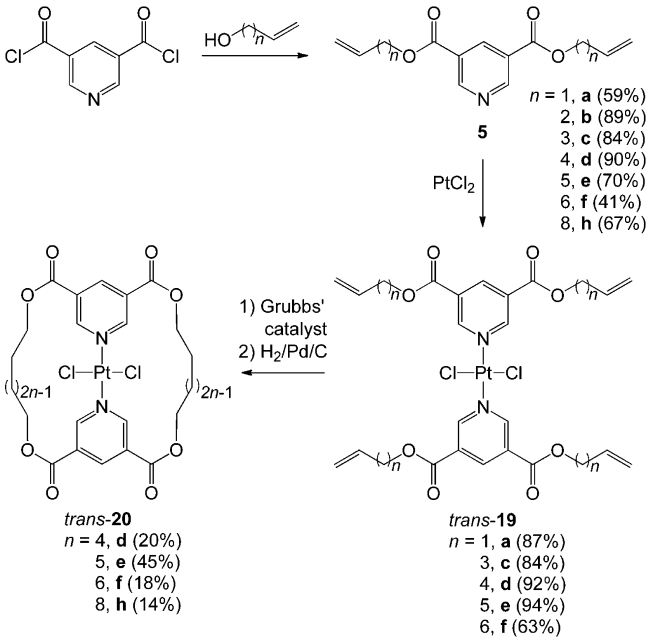
**Scheme 6. Syntheses of Complexes with 2,6-Disubstituted Doubly Trans-Spanning Bis(pyridine) Ligands**




**Scheme 7. Syntheses of Complexes with 3,5-Disubstituted Doubly Trans-Spanning Bis(pyridine) Ligands**




Similar reactions of Grubbs' catalyst with *trans*-**12d,h,i** and subsequent hydrogenations gave the ring-closing metathesis products *trans*-**13d,h,i** as light yellow to off-white solids in 93–80% overall yields. These feature 14-, 22-, and 24-atom linkers connecting the pyridine ligands, or 21-, 29-, and 31-membered macrocycles. The attempted metathesis of *trans*-**12c**, which would have given a 19-membered macrocycle, did not give any products that could be chromatographed, implicating polymer formation. Single crystals of *trans*-**13d** and the solvate *trans*-**13h**·$CH_2Cl_2$ were obtained as described in the Experimental Section. The crystal structures, described in the following section, confirmed the formulations.

*2.2. Doubly Bridged Complexes.* An initial objective was to round out and extend the fragmentary data of Lambert (Scheme 2). As shown in Scheme 5, the reaction of *trans*-$(PhCN)_2PdCl_2$ and **3** (2.3 equiv) afforded the dichloropalladium bis(pyridine) complex *trans*-**14** (**VI**) in 15% yield following chromatography. A $CH_2Cl_2$ solution of *trans*-**14** (0.0301 M) was treated with Grubbs' catalyst (15 mol % added in three equal charges over 24 h). Chromatography gave the metathesis product *trans*-**15** (**VII**) in 58% yield. Lambert obtained an 80% yield and assigned a *Z* C=C stereochemistry on the basis of the incompletely reported crystal structure mentioned above.[13]

In a new reaction, this material was hydrogenated (balloon pressure, $PtO_2$ catalyst). Chromatography afforded the saturated analogue *trans*-**16** as a light yellow solid in 62% yield. Single crystals were obtained as described in the Experimental Section, and the crystal structure is detailed below. Complex *trans*-**16** features 6-atom linkers connecting the pyridine ligands, making for an 11-membered cycle—the smallest ring system in this study.

Analogous sequences were attempted with the 2,6-disubstituted ether containing pyridines, as summarized in Scheme 6. Reactions with $PtCl_2$ with **4a,b** gave the dichloroplatinum bis(pyridine) complexes *trans*-**17a,b** as yellow solids in 88–26% yields after chromatography. The lower yield with **4b** appeared to relate to the size of the 2,6-substituents; the ligands **4c,d** did not give detectable amounts of complexes under comparable conditions, and the yield of *trans*-**14** was also modest. The crystal structure of *trans*-**17a**, which is detailed in the following section, shows that both pyridine ligands are roughly coplanar and orthogonal to the Cl–Pt–Cl vector.

Ring-closing metatheses of *trans*-**17a,b** were carried out under more dilute conditions (0.001 99–0.002 01 M) with 10 mol % of Grubbs' catalyst. Reactions were monitored by $^1H$ NMR to ensure that all of the vinyl groups were consumed. However, following hydrogenations and chromatography, the cyclized products *trans*-**18a,b** were obtained as white or off-white solids in only 22–10% yields. When the synthesis of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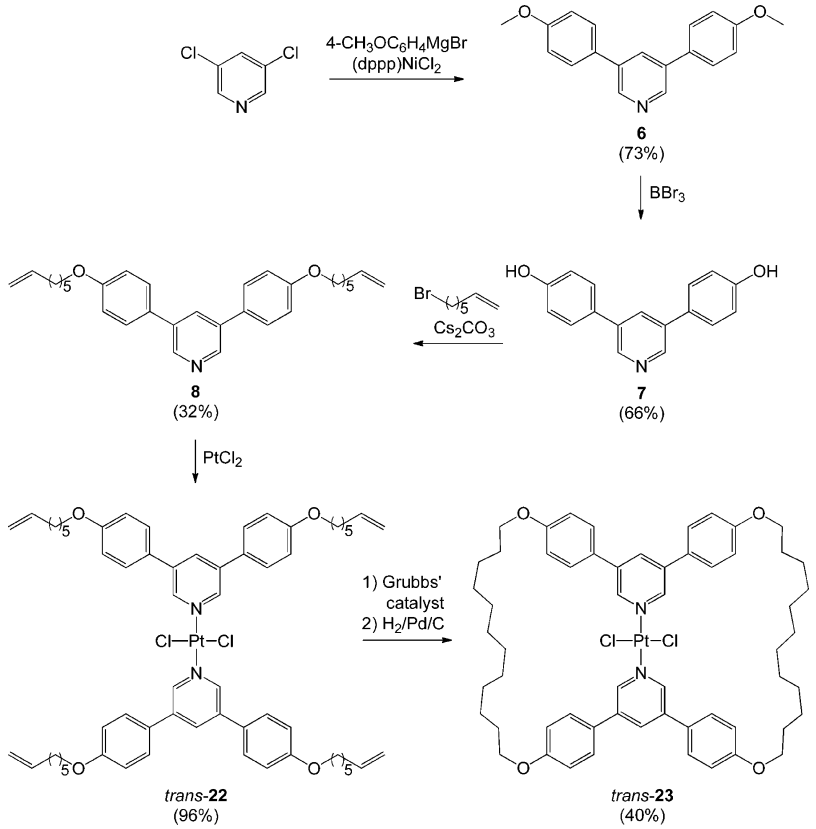
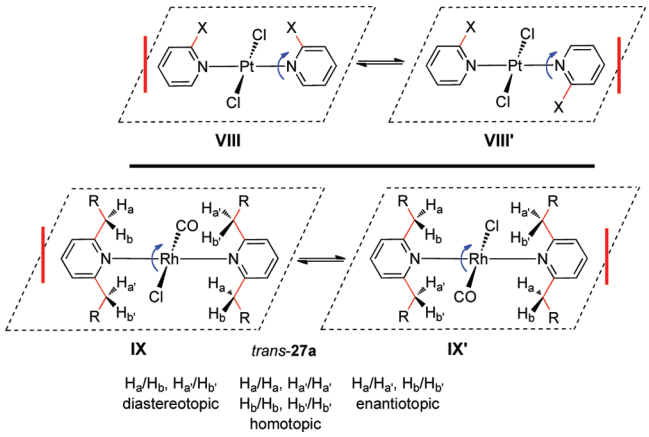
**Scheme 8. Synthesis of a Complex with an Expanded 3,5-Disubstituted Doubly Trans Spanning Bis(pyridine) Ligand**




**Scheme 9. Atropisomeric Equilibrium (Top) and Exchange of Diastereotopic Groups via MLL′ Rotation (Bottom)**




*trans*-**18a** was repeated with Grubbs' second-generation catalyst, an 8% yield was obtained. Complexes *trans*-**18a,b** feature 8- and 10-atom linkers connecting the pyridine ligands, or 13- and 15-membered macrocycles. The crystal structures of both adducts could be determined, as described below.

As shown in Scheme 7, reactions of $PtCl_2$ with the 3,5-disubstituted ester containing pyridines **5a,c–f,h** gave dichloroplatinum bis(pyridine) complexes *trans*-**19a,c–f,h** as yellow solids in 94–63% yields after chromatography. These yields are much higher than those for most of the 2,6-disubstituted adducts in the preceding section.

Ring-closing metatheses of *trans*-**19d–f,h** were carried out under dilute conditions (0.002 00–0.002 02 M) comparable to those used for *trans*-**17a,b**. Hydrogenations afforded the target molecules *trans*-**20d–f,h** as light yellow solids in 45–14% overall yields following chromatography. When the synthesis of *trans*-**20d** was repeated with Grubbs' second-generation catalyst, a 12% yield was obtained. This series of complexes features 14-, 16-, 18-, and 22-atom tethers connecting the two pyridine rings. This corresponds to 21-, 23-, 25-, and 29-membered macrocycles. Single crystals of a solvate of the 23-membered macrocycle *trans*-**20e** were obtained, and the crystal structure is described in the following section.

Finally, $PtCl_2$ and the expanded 3,5-disubstituted pyridine framework **8** were similarly reacted as shown in Scheme 8. Workup gave the dichloroplatinum bis(pyridine) complex **22** as a light yellow solid in 96% yield. Ring-closing metathesis and hydrogenation as above gave **23** as a yellow solid in 40% yield after chromatography. This complex features a 14-atom tether connecting the 3,5-diarylpyridine moieties, making for two 29-membered macrocycles.

**3. Crystal Structures.** Bond lengths and angles around platinum or palladium for the seven crystal structures mentioned above are summarized in Table 1. Additional tables of crystallographic data are presented in the Supporting Information. All bond angles are quite similar, and indicate nearly idealized square-planar coordination geometries. The bond lengths are very close to those found earlier for *trans*-$PtCl_2$ adducts of pyridine, 3-methylpyridine, 4-methylpyridine, and 2,6-bis(hydroxymethyl)pyridine[24a,26] and are not analyzed further.

Figure 1 illustrates two views of the molecular structure of the unbridged complex *trans*-**17a**. There is a 2-fold symmetry axis that contains the N–Pt–N vector and an orthogonal mirror plane containing the Cl–Pt–Cl vector. One methylene carbon atom (C3) was disordered, but this could not be resolved.


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**Table 1. Key Bond Lengths (Å) and Angles (deg) in Crystallographically Characterized Complexes[a]**

| | *trans*-**17a** | *trans*-**11b** | *trans*-**13d**[b] | *trans*-**13h**·$CH_2Cl_2$ | *trans*-**16** | *trans*-**18a** | *trans*-**18b** | *trans*-**20e**·$2CHCl_3$ |
|---|---|---|---|---|---|---|---|---|
| | | | Bond Lengths | | | | | |
| M−Cl1 | 2.2926(14) | 2.3204(9) | 2.299(2)<br>2.3082(19) | 2.2968(16) | 2.3126(4) | 2.3048(8) | 2.3060(7) | 2.2824(17) |
| M−Cl2 | 2.2926(14) | 2.3091(9) | 2.293(2)<br>2.288(2) | 2.2985(16) | 2.3126(4) | 2.3048(8) | 2.3060(7) | 2.2919(16) |
| M−N1 | 2.033(5) | 2.028(2) | 2.026(5)<br>2.027(6) | 1.998(5) | 2.0637(12) | 2.050(3) | 2.048(2) | 2.004(4) |
| M−N2 | 2.033(5) | 2.021(2) | 2.018(5)<br>2.019(6) | 2.002(5) | 2.0637(12) | 2.050(3) | 2.048(2) | 2.011(4) |
| | | | Bond and Other Angles | | | | | |
| N1−M−N2 | 180.0 | 178.4(8) | 177.9(2)<br>178.4(2) | 178.22(18) | 180.0 | 180.0 | 180.000(1) | 179.20(16) |
| Cl1−M−Cl2 | 180.0 | 179.17(2) | 177.77(7)<br>177.80(9) | 178.73(6) | 180.000(3) | 180.00(3) | 180.00(2) | 178.71(6) |
| Cl1−M−N1 | 90.0 | 90.49(7) | 89.54(18)<br>89.38(19) | 90.25(14) | 90.84(3) | 90.66(8) | 90.64(7) | 90.00(3) |
| Cl2−M−N2 | 90.0 | 89.81(7) | 90.64(18)<br>90.65(19) | 89.76(14) | 90.84(3)) | 90.66(8) | 90.64(7) | 90.78(12) |
| Cl1−M−N2 | 90.000(1) | 90.15(7) | 89.43(18)<br>89.50(19) | 89.44(14) | 89.16(3) | 89.34(8) | 89.36(7) | 89.35(13) |
| Cl2−M−N1 | 90.000(1) | 90.4(2) | 90.47(18)<br>90.50(19) | 90.59(14) | 89.16(3) | 89.34(8) | 89.36(7) | 89.85(13) |
| pyridine/pyridine[c] | 0.0 | 27.9 | 1.7<br>6.1 | 12.4 | 0.0 | 0.0 | 0.0 | 0.1 |
| Cl−M−Cl/pyridine[d] | 89.2 | 86.7 | 52.8<br>50.3 | 54.9 | 76.4 | 79.1 | 79.2 | 63.3 |

[a]M = Pt except for *trans*-**16** (Pd). [b]The doubled values are for two independent molecules in the unit cell. [c]The angle defined by the planes of the two pyridine ligands. [d]Angle defined by the Cl−M−Cl vector and the plane or average plane of the two pyridine ligands.

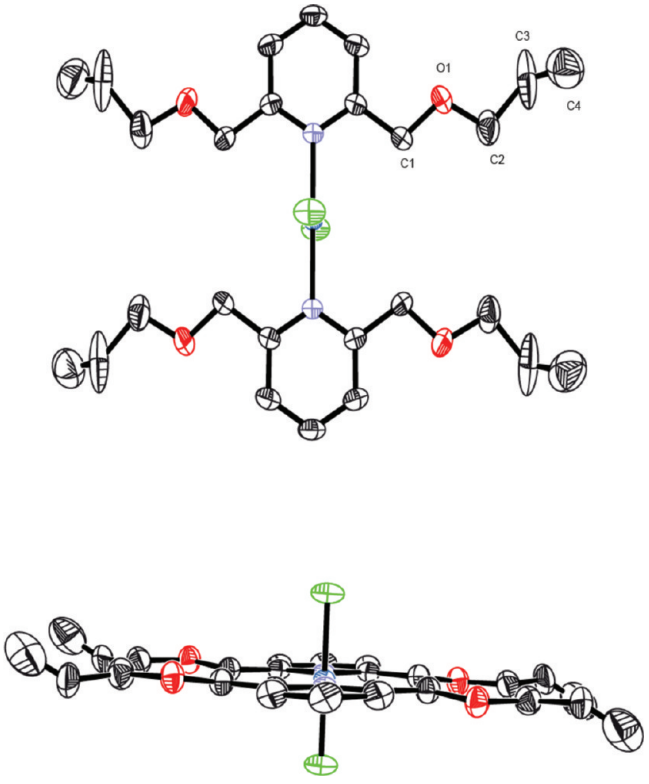


**Figure 1.** Thermal ellipsoid plots (50% probability level) of *trans*-**17a**: (top) view along the Cl−Pt−Cl axis; (bottom) view along the N−Pt−N axis.

Importantly, the pyridine rings are coplanar and essentially orthogonal to the Cl−Pt−Cl vector (89.2°; see Table 1), as proposed for the atropisomers in Scheme 9 (top). This minimizes steric interactions between the chloride ligands and the 2,6-substituents and in turn "preorganizes" the CH═$CH_2$ moieties with respect to intramolecular metathesis.

The crystal structure of the 13-membered macrocycle *trans*-**11b** is depicted in Figure 2. The pyridine rings are no longer coplanar and define an angle of 27.9°. However, the Cl−Pt−Cl vectors remain approximately orthogonal (86.6−86.7°) to the "average" of the two planes (Figure 2, bottom).

The crystal structure of the 21-membered macrocycle *trans*-**13d** revealed two independent molecules in the unit cell. In one, two of the methylene groups in the $O(CH_2)_{10}O$ segment were disordered (80:20 occupancies), and in the other, six ((70−50):(30−50) occupancies). In the former, which is depicted in Figure 3, the ═C−$CH_2$−*O*−$CH_2$ bonds are nearly perpendicular to the planes of the pyridine rings, as reflected by torsion angles of 84.0−89.2°. In the latter, the same bonds are nearly coplanar with the pyridine rings, with torsion angles of 4.8−6.6°. The pyridine rings in both molecules are nearly coplanar (6.1−1.7° angles). However, the Cl−Pt−Cl vectors show the greatest deviations from orthogonality in this series of complexes (52.8−50.3°), as readily seen in Figure 3 (bottom).

The crystal structure of the 29-membered macrocycle *trans*-**13h**·$CH_2Cl_2$ is depicted in Figure 4. The pyridine rings are approximately coplanar (middle view), defining a quite small angle (12.4°). However, the Cl−Pt−Cl vector again shows a large deviation from orthogonality (54.9°). Interestingly, the solvate molecule lies within the macrocycle and, as shown in the bottom view, fills a substantial portion of the enclosed space.


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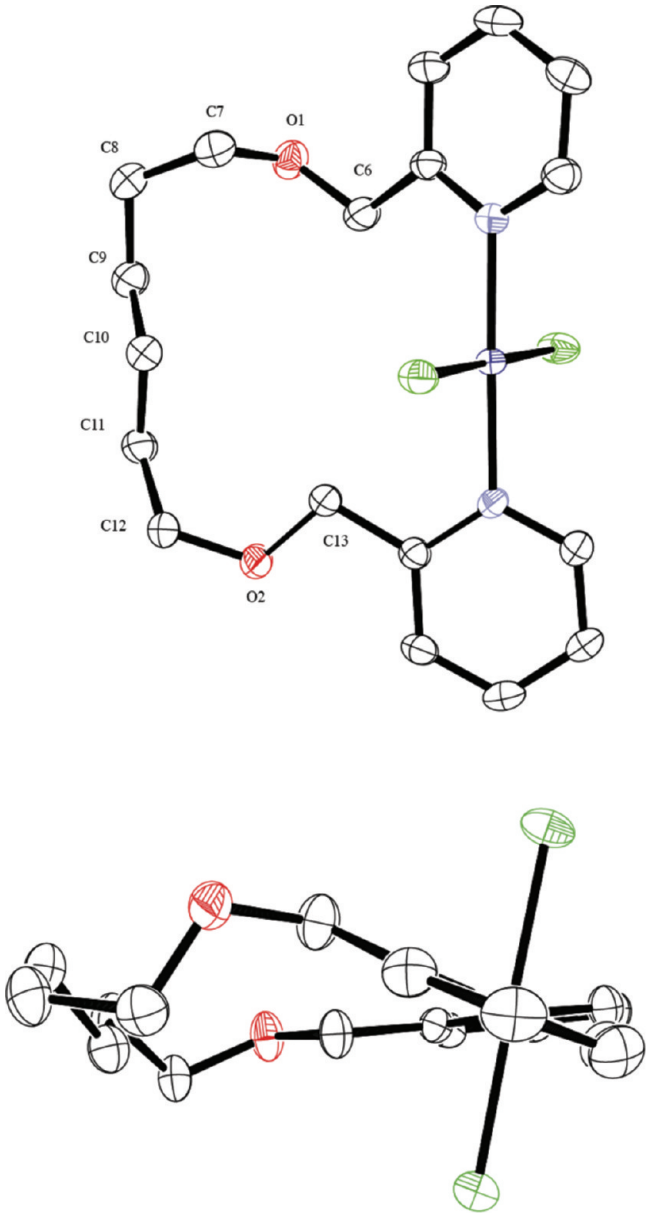


**Figure 2.** Thermal ellipsoid plots (50% probability level) of *trans*-**11b**: (top) view in the general direction of the Cl−Pt−Cl axis; (bottom) view along the N−Pt−N axis.

The molecular structure of the doubly bridged 11-membered cycle *trans*-**16**, derived from the hydrogenation of Lambert's *trans*-**15** (**VII**), is depicted in Figure 5. It exhibits an inversion center at palladium, rendering many of the bond lengths and angles in Table 1 identical. The pyridine rings are coplanar, but the Cl−Pd−Cl vector is not orthogonal (76.4°).

The molecular structures of the 13- and 15-membered macrocycles *trans*-**18a**,**b** are illustrated in Figures 6 and 7, respectively. Both exhibit an inversion center at platinum. For the latter, three methylene groups are disordered and refine to a 81:19 occupancy ratio. Only the dominant conformation is depicted. For both molecules, the pyridine rings are coplanar, and the angles with the Cl−Pt−Cl vectors (79.1 and 79.2°) are close to that of *trans*-**16**.

Three methylene groups of the 23-membered macrocycle *trans*-**20e**·2CHCl$_3$ were disordered (65:35 to 73:27 occupancy ratios). The dominant conformation is shown in Figure 8. The

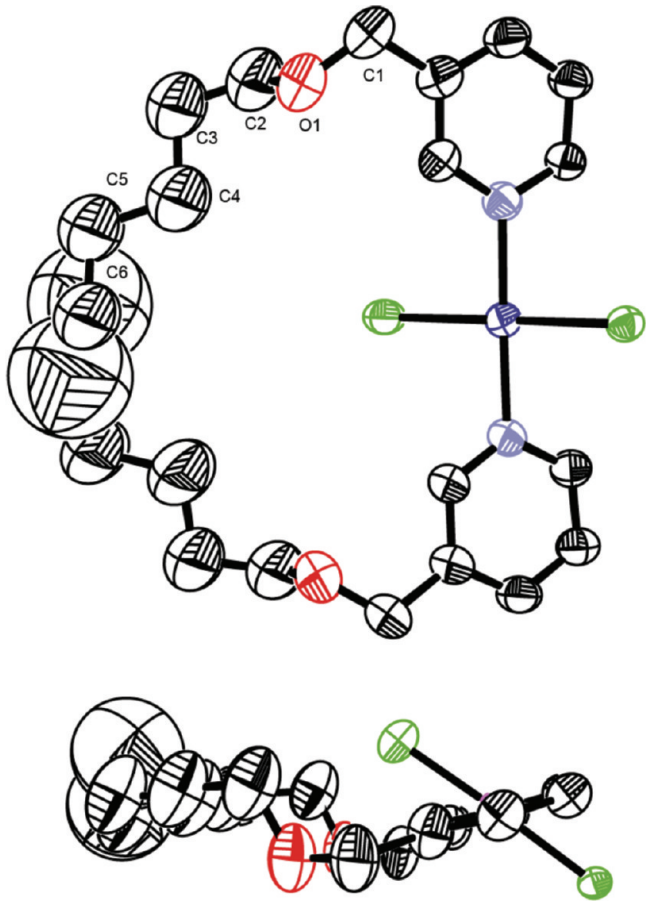


**Figure 3.** Thermal ellipsoid plots (50% probability level) of *trans*-**13d** (dominant conformation of one of two independent molecules in the unit cell): (top) view of the coordination plane; (bottom) view along the N−Pt−N axis.

O═C linkages of all four ester groups are anti to the C≡C≡N moieties, as reflected by O−C−C−C(N) torsion angles of 176.5−163.4°. Furthermore, all of the O═C−O−CH$_2$ linkages exhibit *Z* conformations, as reflected by torsion angles of 4.0−0.1°. The pyridine rings are essentially coplanar (0.1° angle), but the Cl−Pt−Cl vector shows a large deviation from orthogonality (63.3°). In contrast to *trans*-**13h**·CH$_2$Cl$_2$, only one chlorine atom of each solvate molecule projects (partially) into the macrocycle cavity.

**4. Other Reactions.** For reasons amplified in the Discussion, the substitution chemistry of several complexes was briefly explored. In response to some unanticipated results below, the unbridged 3-substituted pyridine complexes *trans*-**12b**,**h** were combined with the Grignard reagent CH$_3$MgBr (2.5−3.0 equiv), as shown in Scheme 10. Chromatography gave the monosubstituted chloroplatinum methyl complexes *trans*-**24b**,**h** as white solids in 94−67% yields. Analogous reactions of the monobridged analogues *trans*-**13d**,**h** afforded the chloroplatinum methyl complexes *trans*-**25d**,**h**, albeit in slightly lower yields of 65−41%. The methyl ligands gave characteristic upfield $^1$H and $^{13}$C NMR signals ($\delta$ 0.87 to 0.93 and −6.4 to −6.6 ppm).

In contrast, the 2,6-disubstituted pyridine complex *trans*-**17a** (Scheme 6) was recovered in at least 80% yield when treated with CH$_3$MgBr, various cyanide ion sources, or phenylacetylene in the presence of the catalyst CuI and base *i*-Pr$_2$NH. However, the 3,5-disubstituted pyridine complex *trans*-**19c** and


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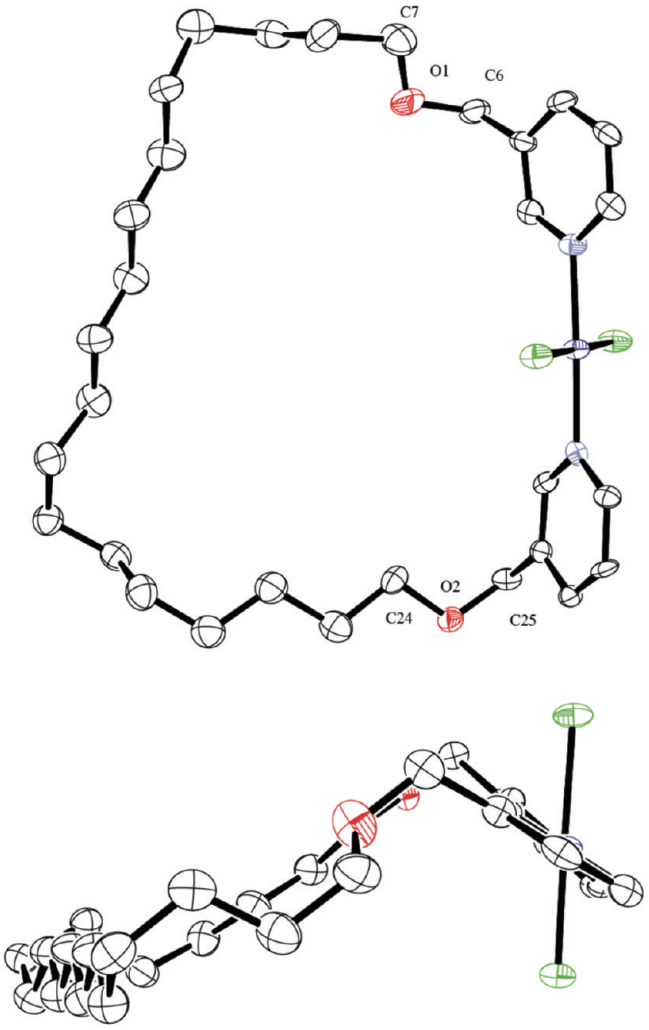


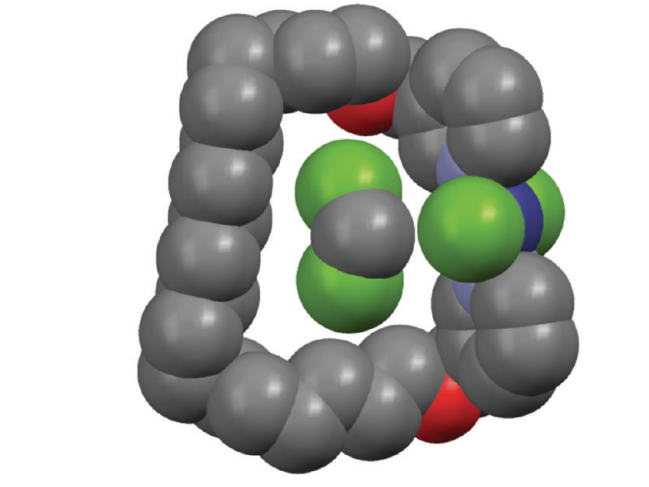

**Figure 4.** Structural representations of *trans*-**13h**·$CH_2Cl_2$: thermal ellipsoid plots (50% probability level) with the solvate molecule omitted in the general direction of the Cl−Pt−Cl axis (top) and along the N−Pt−N axis (middle); space-filling model (bottom).

phenylacetylene reacted in the presence of CuI and *i*-$Pr_2NH$ to give the phenylacetylide complex *trans*-**26c** (Scheme 10, bottom) as a pale yellow solid in 18% yield after chromatography.

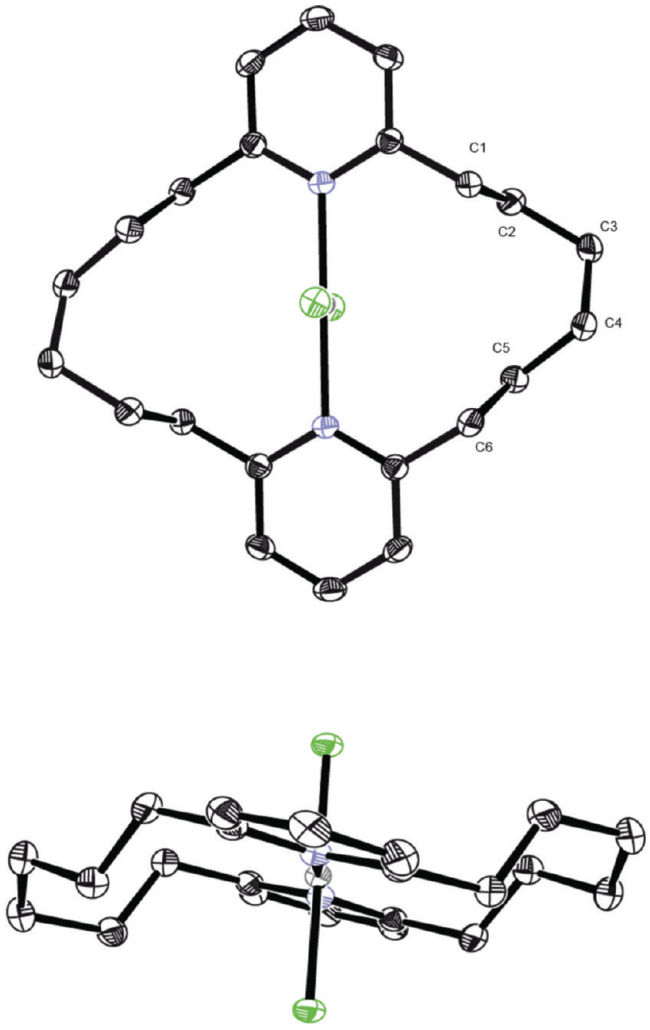


**Figure 5.** Thermal ellipsoid plots (50% probability level) of *trans*-**16**: (top) view along the Cl−Pd−Cl axis; (bottom) view along the N−Pd−N axis.

As shown in Scheme 11, reaction of the 2,6-disubstituted pyridine **4a** and the rhodium bis(cyclooctene) complex $[RhCl(coe)_2]_2$ under CO afforded the trans rhodium carbonyl chloride bis(pyridine) complex *trans*-**27a** as an orange solid in 26% yield after chromatography. However, in contrast to the platinum analogues in Scheme 6, reactions of 0.017−0.0020 M $CH_2Cl_2$ solutions with Grubbs' catalyst never gave a detectable quantity of a monorhodium metathesis product, although the starting material was consumed. Unsuccessful attempts to improve the yield of *trans*-**27a**, or prepare analogous adducts of **4b−d**, are described elsewhere.[14a]

Nonetheless, the $^1H$ NMR spectrum of *trans*-**27a** proved relevant. The two protons on the methylene group between the pyridine ring and ether oxygen atom ($NCCH_2O$) gave two significantly separated doublets ($\delta$ 5.76 and 5.64 ppm; $^2J_{HH}$ = 15 Hz), indicating a diastereotopic relationship. This is highlighted in the partial structure **IX** in Scheme 9 (bottom). Importantly, the diasteretopic protons ($H_a/H_b$) would be exchanged when the Cl−Rh−CO moiety rotates by 180°.[27] Apparently, this is slow on the NMR time scale, even in this unbridged system.


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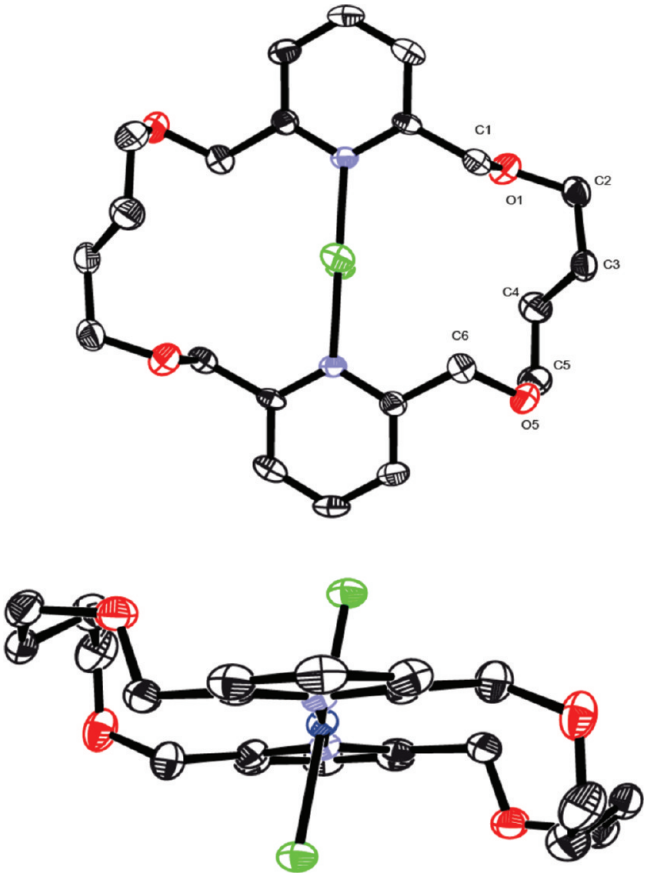


**Figure 6.** Thermal ellipsoid plots (50% probability level) of *trans*-**18a**: (top) view along the Cl−Pt−Cl axis; (bottom) view along the N−Pt−N axis.

## DISCUSSION

**1. Scope of Syntheses.** Schemes 3−8 establish that a variety of platinum and palladium complexes with macrocyclic singly and doubly trans-spanning bis(pyridine) ligands can be accessed by ring-closing alkene metatheses of precursors with appropriately functionalized trans pyridine ligands. Although the one rhodium species studied, *trans*-**27a** (Scheme 11), could not be similarly cyclized, phosphine analogues have been successfully converted to gyroscope-like complexes of the type **IV** in Scheme 1.[6,7] Note that the platinum analogue of *trans*-**27a**, *trans*-**17a**, gives the lowest yield of all the bis-macrocyclizations reported (10%; Scheme 6). Hence, we believe that rhodium adducts of other disubstituted pyridine ligands employed above would give reasonable yields of doubly trans-spanning bis(pyridine) complexes.

In relevant earlier work, van Koten, Kang, and Ko have studied metatheses of platinum pincer complexes of dialkenylated pyridines.[28,29] Three of many examples are collected in Scheme 12. The first two involve *intra*ligand metatheses of 3,5- and 2,6-disubstituted systems (eqs i and ii). The third example features a 3-fold *inter*ligand metathesis to a metacyclophane-like macrocycle.

Equation i of Scheme 12 features the same ligand as in *trans*-**19d** (Scheme 7), but we observed only *inter*ligand metathesis to *trans*-**20d** (one chromatographically mobile product). Importantly, no special attempt has been made to establish thermodynamic control in any of our reactions, although this has been unambiguously reached in certain cases.[30] Furthermore, Fogg

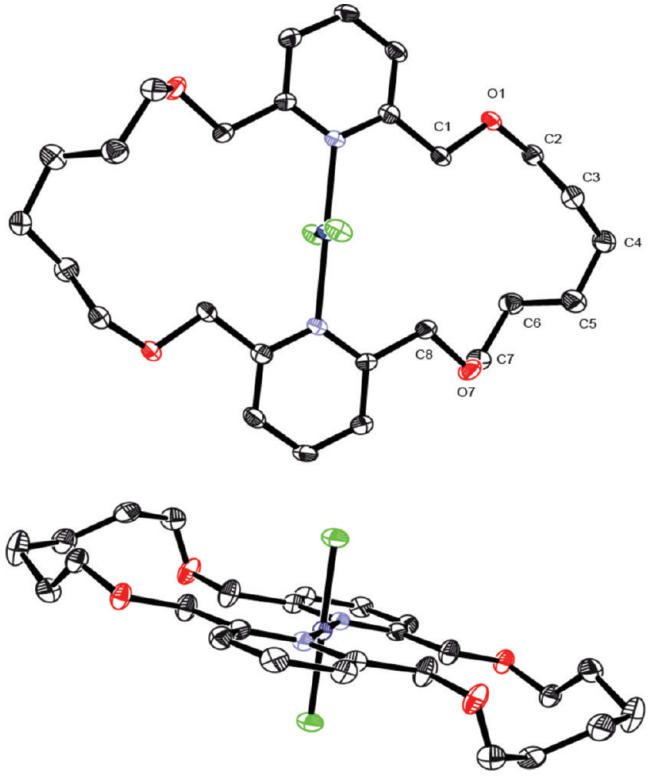


**Figure 7.** Thermal ellipsoid plots (50% probability level) of *trans*-**18b**: (top) view along the Cl−Pt−Cl axis; (bottom) view along the N−Pt−N axis. The three disordered atoms are depicted in their dominant conformations.

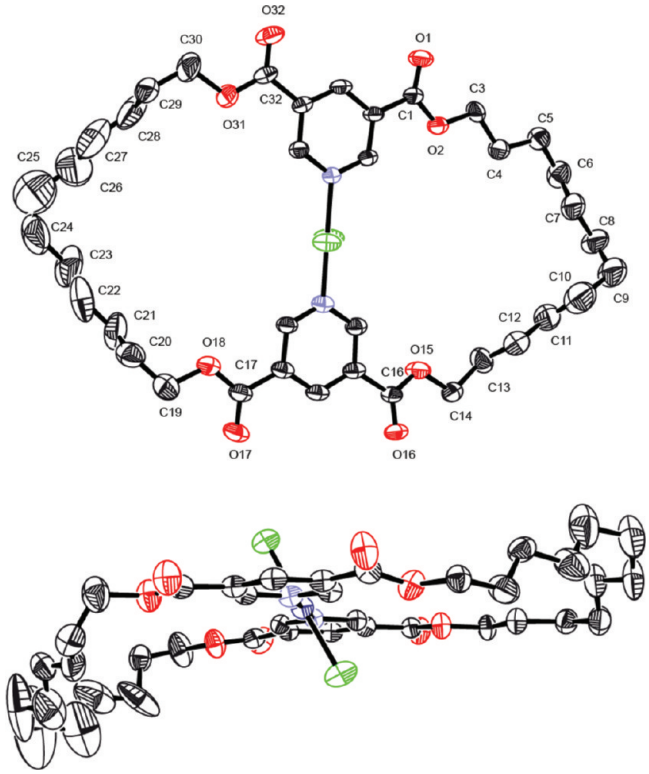


**Figure 8.** Thermal ellipsoid plots (50% probability level) of *trans*-**20e**·2$CHCl_3$ with the solvate molecules omitted: (top) view along the Cl−Pt−Cl axis; (bottom) view along the N−Pt−N axis. The disordered atoms are depicted in their dominant conformations.


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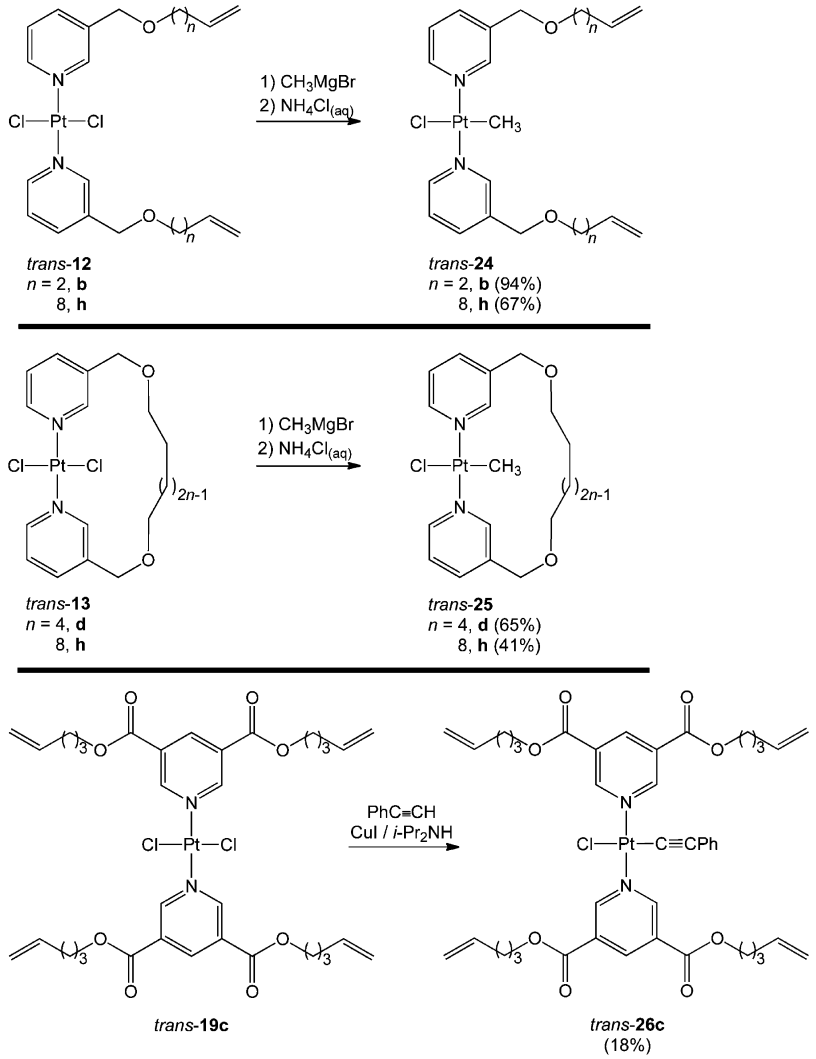
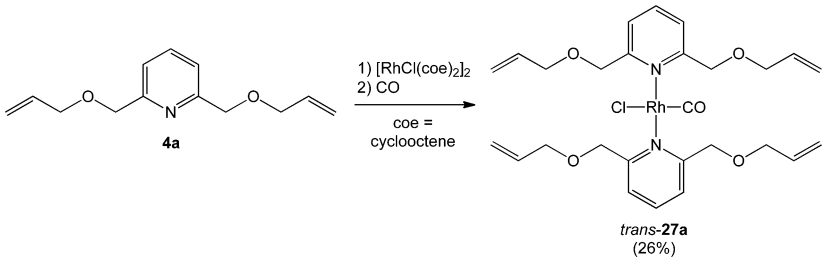
**Scheme 10. Substitution Reactions**




**Scheme 11. Synthesis of a Rhodium 2,6-Disubstituted Bis(pyridine) Complex**




has emphasized that oligomers sometimes dominate kinetically in ring-closing metatheses but can convert to monocyclic products given sufficient time, catalyst, and ethylene coproduct.[31] Thus, there remains much potential for optimization in the preceding chemistry.

The preparative data in Schemes 3−8 and 10 suggest a myriad of steric effects. For example, the yields of the 3-substituted pyridine complexes in Scheme 4 are higher than those of the 2-substituted homologues in Scheme 3. Similarly, the yields of the 2,6-disubstituted pyridine complexes in Schemes 5 and 6 are generally lower than those of the related 3,5-disubstituted pyridine complexes in Schemes 7 and 8. All attempts to effect substitution of the chloride ligands in 2,6-disubstituted pyridine complexes were unsuccessful, in contrast to the examples involving 3-substituted or 3,5-disubstituted pyridine complexes in Scheme 10.

The congestion inherent in the 2,6-disubstituted pyridine complexes is readily seen in the fragment **IX** in Figure 9, which is taken from the crystal structure of the unbridged adduct *trans*-**17a**, including the coplanar pyridine rings (Figure 1). Projection **IXa** highlights the distance between the carbon atoms bound to the 2,6-positions on opposite pyridine ligands, ca. 3.83 Å. This is somewhat greater than twice the van der Waals radius of an $sp^3$ carbon atom (1.70 Å),[32] as illustrated by projection **IXc**, a perpendicular view with the carbon and chlorine atoms shown at van der Waals radii. The difference,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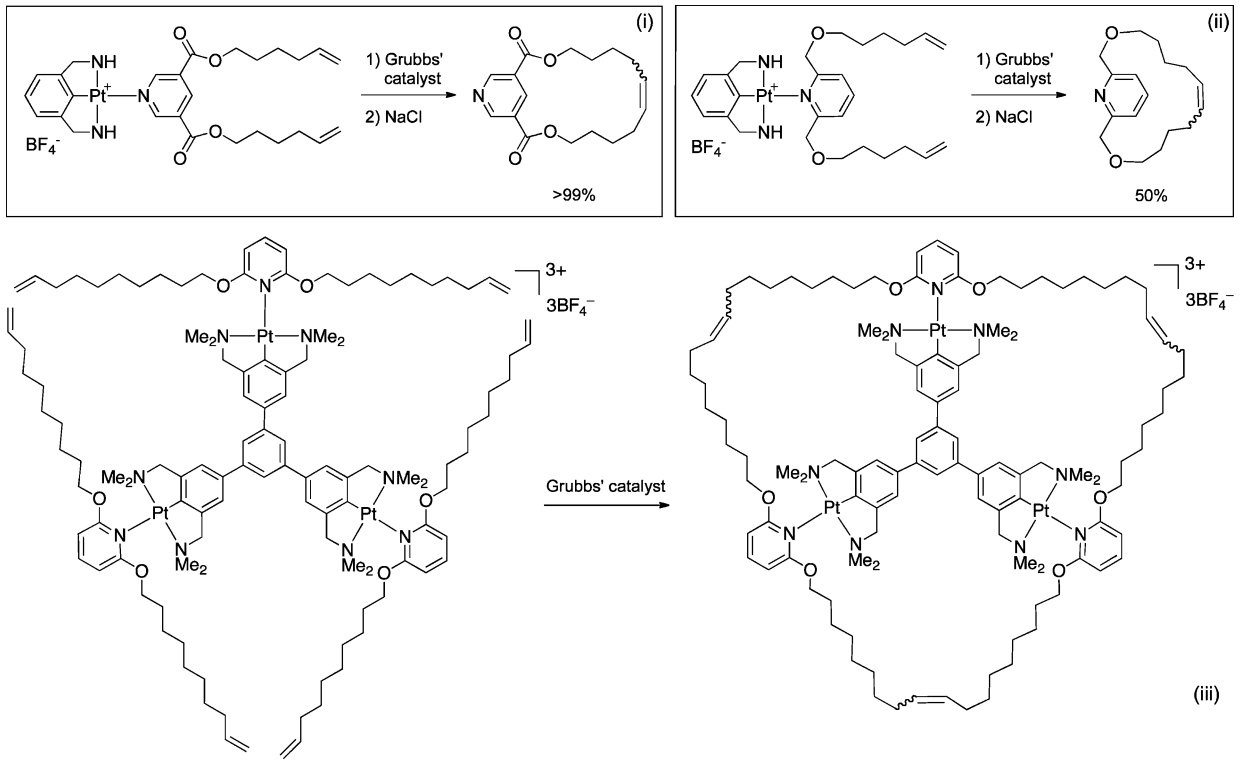
**Scheme 12. Other Alkene Metatheses Involving Pyridine Ligands in Metal Coordination Spheres**



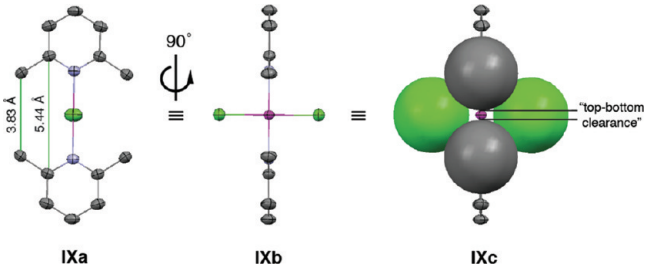




**Figure 9.** Steric relationships between the carbon atoms bound to the 2,6-pyridine positions and the chlorine atoms in *trans*-**17a**.

0.43 Å, can be viewed as a "top−bottom clearance". As summarized in Table 2, comparable values are found for the other 2,6-disubstituted complexes, all of which have coplanar pyridine rings (0.45−0.63 Å; *trans*-**16**, *trans*-**18a,b**). The somewhat greater clearance for the 2-monosubstituted complex *trans*-**11b** (0.87 Å) arises from the noncoplanarity or skewing of the pyridine rings (Table 1).

**Table 2. Distances (Å) Relevant to Rotator Rotation in Crystalline Complexes**

| complex | $MCl_2$ radius | bridge height[a] | top−bottom clearance[b] | closest intermolecular contact |
|---|---|---|---|---|
| *trans*-**17** | 4.04 | | 0.43[c] | 3.38 |
| *trans*-**11** | 4.06 | 3.40 | 0.87[c] | 2.62 |
| *trans*-**13d**[d] | 4.05 | 5.37 | 1.90[e] | 2.51 |
| | 4.06 | 5.00 | 1.91[e] | |
| *trans*-**13h**·$CH_2Cl_2$ | 4.05 | 7.58 | 1.92[e] | 1.87 |
| *trans*-**16** | 4.06[f] | 2.58 | 0.58[c] | 3.59 |
| *trans*-**18a** | 4.06 | 2.49 | 0.63[c] | 3.13 |
| *trans*-**18b** | 4.06 | 4.38 | 0.45[c] | 2.89 |
| *trans*-**20e**·$2CHCl_3$ | 4.04 | 7.66 | 1.93[e] | 3.21 |

[a]See Figure 10. [b]See Figure 9. [c]2- or 2,6-substitution. [d]The two sets of values correspond to the two independent molecules in the unit cell. [e]3- or 3,5-substitution. [f]$PdCl_2$ radius; other values are $PtCl_2$ radii.

**2. Feasibility of $MCl_2$ Rotation.** The long-term goal of this project is to synthesize molecular rotors[12] in which a transition-metal-based rotator can turn within a macrocyclic cage (stator) with as low an energy barrier as possible. In this context, a key issue is the interior space available within the macrocycles vis-à-vis the sizes of the ligands on the metal. Analyses of the type in Figure 10 have proven to be particularly helpful

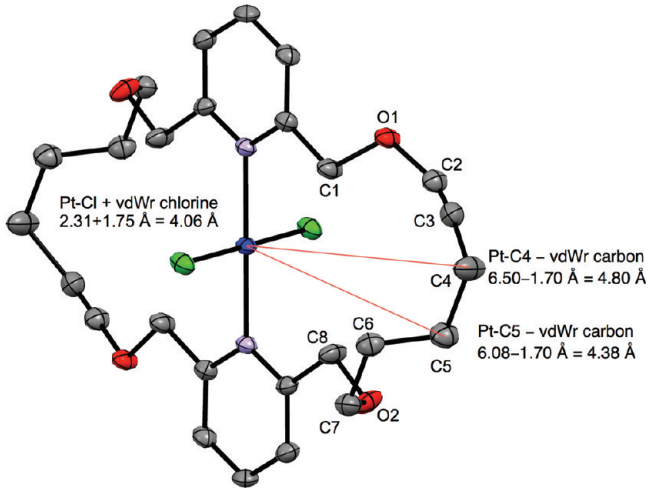



**Figure 10.** Estimation of "horizontal clearance" or "bridge height" in Table 2, illustrated for *trans*-**18b**.

in correlating properties of the bis(phosphine) systems in Scheme 1. First, the radius of the $MCl_2$ moiety is calculated by adding the crystallographically determined metal−chlorine bond distance (Table 1) and the van der Waals radius of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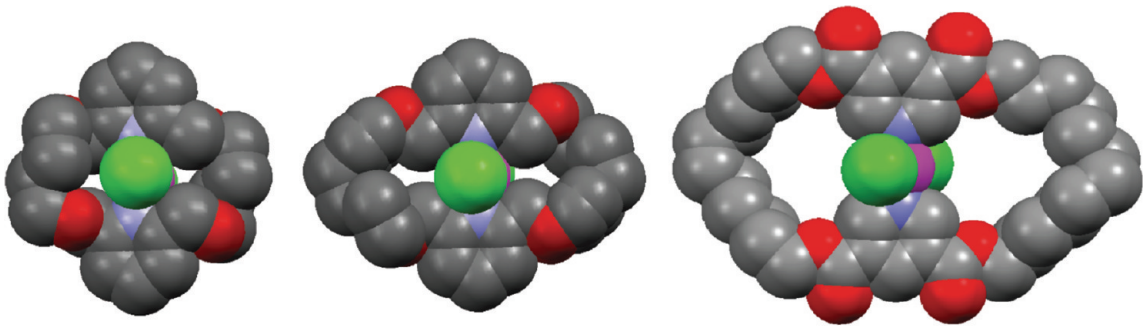

*trans*-**18a** *trans*-**18b** *trans*-**20e**

**Figure 11.** Space-filling representations of the molecular structures of *trans*-**18a**, *trans*-**18b**, and *trans*-**20e**.

chlorine (1.75 Å).[32] As summarized in Table 2, essentially the same value is obtained for all the platinum and palladium complexes (average 4.05 Å).

The distances between the metal atom and the remote carbon atoms of each macrocycle chain are then calculated, utilizing the two carbon atoms closest to the plane that would be defined by $MCl_2$ rotation. As shown in Figure 10, these vary, and the shortest distance among the four possibilities is taken. The van der Waals radius of carbon is then subtracted, giving a "horizontal clearance" or "bridge height". The resulting distances are summarized in Table 2. However, it should be kept in mind that an equilibrium ensemble of macrocycle conformations would be expected in solution, and any impression of a rigid steric barrier is unintended.

In any case, the $PtCl_2$ radii in *trans*-**13d**, *trans*-**13h**·$CH_2Cl_2$, *trans*-**18b**, and *trans*-**20e**·$2CHCl_3$ are less than the respective bridge heights (Table 2), fulfilling one steric condition for $PtCl_2$ rotation. These complexes represent the largest macrocycle based upon a 2,6-disubstituted pyridine (*trans*-**18b**, 15-membered), and all of the macrocycles based upon 3-substituted (*trans*-**13d**, *trans*-**13h**·$CH_2Cl_2$, 21- and 29-membered) and 3,5-disubstituted pyridines (*trans*-**20e**·$2CHCl_3$, 23-membered). However, in the 2,6-disubstituted complex *trans*-**18b**, the top−bottom clearance is much less than the van der Waals *diameter* of a chlorine atom (0.45 Å vs 3.50 Å). This is depicted in projection **IXc** in Figure 9 and would render rotation a very high energy process.

For the 3-substituted and 3,5-disubstituted complexes, the top−bottom clearance can be estimated as follows. First, the shortest distance between the 2,2′- or 6,6′-carbon atoms is identified. In the case of reference molecule *trans*-**17a**, this is 5.44 Å (Figure 9, **IXa**). Next, two times the van der Waals radius of carbon is subtracted. As summarized in Table 2, this gives distances in the range of 1.90−1.98 Å. In the absence of any skewing of the pyridine rings, this would have to accommodate the full diameter of a chlorine atom: ca. 3.50 Å. Obviously, this steric requirement is poorly fulfilled, and none of the compounds in this first-generation synthetic study provide an experimental test of $MCl_2$ rotation. Per the analysis in Scheme 9 (bottom), the $^1$H NMR properties of rhodium carbonyl chloride analogues of any of these complexes would be diagnostic of Cl−Rh−CO rotation.

Furthermore, note that the hydrogen atoms in the 2,2′- or 6,6′-positions have not been taken into account—as was also the case for complexes with 2,6-substituents (Figure 9). Hydrogen atoms have also been omitted in all space-filling representations in this paper. There are many conformational processes that readily occur in organic molecules despite van der Waals interactions involving hydrogen atoms and/or not being able to execute them with space-filling models. Hence, only non-hydrogen atoms have been considered in this admittedly qualitative analysis.

Figure 11 provides side-by-side comparisons that illustrate the preceding concepts. In 2,6-disubstituted *trans*-**18a**, the bridge height is smaller than the $PtCl_2$ radius, and the top−bottom clearance is much smaller than the diameter of chlorine. In *trans*-**18b**, the latter still holds, but the bridge height is larger than the $PtCl_2$ radius. With 3,5-disubstituted *trans*-**20e**, the bridge height is much larger than the $PtCl_2$ radius, and the top−bottom clearance is the maximum possible for this series of compounds. Complexes *trans*-**20h** and *trans*-**23** (Schemes 7 and 8), in which the macrocycles are even larger (29 vs the 23 atoms in *trans*-**20e**), would make a still more spacious visual impression.

In any case, the top−bottom clearance in *trans*-**20e** is admittedly snug with respect to a chlorine ligand, especially in view of the hydrogen atoms that have been neglected. However, this can to some extent be ameliorated if the pyridine ligands skew away from coplanarity, as reflected by the trend with *trans*-**11b** in Table 2. In effect, this would replace an energy maximum with two closely spaced but lower energy maxima. Interactions might also be attenuated by employing second- or third-row donor atoms, which would feature longer metal−heteroatom bonds.

Apart from these intramolecular issues, another question is whether any of the $MCl_2$ moieties would be able to undergo rotation in the crystal lattice. It is a simple matter to calculate the distance between the metal and the closest atom in a neighboring molecule, and these are summarized in Table 2. In every case, the closest contact is less than the $MCl_2$ radius. Hence, the rotational barriers should be extremely high, even in the absence of intramolecular contacts. In principle, the onset of any rotation in the solid state could be evidenced by a phase transition. Out of all the macrocyclic complexes for which DSC data were recorded (*trans*-**18b**, *trans*-**20d**,**e**,**f**,**h**), only one showed an endotherm considerably below the melting or decomposition point (*trans*-**20e**).

We note in passing that, for doubly bridged *trans*-**18b** and *trans*-**20e**·$2CHCl_3$, all molecules exhibit parallel Cl−M−Cl axes in the crystal lattice. In contrast, *trans*-**16** and *trans*-**18a** show two sets of molecules with parallel axes. These axes define angles of 44 and 82°, respectively, as calculated from six atom planes generated from two parallel Cl−M−Cl segments. Representative packing diagrams are given elsewhere.[14]


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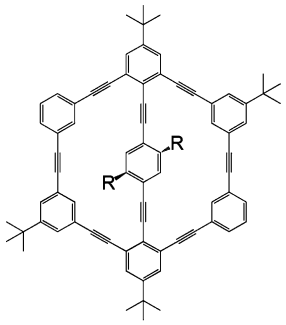
Trigonal-bipyramidal systems such as **III** (Scheme 1) commonly pack in layers with all P−M−P axes parallel,[4] but other coordination geometries do not appear to exhibit strong preferences.

**3. Toward Molecular Gyroscopes.** The singly bridged bis(pyridine) complexes belong to a class of compounds that have been referred to as rope-skipping rotors,[12] and the doubly bridged bis(pyridine) complexes belong to a class of compounds that have been termed molecular turnstiles.[34] The former are in principle quite numerous, whereas the latter are less common if required to closely approximate "revolving door" symmetry. The prototype would be Moore's system **X** in Figure 12, but the descriptor has also been applied to molecules in the rope-skipping category[35] and other assemblies.[36]




R = H, $CH_2OCH_3$, $CH_2O(3,5\text{-}C_6H_3(t\text{-}Bu)_2)$

**X**

**Figure 12.** Other relevant molecular rotors.

Regardless of the $MCl_2$ rotational barriers associated with our complexes, the $MCl_2$ moieties of individual molecules would exhibit both clockwise and counterclockwise motion. However, in order to attain functional gyroscopic properties, unidirectional rotation is required. One strategy for controlling the direction of a rotator involves introducing a dipole moment, such that it can be oriented by a static applied electric field or driven by a rotating electric field.[12,33] Both substitution reactions of the types in Scheme 10, and ring-closing metatheses of less symmetrical substrates—such as rhodium carbonyl chloride analogues of the preceding platinum dichloride complexes—should provide practical routes to such species, especially now that certain limitations of these processes have been defined.

Macroscopic gyroscopes are almost always found within housings to shield the moving parts. The rotators in our doubly bridged bis(pyridine) adducts are somewhat more exposed than those in the diphosphine systems in Scheme 1. However, this renders them superior for other purposes such as gearing, i.e. the coupling of rotation between rotors in ordered arrays. In summary, this study has established much valuable baseline data pertaining to the synthesis of molecular rotors based upon bridged trans bis(pyridine) complexes. Key structural, steric, and conformational properties have also been elucidated. Additional studies, including full papers detailing the types of complexes in Scheme 1, will be reported shortly.

## EXPERIMENTAL SECTION

**General Considerations.** All reactions were carried out under inert atmospheres using standard Schlenk and vacuum line techniques. Workups were conducted in air. Reaction solvents were dried and deoxygenated by standard protocols detailed elsewhere.[14] Workup solvents were purified by simple distillation or used as received. Silica (Acros, 60 A) and alumina (neutral, Macherey-Nagel) were used as received.

The $CDCl_3$ was stored over molecular sieves (Deutero GmbH) or used as received (Cambridge Isotope Laboratories). Other chemicals were used as received: DMSO-$d_6$ (Aldrich), sodium (J. T. Baker, ACS reagent), allyl alcohol (Alfa Aesar, 98%), 3-buten-1-ol (TCI or Acros Organics, 96−95%), 4-penten-1-ol (TCI or Acros Organics, 98−97%), 5-hexen-1-ol (TCI, 95%), 6-hepten-1-ol (TCI, 95%), 7-octen-1-ol (TCI, >96%), 9-decen-1-ol (TCI or Aldrich, 97%-95%), 10-undecen-1-ol (TCI, 95%), 3-(chloromethyl)pyridine hydrochloride (Alfa Aesar, 97%), 2-(chloromethyl)pyridine hydrochloride (TCI, 98%), $C_6H_5CH_2N(CH_3)_3^+Cl^-$ (Aldrich, 97%), 2,6-bis(bromomethyl)-pyridine (Aldrich, 98%), $PtCl_2$ (ABCR, 99.9%), *trans*-$(PhCN)_2PtCl_2$ (Alfa Aesar, 98%), *trans*-$(PhCN)_2PdCl_2$ (Acros, 99%), $[RhCl(coe)_2]_2$ (Acros, 97%), Grubbs' catalyst ($Ru(=CHPh)(PCy_3)_2(Cl)_2$; Aldrich), CuI (Acros, 99.9%), *i*-$Pr_2NH$ (Fluka, 99%), PhC≡CH (Acros, 98%), $PtO_2$ (Aldrich), Pd/C (Lancaster or Acros, 10%), pyridine-3,5-dicarboxylic acid (Aldrich), 3,5-dichloropyridine (TCI or Aldrich, 98%), 4-bromoanisole (Alfa Aesar, 99%), $BBr_3$ (Aldrich, 1.0 M in $CH_2Cl_2$), $Cs_2CO_3$ (Alfa Aesar, 99.9%), 7-bromo-1-heptene (Aldrich, 97%), $CH_3MgBr$ (Acros, 3.0 M in diethyl ether; titration vs $I_2$ gave 2.94 M),[37] $H_2C{=}CHCH_2MgBr$ (Fluka, 1.0 M in diethyl ether), magnesium (Alfa Aesar, 99.8%), $NH_4Cl$ (Mallinckrodt, 99.5%), and $(dppp)NiCl_2$ (Strem, 99%). The bis(acid chloride) 3,5-$NC_5H_3(COCl)_2$[38] and Grubbs' second-generation catalyst $Ru(=CHPh)(H_2IMes)(PCy_3)(Cl)_2$[39] were synthesized by literature procedures.

NMR spectra were recorded on 500−300 MHz spectrometers and referenced as follows: $^1H$, residual internal $CHCl_3$ ($\delta$, 7.26 ppm) or DMSO-$d_5$ ($\delta$, 2.50 ppm); $^{13}C$, internal $CDCl_3$ ($\delta$, 77.23 ppm). The $^1H$ and $^{13}C$ NMR signals of the free and coordinated nitrogen donor ligands were assigned on the basis of literature generalizations.[24,25] IR spectra were recorded using ATR accessories. DSC data were treated by standard methods.[40] Instrument models are detailed elsewhere.[14]

**2-$NC_5H_4(CH_2OCH_2CH{=}CH_2)$ (1a).** A Schlenk flask was charged with sodium (0.8942 g, 36.94 mmol) and allyl alcohol (15.6510 g, 269.47 mmol). The mixture was stirred at 80 °C (oil bath) until the sodium was consumed and cooled to room temperature. Then 2-(chloromethyl)pyridine hydrochloride (2.4870 g, 15.161 mmol) was added and the mixture kept at 80 °C for 16 h. The excess alcohol was removed by oil pump vacuum at 80 °C. Water and $CH_2Cl_2$ were added to the residue. The phases were separated and the aqueous phase extracted with $CH_2Cl_2$ (2 × 50 mL). The combined $CH_2Cl_2$ layers were dried ($MgSO_4$). The solvent was removed by oil pump vacuum. The residue was eluted through a silica column (8 × 1.5 cm) with ethyl acetate (300 mL). The solvent was removed from the product fraction by oil pump vacuum to give spectroscopically pure **1a** as a brown oil (1.3682 g, 9.1776 mmol, 61%). NMR ($\delta$, $CDCl_3$): $^1H$ 8.54 (m, 1H, *o*-$HC_{6pyr}$), 7.68 (m, 1H, *p*-$HC_{4pyr}$), 7.45 (m, 1H, *m*-$HC_{3pyr}$), 7.17 (m, 1H, *m*-$HC_{5pyr}$), 6.01−5.92 (ddt, 1H, $^3J_{HHtrans}$ = 17.3 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 5.5 Hz, $CH{=}$), 5.35−5.19 (m, 2H, $=CH_2$), 4.64 (s, 2H, $CH_2O$), 4.11 (m, 2H, $OCH_2CH$); $^{13}C\{^1H\}$ 158.7 (s, *o*-$C_{2pyr}$), 149.2 (s, *o*-$C_{6pyr}$), 136.8 (s, $CH{=}$), 134.6 (s, *p*-$C_{4pyr}$), 122.5 (s, *m*-$C_{3pyr}$), 121.5 (s, *m*-$C_{5pyr}$), 117.5 (s, $=CH_2$), 73.1 (s, $CH_2O$), 72.0 (s, $OCH_2CH$). These data agreed with those previously reported for an alternative synthesis.[15] IR ($cm^{-1}$, neat oil): 3076 (w), 2859 (w), 1717 (m), 1591 (m), 1306 (m), 1244 (m), 1107 (s), 1084 (s), 993 (s), 926 (s), 758 (s).

**2-$NC_5H_4(CH_2O(CH_2)_2CH{=}CH_2)$ (1b).** 3-Buten-1-ol (14.0023 g, 194.19 mmol), sodium (0.6338 g, 27.57 mmol), and 2-(chloromethyl)pyridine hydrochloride (1.9507 g, 11.892 mmol) were combined in a procedure similar to that for **1a** (12 h reaction time at 80 °C). An analogous workup gave **1b** as a yellow oil (1.8179 g, 11.138 mmol, 59%). NMR ($\delta$, $CDCl_3$): $^1H$ 8.53 (m, 1H, *o*-$HC_{6pyr}$), 7.68 (m, 1H, *p*-$HC_{4pyr}$), 7.44 (m, 1H, *m*-$HC_{3pyr}$), 7.17 (m, 1H, *m*-$HC_{5pyr}$), 5.90−5.81 (ddt, 1H, $^3J_{HHtrans}$ = 17.1 Hz, $^3J_{HHcis}$ = 10.1 Hz, $^3J_{HH}$ = 6.9 Hz, $CH{=}$), 5.14−5.03 (m, 2H, $=CH_2$), 4.64 (s, 2H, $CH_2O$), 3.62 (t, 2H, $^3J_{HH}$ = 6.9 Hz, $OCH_2CH_2$), 2.41 (m, 2H, $OCH_2CH_2$); $^{13}C\{^1H\}$ 158.9 (s, *o*-$C_{2pyr}$), 149.2 (s, *o*-$C_{6pyr}$), 136.9 (s, $CH{=}$), 135.3 (s, *p*-$C_{4pyr}$), 122.5 (s, *m*-$C_{3pyr}$), 121.5 (s, *m*-$C_{5pyr}$),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116.7 (s, $=CH_2$), 73.9 (s, $CH_2O$), 70.6 (s, $OCH_2CH_2$), 34.4 (s, $CH_2CH=$). These data agreed with those previously reported for an alternative synthesis.[16] IR ($cm^{-1}$, neat oil): 2907 (w), 2859 (m), 1717 (m), 1591 (m), 1435 (s), 1121 (s), 1088 (s), 993 (s), 914 (s), 756 (s).

**3-$NC_5H_4(CH_2OCH_2CH=CH_2)$ (2a).** Allyl alcohol (14.1138 g, 243.01 mmol), sodium (0.9319 g, 40.54 mmol), and 3-(chloromethyl)pyridine hydrochloride (2.2593 g, 13.773 mmol) were combined in a procedure similar to that for **1a** (12 h reaction time at 80 °C). An analogous workup gave **2a** as a yellow-brown oil (1.7175 g, 11.512 mmol, 84%). NMR ($\delta$, $CDCl_3$): $^1$H 8.58 (m, 1H, *o*-$HC_{2pyr}$), 8.54 (m, 1H, *o*-$HC_{6pyr}$), 7.69 (m, 1H, *p*-$HC_{4pyr}$), 7.28 (m, 1H, *m*-$HC_{5pyr}$), 6.01−5.88 (ddt, 1H, $^3J_{HHtrans}$ = 17.3 Hz, $^3J_{HHcis}$ = 10.4 Hz, $^3J_{HH}$ = 5.6 Hz, C*H*=), 5.32 (dt, 1H, $^3J_{HH}$ = 17.3 Hz, $^2J_{HH}$ = 1.7 Hz, $=CH_EH_Z$), 5.23 (dt, 1H, $^3J_{HH}$ = 10.4 Hz, $^2J_{HH}$ = 1.7 Hz $=CH_EH_Z$), 4.53 (s, 2H, $CH_2O$), 4.05 (dt, 2H, $^3J_{HH}$ = 5.6 Hz, $^4J_{HH}$ = 1.4 Hz, $OCH_2CH$); $^{13}C\{^1H\}$ 149.4 and 149.3 (2 s, *o*-$C_{2pyr}$ and *o*-$C_{6pyr}$), 135.6 (s, *C*H=), 134.5 (s, *p*-$C_{4pyr}$), 133.9 (s, *m*-$C_{3pyr}$), 123.6 (s, *m*-$C_{5pyr}$), 117.8 (s, $=CH_2$), 71.8 (s, $CH_2O$), 69.7 (s, $CH_2CH=$). IR ($cm^{-1}$, neat oil): 2857 (w), 1724 (w), 1578 (m), 1425 (m), 1082 (s), 1026 (m), 926 (m), 791 (m), 712 (s).

**3-$NC_5H_4(CH_2O(CH_2)_2CH=CH_2)$ (2b).** 3-Buten-1-ol (23.1913 g, 321.62 mmol), sodium (1.0569 g, 45.973 mmol), and 3-(chloromethyl)pyridine hydrochloride (2.4873 g, 15.163 mmol) were combined in a procedure similar to that for **1a** (12 h reaction time at 80 °C). An analogous workup gave **2b** as a yellow-brown oil (2.2722 g, 13.921 mmol, 92%). NMR ($\delta$, $CDCl_3$): $^1$H 8.57 (m, 1H, *o*-$HC_{2pyr}$), 8.53 (m, 1H, *o*-$HC_{6pyr}$), 7.67 (m, 1H, *p*-$HC_{4pyr}$), 7.27 (m, 1H, *m*-$HC_{5pyr}$), 5.90−5.76 (ddt, 1H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.2 Hz, $^3J_{HH}$ = 6.8 Hz, C*H*=), 5.14−5.02 (m, 2H, $=CH_2$), 4.53 (s, 2H, $CH_2O$), 3.54 (t, 2H, $^3J_{HH}$ = 6.8 Hz, $OCH_2CH_2$), 2.38 (apparent qt, 2H, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH}$ = 1.4 Hz, $OCH_2CH_2$); $^{13}C\{^1H\}$ 149.34 and 149.28 (2 s, *o*-$C_{2pyr}$ and *o*-$C_{6pyr}$), 135.5 (s, *C*H=), 135.2 (s, *p*-$C_{4pyr}$), 134.0 (s, *m*-$C_{3pyr}$), 123.6 (s, *m*-$C_{5pyr}$), 116.8 (s, $=CH_2$), 70.6 (s, $CH_2O$), 70.1 (s, $OCH_2CH_2$), 34.3 (s, $CH_2$). IR ($cm^{-1}$, neat oil): 2860 (w), 1722 (s), 1591 (m), 1427 (m), 1283 (s), 1096 (s), 1024 (s), 916 (s), 791 (m), 743 (s), 712 (s).

**3-$NC_5H_4(CH_2O(CH_2)_3CH=CH_2)$ (2c).** 4-Penten-1-ol (27.3842 g, 39.793 mmol), sodium (1.0307 g, 44.833 mmol), and 2-(chloromethyl)pyridine hydrochloride (2.9548 g, 18.013 mmol) were combined in a procedure similar to that for **1a** (12 h for sodium consumption at 80 °C; 12 h reaction time at 100 °C). An analogous workup gave **2c** as a yellow oil (2.2281 g, 12.571 mmol, 70%). NMR ($\delta$, $CDCl_3$): $^1$H 8.57 (m, 1H, *o*-$HC_{2pyr}$), 8.53 (m, 1H, *o*-$HC_{6pyr}$), 7.68 (m, 1H, *p*-$HC_{4pyr}$), 7.28 (m, 1H, *m*-$HC_{5pyr}$), 5.87−5.73 (ddt, 1H, $^3J_{HHtrans}$ = 17.1 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*=), 5.05−4.93 (m, 2H, $=CH_2$), 4.51 (s, 2H, $CH_2O$), 3.50 (t, 2H, $^3J_{HH}$ = 6.5 Hz, $OCH_2CH_2$), 2.14 (m, 2H, $CH_2CH=CH_2$), 1.71 (m, 2H, $OCH_2CH_2$); $^{13}C\{^1H\}$ 149.2 and 149.1 (2 s, *o*-$C_{2pyr}$ and *o*-$C_{6pyr}$), 138.3 (s, *C*H=), 135.6 (s, *p*-$C_{4pyr}$), 134.2 (s, *m*-$C_{3pyr}$), 123.6 (s, *m*-$C_{5pyr}$), 115.1 (s, $=CH_2$), 70.5 (s, $CH_2O$), 70.3 (s, $OCH_2CH_2$), 30.5 (s, $CH_2$), 29.0 (s, $CH_2$). IR ($cm^{-1}$, neat oil): 2938 (m), 2860 (m), 1722 (s), 1427 (m), 1281 (s), 1097 (s), 912 (s), 712 (s).

**3-$NC_5H_4(CH_2O(CH_2)_4CH=CH_2)$ (2d).** 5-Hexen-1-ol (12.9850 g, 129.64 mmol), sodium (0.7838 g, 34.09 mmol), and 3-(chloromethyl)pyridine hydrochloride (1.9432 g, 11.846 mmol) were combined in a procedure similar to that for **1a** (sodium dissolved at 100 °C; 12 h reaction time at 100 °C). An analogous workup gave **2d** as a yellow-brown oil (1.0806 g, 5.6496 mmol, 48%). NMR ($\delta$, $CDCl_3$): $^1$H 8.56 (m, 1H, *o*-$HC_{2pyr}$), 8.53 (m, 1H, *o*-$HC_{6pyr}$), 7.67 (m, 1H, *p*-$HC_{4pyr}$), 7.27 (m, 1H, *m*-$HC_{5pyr}$), 5.87−5.72 (ddt, 1H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*=), 5.04−4.91 (m, 2H, $=CH_2$), 4.50 (s, 2H, $CH_2O$), 3.49 (t, 2H, $^3J_{HH}$ = 6.5 Hz, $OCH_2CH_2$), 2.06 (m, 2H, $CH_2CH=CH_2$), 1.63 (m, 2H, $OCH_2CH_2$), 1.46 (m, 2H, $OCH_2CH_2CH_2$); $^{13}C\{^1H\}$ 152.7 and 152.5 (2 s, *o*-$C_{2pyr}$ and *o*-$C_{6pyr}$), 138.8 (s, *C*H=), 137.4 (s, *p*-$C_{4pyr}$), 136.8 (s, *m*-$C_{3pyr}$), 125.1 (s, *m*-$C_{5pyr}$), 114.9 (s, $=CH_2$), 71.2 (s, $CH_2O$), 69.3 (s, $OCH_2CH_2$), 33.7, 29.2, and 25.6 (3 s, $3CH_2$). IR ($cm^{-1}$, neat oil): 2934 (m), 2859 (m), 1639 (m), 1429 (m), 1097 (s), 1028 (m), 933 (m), 791 (m), 712 (s).

**3-$NC_5H_4(CH_2O(CH_2)_5CH=CH_2)$ (2e).** 6-Hepten-1-ol (23.7783 g, 208.24 mmol), sodium (0.6665 g, 28.93 mmol), and 2-(chloromethyl)pyridine hydrochloride (1.9377 g, 11.813 mmol) were combined in a procedure similar to that for **1a** (sodium dissolved at 100 °C; 12 h reaction time at 100 °C). An analogous workup gave **2e** as a yellow-brown oil (1.9577 g, 9.5358 mmol, 81%). NMR ($\delta$, $CDCl_3$): $^1$H 8.56 (m, 1H, *o*-$HC_{2pyr}$), 8.52 (m, 1H, *o*-$HC_{6pyr}$), 7.68 (m, 1H, *p*-$HC_{4pyr}$), 7.28 (m, 1H, *m*-$HC_{5pyr}$), 5.86−5.73 (ddt, 1H, $^3J_{HHtrans}$ = 17.1 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*=), 5.03−4.90 (m, 2H, $=CH_2$), 4.50 (s, 2H, $CH_2O$), 3.48 (t, 2H, $^3J_{HH}$ = 6.6 Hz, $OCH_2CH_2$), 2.04 (m, 2H, $CH_2CH=CH_2$), 1.62 (m, 2H, $OCH_2CH_2$), 1.44−1.34 (m, 4H, $CH_2$); $^{13}C\{^1H\}$ 149.2 and 149.0 (2 s, *o*-$C_{2pyr}$ and *o*-$C_{6pyr}$), 139.1 (s, *C*H=), 135.6 (s, *p*-$C_{4pyr}$), 134.3 (s, *m*-$C_{3pyr}$), 123.6 (s, *m*-$C_{5pyr}$), 114.6 (s, $=CH_2$), 71.0 (s, $CH_2O$), 70.5 (s, $OCH_2CH_2$), 33.9, 29.7, 28.9, and 25.8 (4 s, $4CH_2$). IR ($cm^{-1}$, neat oil): 2932 (m), 2859 (m), 1722 (s), 1420 (m), 1281 (s), 1113 (s), 1024 (m), 910 (m), 743 (s), 702 (s).

**3-$NC_5H_4(CH_2O(CH_2)_8CH=CH_2)$ (2h).** 9-Decen-1-ol (16.7254 g, 107.03 mmol), sodium (0.3096 g, 13.47 mmol), and 3-(chloromethyl)pyridine hydrochloride (0.8856 g, 5.399 mmol) were combined in a procedure similar to that for **1a** (sodium dissolved at 100 °C; 16 h reaction time at 125 °C). An analogous workup gave **2h** as a yellow-brown oil (1.1231 g, 4.5400 mmol, 84%). NMR ($\delta$, $CDCl_3$): $^1$H 8.57 (m, 1H, *o*-$HC_{2pyr}$), 8.53 (m, 1H, *o*-$HC_{6pyr}$), 7.68 (m, 1H, *p*-$HC_{4pyr}$), 7.27 (m, 1H, *m*-$HC_{5pyr}$), 5.87−5.73 (ddt, 1H, $^3J_{HHtrans}$ = 17.1 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*=), 5.02−4.89 (m, 2H, $=CH_2$), 4.51 (s, 2H, $CH_2O$), 3.48 (t, 2H, $^3J_{HH}$ = 6.6 Hz, $OCH_2CH_2$), 2.03 (m, 2H, $CH_2CH=CH_2$), 1.61 (m, 2H, $OCH_2CH_2$), 1.45−1.27 (m, 10H, $CH_2$); $^{13}C\{^1H\}$ 149.4 and 149.2 (2 s, *o*-$C_{2pyr}$ and *o*-$C_{6pyr}$), 139.4 (s, *C*H=), 135.5 (s, *p*-$C_{4pyr}$), 134.2 (s, *m*-$C_{3pyr}$), 123.6 (s, *m*-$C_{5pyr}$), 114.3 (s, $=CH_2$), 71.1 (s, $CH_2O$), 70.5 (s, $OCH_2CH_2$), 34.0, 29.9, 29.6 (2×), 29.3, 29.1, and 26.3 (6 s, $7CH_2$). IR ($cm^{-1}$, neat oil): 2926 (s), 2854 (s), 1724 (s), 1281 (s), 1111 (s), 1024 (m), 908 (s), 743 (s), 710 (s).

**3-$NC_5H_4(CH_2O(CH_2)_9CH=CH_2)$ (2i).** 10-Undecen-1-ol (23.3818 g, 137.31 mmol), sodium (0.4430 g, 19.27 mmol), and 2-(chloromethyl)-pyridine hydrochloride (1.4139 g, 8.6195 mmol) were combined in a procedure similar to that for **1a** (sodium dissolved at 100 °C; 16 h reaction time at 125 °C). An analogous workup gave **2i** as a yellow-brown oil (1.7982 g, 6.8791 mmol, 80%). NMR ($\delta$, $CDCl_3$): $^1$H 8.57 (m, 1H, *o*-$HC_{2pyr}$), 8.53 (m, 1H, *o*-$HC_{6pyr}$), 7.68 (m, 1H, *p*-$HC_{4pyr}$), 7.28 (m, 1H, *m*-$HC_{5pyr}$), 5.85−5.76 (ddt, 1H, $^3J_{HHtrans}$ = 17.1 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.8 Hz, C*H*=), 5.01−4.91 (m, 2H, $=CH_2$), 4.51 (s, 2H, $CH_2O$), 3.48 (t, 2H, $^3J_{HH}$ = 6.5 Hz, $OCH_2CH_2$), 2.03 (m, 2H, $CH_2CH=CH_2$), 1.61 (m, 2H, $OCH_2CH_2$), 1.40−1.24 (m, 12H, $CH_2$); $^{13}C\{^1H\}$ 148.9 and 148.8 (2 s, *o*-$C_{2pyr}$ and *o*-$C_{6pyr}$), 139.2 (s, *C*H=), 135.5 (s, *p*-$C_{4pyr}$), 134.1 (s, *m*-$C_{3pyr}$), 123.4 (s, *m*-$C_{5pyr}$), 114.1 (s, $=CH_2$), 70.9 (s, $CH_2O$), 70.3 (s, $OCH_2CH_2$), 33.8, 29.7, 29.4 (2×), 29.4, 29.1 (2×), and 26.1 (6 s, $8CH_2$). IR ($cm^{-1}$, neat oil): 2924 (s), 2853 (s), 1724 (s), 1427 (m), 1281 (s), 1098 (s), 908 (s), 712 (s).

**2,6-$NC_5H_3(CH_2CH_2CH=CH_2)_2$ (3).**[13] A round-bottom flask was charged with 2,6-bis(bromomethyl)pyridine (2000 g, 7.549 mmol) and THF (76 mL). The solution was cooled to 0 °C with stirring. After 15 min, $H_2C=CHCH_2MgBr$ (1.0 M in diethyl ether; 19 mL, 19.0 mmol) was added dropwise over 20 min. The cold bath was removed. After 18 h, cold saturated aqueous $NH_4Cl$ (20 mL) was added dropwise over 20 min. The organic layer was collected, washed with water (3 × 20 mL), and dried ($MgSO_4$). The solvent was removed by rotary evaporation. The orange residue was chromatographed on a silica column (40 × 3 cm, 5/1 v/v hexanes/ethyl acetate). The solvents were removed from the product-containing fractions by rotary evaporation and oil pump vacuum to give **3** as a yellow oil (0.847 g, 4.52 mmol, 60%). NMR ($\delta$, $CDCl_3$): $^1$H 7.50 (t, 1H, $^3J_{HH}$ = 7.7 Hz, *p*-$HC_{4pyr}$), 6.96 (d, 2H, $^3J_{HH}$ = 7.7 Hz, *m*-$HC_{3,5pyr}$), 5.88 (ddt, 2H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*=), 5.05 (dd, 2H, $^3J_{HHtrans}$ = 17.1 Hz, $^2J_{HH}$ = 1.9 Hz, $=CH_EH_Z$), 4.97 (dd, 2H, $^3J_{HHcis}$ = 10.2 Hz, $^2J_{HH}$ = 1.3 Hz, $=CH_EH_Z$), 2.87 (t, 4H, $^3J_{HH}$ = 7.8 Hz, $CH_2$), 2.49 (q, 4H, $^3J_{HH}$ = 7.4 Hz, $CH_2$); $^{13}C\{^1H\}$ 160.9 (s, *o*-$C_{2,6pyr}$), 137.9 (s, *C*H=), 136.4 (s, *p*-$C_{4pyr}$), 120.0 (s, *m*-$C_{3,5pyr}$),


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114.9 (s, =$CH_2$), 37.8 (s, $CH_2$), 34.0 (s, $CH_2$). IR ($cm^{-1}$, oil film): 3076 (w), 2922 (m), 2853 (w), 1640 (m), 1579 (s), 1455 (s), 996 (s), 911 (s), 804 (m), 749 (m). MS:[41] 188 ([**21** + H]$^+$, 80%), 133 ([**21** − $CH_2CH_2CH{=}CH_2$]$^+$, 100%).

**2,6-$NC_5H_3(CH_2OCH_2CH{=}CH_2)_2$ (4a).** A Schlenk flask was charged with 2,6-bis(bromomethyl)pyridine (3.300 g, 12.45 mmol), allyl alcohol (3.620 g, 62.32 mmol), and $C_6H_5CH_2N(CH_3)_3^+Cl^-$ (0.464 g, 2.50 mmol, 20 mol %) and fitted with a condenser. The solution was refluxed with stirring (24 h), cooled to room temperature, and poured into water (20 mL). The organic layer was separated. The aqueous layer was extracted with $CH_2Cl_2$ (4 × 10 mL). The organic layer and the extracts were combined, washed with water (3 × 20 mL) and saturated aqueous $NaHCO_3$ (4 × 20 mL), and dried ($MgSO_4$). The solvent was removed by rotary evaporation. The yellow residue was chromatographed on a silica column (40 × 3 cm, 4/1 v/v hexanes/ethyl acetate). The solvents were removed from the product-containing fractions by rotary evaporation and oil pump vacuum to give **4a** as a light yellow oil (1.503 g, 6.86 mmol, 55%). Continued elution of the column afforded the byproduct 2,6-$NC_5H_3(CH_2Br)(CH_2OCH_2CH{=}CH_2)$, identified from an $^1$H NMR spectrum reported elsewhere.[14a] NMR ($\delta$, $CDCl_3$): $^1$H 7.68 (t, 1H, $^3J_{HH}$ = 7.7 Hz, *p*-$HC_{4pyr}$), 7.33 (d, 2H, $^3J_{HH}$ = 7.7 Hz, *m*-$HC_{3,5pyr}$), 5.98 (ddt, 2H, $^3J_{HHtrans}$ = 17.2 Hz, $^3J_{HHcis}$ = 10.4 Hz, $^3J_{HH}$ = 5.6 Hz, C*H*=), 5.34 (dd, 2H, $^3J_{HHtrans}$ = 17.2 Hz, $^2J_{HH}$ = 1.6 Hz, =$CH_EH_Z$), 5.23 (dd, 2H, $^3J_{HHcis}$ = 10.4 Hz, $^2J_{HH}$ = 1.5 Hz, =$CH_EH_Z$), 4.64 (s, 4H, $CH_2O$), 4.12 (dt, 4H, $^3J_{HH}$ = 5.6 Hz, $^4J_{HH}$ = 1.4 Hz, $OCH_2CH$=); $^{13}C\{^1H\}$ 157.9 (s, *o*-$C_{2,6pyr}$), 137.2 (s, *p*-$C_{4pyr}$), 134.4 (s, *C*H=), 119.8 (s, *m*-$C_{3,5pyr}$), 117.3 (s, =$CH_2$), 72.9 and 71.8 (2 s, $CH_2OCH_2$). These data agreed with those previously reported for an alternative synthesis.[18] IR ($cm^{-1}$, oil film): 3084 (w), 2918 (s), 2853 (m), 1648 (w), 1594 (m), 1459 (m), 1347 (m), 1100 (s), 992 (s), 922 (s), 787 (m). MS:[41] 220 ([**4a** + H]$^+$, 100%).

**2,6-$NC_5H_3(CH_2O(CH_2)_2CH{=}CH_2)_2$ (4b).** 2,6-Bis(bromomethyl)-pyridine (2.000 g, 7.548 mmol), 3-buten-1-ol (2.721 g, 37.74 mmol), and $C_6H_5CH_2N(CH_3)_3^+Cl^-$ (0.280 g, 1.51 mmol, 20 mol %) were combined in a procedure similar to that for **4a**. An analogous workup gave **4b** as a light yellow oil (1.020 g, 4.326 mmol, 55%). NMR ($\delta$, $CDCl_3$): $^1$H 7.73 (t, 1H, $^3J_{HH}$ = 7.7 Hz, *p*-$HC_{4pyr}$), 7.36 (d, 2H, $^3J_{HH}$ = 7.7 Hz, *m*-$HC_{3,5pyr}$), 5.87 (ddt, 2H, $^3J_{HHtrans}$ = 17.1 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.8 Hz, C*H*=), 5.09 (dd, 2H, $^3J_{HHtrans}$ = 17.2 Hz, $^2J_{HH}$ = 1.6 Hz, =$CH_EH_Z$), 4.99 (dd, 2H, $^3J_{HHcis}$ = 10.2 Hz, $^2J_{HH}$ = 1.3 Hz, 2 =$CH_EH_Z$), 4.64 (s, 4H, $CH_2O$), 3.63 (t, 4H, $^3J_{HH}$ = 6.7 Hz, $OCH_2CH_2$), 2.44 (q, 4H, $^3J_{HH}$ = 6.7 Hz, $CH_2$); $^{13}C\{^1H\}$ 158.0 (s, *o*-$C_{2,6pyr}$), 137.2 (s, *p*-$C_{4pyr}$), 135.1 (s, *C*H=), 119.7 (s, *m*-$C_{3,5pyr}$), 116.5 (s, =$CH_2$), 73.7 (s, $CH_2O$), 70.3 (s, $OCH_2CH_2$), 34.2 (s, $CH_2$). IR ($cm^{-1}$, oil film): 3080 (w), 2910 (s), 2860 (m), 1640 (w), 1455 (m), 1351 (m), 1112 (s), 992 (s), 915 (s), 787 (s). MS:[41] 248 ([**4b** + H]$^+$, 100%).

**2,6-$NC_5H_3(CH_2O(CH_2)_3CH{=}CH_2)_2$ (4c).** 2,6-Bis(bromomethyl)-pyridine (3.000 g, 11.32 mmol), 4-penten-1-ol (5.860 g, 68.03 mmol), and $C_6H_5CH_2N(CH_3)_3^+Cl^-$ (0.420 g, 2.26 mmol, 20 mol %) were combined in a procedure similar to that for **4a**. An analogous workup gave **4c** as a colorless oil (1.412 g, 5.127 mmol, 45%). NMR ($\delta$, $CDCl_3$): $^1$H 7.71 (t, 1H, $^3J_{HH}$ = 7.7 Hz, *p*-$HC_{4pyr}$), 7.35 (d, 2H, $^3J_{HH}$ = 7.7 Hz, *m*-$HC_{3,5pyr}$), 5.83 (ddt, 2H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.7 Hz, C*H*=), 5.03 (dd, 2H, $^3J_{HHtrans}$ = 17.2 Hz, $^2J_{HH}$ = 2.0 Hz, =$CH_EH_Z$), 4.99 (dd, 2H, $^3J_{HHcis}$ = 10.2 Hz, $^2J_{HH}$ = 2.0 Hz, =$CH_EH_Z$), 4.60 (s, 4H, $CH_2O$), 3.57 (t, 4H, $^3J_{HH}$ = 6.5 Hz, $OCH_2CH_2$), 2.20−2.14 (m, 4H, $CH_2$), 1.79−1.72 (m, 4H, $CH_2$); $^{13}C\{^1H\}$ 158.2 (s, *o*-$C_{2,6pyr}$), 138.2 (s, *p*-$C_{4pyr}$), 137.2 (s, *C*H=), 119.7 (s, *m*-$C_{3,5pyr}$), 114.8 (s, =$CH_2$), 73.7 (s, $CH_2O$), 70.6 (s, $OCH_2CH_2$), 30.3 (s, $CH_2$), 28.9 (s, $CH_2$). IR ($cm^{-1}$, oil film): 3076 (w), 2937 (m), 2864 (m), 1640 (s), 1594 (s), 1445 (s), 1347 (s), 1116 (s), 992 (s), 911 (s), 787 (s). MS:[41] 276 ([**4c** + H]$^+$, 100%).

**2,6-$NC_5H_3(CH_2O(CH_2)_4CH{=}CH_2)_2$ (4d).** 2,6-Bis(bromomethyl)-pyridine (1.000 g, 3.774 mmol), 5-hexen-1-ol (1.512 g, 15.10 mmol), and $C_6H_5CH_2N(CH_3)_3^+Cl^-$ (0.140 g, 0.754 mmol, 20 mol %) were combined in a procedure similar to that for **4a**. An analogous workup gave **4d** as a light yellow oil (0.542 g, 1.79 mmol, 47%). NMR ($\delta$, $CDCl_3$): $^1$H 7.68 (t, 1H, $^3J_{HH}$ = 7.7 Hz, *p*-$HC_{4pyr}$), 7.32 (d, 2H, $^3J_{HH}$ = 7.7 Hz, *m*-$HC_{3,5pyr}$), 5.79 (ddt, 2H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.7 Hz, C*H*=), 4.98 (dd, 2H, $^3J_{HHtrans}$ = 17.1 Hz, $^2J_{HH}$ = 1.8 Hz, =$CH_EH_Z$), 4.93 (dd, 2H, $^3J_{HHcis}$ = 10.2 Hz, $^2J_{HH}$ = 1.6 Hz, =$CH_EH_Z$), 4.59 (s, 4H, $CH_2O$), 3.54 (t, 4H, $^3J_{HH}$ = 6.5 Hz, $OCH_2CH_2$), 2.09−2.01 (m, 4H, $CH_2$), 1.68−1.62 (m, 4H, $CH_2$), 1.51−1.45 (m, 4H, $CH_2$); $^{13}C\{^1H\}$ 157.8 (s, *o*-$C_{2,6pyr}$), 138.5 (s, *p*-$C_{4pyr}$), 136.8 (s, *C*H=), 120.8 (s, *m*-$C_{3,5pyr}$), 115.1 (s, =$CH_2$), 74.5 (s, $CH_2O$), 70.2 (s, $OCH_2CH_2$), 33.8, 30.3, and 28.7 (3 s, $CH_2$). These data agreed reasonably well with those previously reported (in acetone-$d_6$) for an alternative synthesis.[19] IR ($cm^{-1}$, oil film): 3078 (w), 2941 (m), 2870 (m), 1645 (s), 1600 (s), 1448 (s), 1350 (s), 1120 (s), 994 (s), 915 (s), 785 (s). MS:[42] 304 ([**4d** + H]$^+$, 100%).

**3,5-$NC_5H_3(COOCH_2CH{=}CH_2)_2$ (5a).** A round-bottom flask was charged with 3,5-$NC_5H_3(COCl)_2$ (1.224 g, 6.002 mmol) and $CH_2Cl_2$ (20 mL) and cooled to 0 °C. Allyl alcohol (0.7442 g, 13.16 mmol) was added dropwise over 20 min with stirring. The cold bath was removed. After 1 h, the flask was fitted with a condenser. The solution was refluxed (5 h) and cooled to room temperature. The solvent was removed by rotary evaporation. Hexanes was added (10 mL). The off-white residue was collected by filtration and washed with hexanes until a white solid was obtained (8 × 5 mL). The solid was dissolved in $CH_2Cl_2$ (20 mL), washed with aqueous NaOH (1.0 M, 4 × 5 mL), and dried ($MgSO_4$). The solvent was removed by oil pump vacuum to give spectroscopically pure **5a** as a light yellow oil (0.8732 g, 3.535 mmol, 59%). NMR ($\delta$, $CDCl_3$): $^1$H 9.35 (d, 2H, $^4J_{HH}$ = 2.1 Hz, *o*-$HC_{2,6pyr}$), 8.85 (t, 1H, $^4J_{HH}$ = 2.1 Hz, *p*-$HC_{4pyr}$), 6.02 (ddt, 2H, $^3J_{HHtrans}$ = 17.2 Hz, $^3J_{HHcis}$ = 10.4 Hz, $^3J_{HH}$ = 5.8 Hz, C*H*=), 5.40 (dd, 2H, $^3J_{HHtrans}$ = 17.2 Hz, $^2J_{HH}$ = 1.4 Hz, =$CH_EH_Z$), 5.30 (dd, 2H, $^3J_{HHcis}$ = 10.4 Hz, $^2J_{HH}$ = 1.2 Hz, =$CH_EH_Z$), 4.85 (dt, 4H, $^3J_{HH}$ = 5.8 Hz, $^4J_{HH}$ = 1.3 Hz, $OCH_2$); $^{13}C\{^1H\}$ 163.9 (s, CO), 154.1 (s, *o*-$C_{2,6pyr}$), 137.9 (s, *p*-$C_{4pyr}$), 131.4 (s, *C*H=), 125.9 (s, *m*-$C_{3,5pyr}$), 119.0 (s, =$CH_2$), 66.2 (s, $OCH_2$). IR ($cm^{-1}$, oil film): 3080 (w), 2931 (m), 2863 (w), 1727 (s), 1312 (m), 1240 (s), 1112 (m), 912 (m), 747 (s). MS:[41] 248 ([**5a** + H]$^+$, 100%).

**3,5-$NC_5H_3(COO(CH_2)_2CH{=}CH_2)_2$ (5b).** 3,5-$NC_5H_3(COCl)_2$ (0.400 g, 1.96 mmol), $CH_2Cl_2$ (6.5 mL), and 3-buten-1-ol (0.423 g, 5.88 mmol) were combined in a procedure similar to that for **5a**. An analogous workup gave **5b** as a light yellow oil (0.482 g, 1.75 mmol, 89%). NMR ($\delta$, $CDCl_3$): $^1$H 9.33 (d, 2H, $^4J_{HH}$ = 2.1 Hz, *o*-$HC_{2,6pyr}$), 8.82 (t, 1H, $^4J_{HH}$ = 2.1 Hz, *p*-$HC_{4pyr}$), 5.84 (ddt, 2H, $^3J_{HHtrans}$ = 17.1 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.8 Hz, C*H*=), 5.22 (dd, 2H, $^3J_{HHtrans}$ = 17.1 Hz, $^2J_{HH}$ = 1.3 Hz, =$CH_EH_Z$), 5.11 (dd, 2H, $^3J_{HHcis}$ = 10.2 Hz, $^2J_{HH}$ = 1.1 Hz, =$CH_EH_Z$), 4.42 (t, 4H, $^3J_{HH}$ = 6.7 Hz, $OCH_2$), 2.53 (q, 4H, $^3J_{HH}$ = 6.7 Hz, $CH_2CH$=); $^{13}C\{^1H\}$ 165.2 (s, CO), 153.2 (s, *o*-$C_{2,6pyr}$), 138.0 (s, *p*-$C_{4pyr}$), 135.7 (s, *C*H=), 126.0 (s, *m*-$C_{3,5pyr}$), 115.4 (s, =$CH_2$), 64.3 (s, $OCH_2$), 33.5 (s, $CH_2CH$=). IR ($cm^{-1}$, oil film): 3082 (w), 2940 (m), 2865 (w), 1730 (s), 1312 (m), 1242 (s), 1112 (m), 913 (m), 746 (s). MS:[41] 276 ([**5b** + H]$^+$, 100%).

**3,5-$NC_5H_3(COO(CH_2)_3CH{=}CH_2)_2$ (5c).** 3,5-$NC_5H_3(COCl)_2$ (1.500 g, 7.349 mmol), $CH_2Cl_2$ (24 mL), and 4-penten-1-ol (1.392 g, 16.16 mmol) were combined in a procedure similar to that for **5a**. An analogous workup gave **5c** as a light yellow oil (1.865 g, 6.148 mmol, 84%). NMR ($\delta$, $CDCl_3$): $^1$H 9.33 (d, 2H, $^4J_{HH}$ = 2.1 Hz, *o*-$HC_{2,6pyr}$), 8.81 (t, 1H, $^4J_{HH}$ = 2.1 Hz, *p*-$HC_{4pyr}$), 5.87 (ddt, 2H, $^3J_{HHtrans}$ = 17.2 Hz, $^3J_{HHcis}$ = 11.0 Hz, $^3J_{HH}$ = 5.9 Hz, C*H*=), 5.03 (dd, 2H, $^3J_{HHtrans}$ = 17.1 Hz, $^2J_{HH}$ = 1.7 Hz, =$CH_EH_Z$), 4.98 (dd, 2H, $^3J_{HHcis}$ = 10.2 Hz, $^2J_{HH}$ = 1.2 Hz, =$CH_EH_Z$), 4.41 (t, 4H, $^3J_{HH}$ = 6.7 Hz, $OCH_2$), 2.25−2.20 (m, 4H, $CH_2$), 1.93−1.86 (m, 4H, $CH_2$); $^{13}C\{^1H\}$ 164.8 (s, CO), 154.4 (s, *o*-$C_{2,6pyr}$), 138.0 (s, *p*-$C_{4pyr}$), 137.9 (s, *C*H=), 126.6 (s, *m*-$C_{3,5pyr}$), 115.4 (s, =$CH_2$), 65.5 (s, $OCH_2$), 30.4 (s, $CH_2$), 28.1 (s, $CH_2$). IR ($cm^{-1}$, oil film): 3076 (w), 2932 (m), 2858 (w), 1720 (s), 1312 (m), 1231 (s), 1103 (m), 913 (m), 749 (s). MS:[41] 304 ([**5c** + H]$^+$, 100%).

**3,5-$NC_5H_3(COO(CH_2)_4CH{=}CH_2)_2$ (5d).** 3,5-$NC_5H_3(COCl)_2$ (2.000 g, 9.799 mmol), $CH_2Cl_2$ (32 mL), and 5-hexen-1-ol (2.160 g, 21.57 mmol) were combined in a procedure similar to that for **5a**. An analogous workup gave **5d** as a light yellow oil (2.917 g, 8.802 mmol, 90%). NMR ($\delta$, $CDCl_3$): $^1$H 9.37 (d, 2H, $^4J_{HH}$ = 2.1 Hz, *o*-$HC_{2,6pyr}$), 8.85 (t, 1H, $^4J_{HH}$ = 2.1 Hz, *p*-$HC_{4pyr}$), 5.80 (ddt, 2H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.7 Hz, C*H*=), 5.02 (dd,

2H, $^3J_{HHtrans}$ = 17.1 Hz, $^2J_{HH}$ = 1.5 Hz, =$CH_EH_Z$), 4.97 (dd, 2H, $^3J_{HHcis}$ = 10.2 Hz, $^2J_{HH}$ = 1.1 Hz, =$CH_EH_Z$), 4.41 (t, 4H, $^3J_{HH}$ = 6.7 Hz, O$CH_2$), 2.18−2.13 (m, 4H, $CH_2$), 1.87−1.80 (m, 4H, $CH_2$), 1.61−1.54 (m, 4H, $CH_2$); $^{13}C\{^1H\}$ 164.6 (s, CO), 154.1 (s, *o*-$C_{2,6pyr}$), 138.7 (s, *p*-$C_{4pyr}$), 137.6 (s, CH=), 126.3 (s, *m*-$C_{3,5pyr}$), 114.7 (s, =$CH_2$), 65.7 (s, O$CH_2$), 33.6, 25.8, and 25.3 (3 s, 3$CH_2$). These data agreed reasonably well with those previously reported in other solvents for a similar synthesis.[19] IR (cm$^{-1}$, oil film): 3078 (w), 2937 (m), 2860 (w), 1724 (s), 1309 (m), 1235 (s), 1107 (m), 909 (m), 745 (s). MS:[41] 332 ([**5d** + H]$^+$, 100%).

**3,5-$NC_5H_3$(COO$(CH_2)_5$CH=$CH_2)_2$ (5e).** 3,5-$NC_5H_3(COCl)_2$ (1.500 g, 7.349 mmol), $CH_2Cl_2$ (24 mL), and 6-hepten-1-ol (1.850 g, 16.20 mmol) were combined in a procedure similar to that for **5a**. An analogous workup gave **5e** as a light yellow oil (1.838 g, 5.113 mmol, 70%). NMR ($\delta$, $CDCl_3$): $^1$H 9.36 (d, 2H, $^4J_{HH}$ = 2.1 Hz, *o*-$HC_{2,6pyr}$), 8.85 (t, 1H, $^4J_{HH}$ = 2.1 Hz, *p*-$HC_{4pyr}$), 5.80 (ddt, 2H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.7 Hz, C*H*=), 5.01 (dd, 2H, $^3J_{HHtrans}$ = 17.1 Hz, $^2J_{HH}$ = 1.7 Hz, =$CH_EH_Z$), 4.96 (dd, 2H, $^3J_{HHcis}$ = 10.2 Hz, $^2J_{HH}$ = 1.0 Hz, =$CH_EH_Z$), 4.39 (t, 4H, $^3J_{HH}$ = 6.7 Hz, O$CH_2$), 2.10−2.08 (m, 4H, $CH_2$), 1.84−1.77 (m, 4H, $CH_2$), 1.50−1.45 (m, 8H, $CH_2$); $^{13}C\{^1H\}$ 164.5 (s, CO), 154.1 (s, *o*-$C_{2,6pyr}$), 138.5 (s, *p*-$C_{4pyr}$), 137.9 (s, CH=), 126.2 (s, *m*-$C_{3,5pyr}$), 114.6 (s, =$CH_2$), 65.8 (s, O$CH_2$), 33.5, 28.5, 28.3, and 25.3 (4 s, 4$CH_2$). IR (cm$^{-1}$, oil film): 3076 (w), 2934 (m), 2860 (w), 1725 (s), 1309 (m), 1235 (s), 1104 (m), 911 (m), 745 (s). MS:[41] 360 ([**5e** + H]$^+$, 100%).

**3,5-$NC_5H_3$(COO$(CH_2)_6$CH=$CH_2)_2$ (5f).** 3,5-$NC_5H_3(COCl)_2$ (1.800 g, 8.819 mmol), $CH_2Cl_2$ (29 mL), and 7-octen-1-ol (2.488 g, 19.42 mmol) were combined in a procedure similar to that for **5a**. After workup, the yellow residue was chromatographed on a silica column (45 × 3 cm, 4/1 v/v hexanes/ethyl acetate). The solvent was removed from the product-containing fractions by rotary evaporation to give **5f** as a light yellow oil (1.408 g, 3.633 mmol, 41%). NMR ($\delta$, $CDCl_3$): $^1$H 9.36 (d, 2H, $^4J_{HH}$ = 2.1 Hz, *o*-$HC_{2,6pyr}$), 8.85 (t, 1H, $^4J_{HH}$ = 2.1 Hz, *p*-$HC_{4pyr}$), 5.81 (ddt, 2H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.2 Hz, $^3J_{HH}$ = 6.7 Hz, C*H*=), 5.00 (dd, 2H, $^3J_{HHtrans}$ = 17.2 Hz, $^2J_{HH}$ = 2.1 Hz, =$CH_EH_Z$), 4.94 (dd, 2H, $^3J_{HHcis}$ = 10.2 Hz, $^2J_{HH}$ = 2.1 Hz, =$CH_EH_Z$), 4.39 (t, 4H, $^3J_{HH}$ = 6.7 Hz, O$CH_2$), 2.07−2.03 (m, 4H, $CH_2$), 1.85−1.76 (m, 4H, $CH_2$), 1.45−1.51 (m, 12H, $CH_2$); $^{13}C\{^1H\}$ 164.5 (s, CO), 154.1 (s, *o*-$C_{2,6pyr}$), 138.8 (s, *p*-$C_{4pyr}$), 137.9 (s, CH=), 126.2 (s, *m*-$C_{3,5pyr}$), 114.4 (s, =$CH_2$), 65.9 (s, O$CH_2$), 33.6, 28.7, 28.6, 28.5, and 25.8 (5 s, 5$CH_2$). IR (cm$^{-1}$, oil film): 3076 (w), 2930 (s), 2856 (m), 1725 (s), 1309 (s), 1235 (s), 1104 (s), 911 (s), 745 (s). MS:[41] 388 ([**5f** + H]$^+$, 100%).

**3,5-$NC_5H_3$(COO$(CH_2)_8$CH=$CH_2)_2$ (5h).** 3,5-$NC_5H_3(COCl)_2$ (1.480 g, 7.251 mmol), $CH_2Cl_2$ (24 mL), and 9-decen-1-ol (2.503 g, 16.02 mmol) were combined in a procedure similar to that for **5a**. An analogous workup gave **5h** as a light yellow oil (2.152 g, 4.858 mmol, 67%). NMR ($\delta$, $CDCl_3$): $^1$H 9.36 (d, 2H, $^4J_{HH}$ = 2.1 Hz, *o*-$HC_{2,6pyr}$), 8.86 (t, 1H, $^4J_{HH}$ = 2.1 Hz, *p*-$HC_{4pyr}$), 5.81 (ddt, 2H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.7 Hz, C*H*=), 5.23 (dd, 2H, $^3J_{HHtrans}$ = 17.1 Hz, $^2J_{HH}$ = 1.8 Hz, =$CH_EH_Z$), 4.99 (dd, 2H, $^3J_{HHcis}$ = 10.2 Hz, $^2J_{HH}$ = 1.2 Hz, =$CH_EH_Z$), 4.39 (t, 4H, $^3J_{HH}$ = 6.7 Hz, O$CH_2$), 2.06−2.02 (m, 4H, $CH_2$), 1.81−1.76 (m, 4H, $CH_2$), 1.46−1.33 (m, 20H, $CH_2$); $^{13}C\{^1H\}$ 164.5 (s, CO), 154.1 (s, *o*-$C_{2,6pyr}$), 139.1 (s, *p*-$C_{4pyr}$), 137.9 (s, CH=), 126.2 (s, *m*-$C_{3,5pyr}$), 114.2 (s, =$CH_2$), 65.9 (s, O$CH_2$), 33.7, 29.3, 29.1, 29.0, 28.8, 28.6, and 25.9 (7 s, 7$CH_2$). These data agreed reasonably well with those previously reported for a similar synthesis.[20] IR (cm$^{-1}$, oil film): 3076 (w), 2926 (s), 2856 (m), 1729 (s), 1309 (s), 1235 (s), 1100 (s), 907 (s), 745 (s). MS:[41] 444 ([**5h** + H]$^+$, 100%).

**3,5-$NC_5H_3$(4-$C_6H_4OCH_3)_2$ (6).**[23a] A 100 mL three-necked round-bottom flask was charged with magnesium (0.5821 g, 23.95 mmol) and fitted with a septum, a stopper, and a condenser capped with a 180° glass needle valve. The flask was evacuated and back-filled with $N_2$. THF (30 mL) was added via cannula. Then 1,2-dibromoethane (0.30 mL) was added with stirring. After 10 min, 4-bromoanisole (2.50 mL, 20.0 mmol) was added by syringe. A Schlenk flask was charged with 3,5-dichloropyridine (1.3697 g, 9.2552 mmol), (dppp)-$NiCl_2$ (0.0503 g, 0.0928 mmol, 1.0 mol %), and THF (20 mL) and cooled to 0 °C. The Grignard mixture from the round-bottom flask was then added dropwise with stirring over 10 min. The cold bath was removed. After 15 h, the sample was refluxed (oil bath). After 2 h, the mixture was cooled (0 °C), and methanol (10 mL) was added. The volatiles were removed by oil pump vacuum. Water (200 mL) was added, which was extracted with $CH_2Cl_2$ (3 × 200 mL). The combined extracts were washed with water (150 mL) and brine (150 mL) and dried ($MgSO_4$). The solvent was removed by oil pump vacuum. The residue was recrystallized from toluene to afford **6** as colorless plates (1.8531 g, 6.3606 mmol, 73%). Mp (capillary): 228−231 °C; lit.[43] mp 233−235 °C. NMR ($\delta$, $CDCl_3$): $^1$H 8.75 (br s, 2H, *o*-$HC_{2,6pyr}$), 7.97 (s, 1H, *p*-$HC_{4pyr}$), 7.58 (d, 4H, $^3J_{HH}$ = 8.6 Hz, MeOCC*H*), 7.04 (d, 4H, $^3J_{HH}$ = 8.6 Hz, MeOCCHC*H*), 3.88 (s, 6H, $CH_3$). These data agreed with those previously reported.[43]

**3,5-$NC_5H_3$(4-$C_6H_4OH)_2$ (7).**[23b] A round-bottom flask was charged with **6** (10944 g, 3.7564 mmol), $CH_2Cl_2$ (25 mL), and $BBr_3$ (1.0 M in $CH_2Cl_2$; 16.0 mL, 16.0 mmol) with stirring. After 14 h, methanol (10 mL) was added. The volatiles were removed by oil pump vacuum, and the residue was chromatographed on a silica column (37 × 4 cm, 1/9 v/v petroleum ether/ethyl acetate). The solvent was removed from a faint yellow band by rotary evaporation to give **7** as an off-white solid (0.6539 g, 2.484 mmol, 66%). NMR ($\delta$, DMSO-$d_6$): $^1$H 10.06 (br s, 2H, O*H*), 9.37 (br s, 2H, *o*-$HC_{2,6pyr}$), 8.90 (t, 1H, $^4J_{HH}$ = 2.0 Hz, *p*-$HC_{4pyr}$), 7.77 (m, 4H, HOCC*H*), 6.99 (m, 4H, HOCCHC*H*). These data agreed with those previously reported.[23b]

**3,5-$NC_5H_3$(4-$C_6H_4O(CH_2)_5CH$=$CH_2)_2$ (8).** A round-bottom flask was charged with **7** (0.5179 g, 1.967 mmol), $Cs_2CO_3$ (1.5166 g, 4.6549 mmol), and DMF (50 mL). The flask was fitted with a septum connected by a needle to an oil bubbler and purged with $N_2$ (10 min). Then 7-bromo-1-heptene was added by syringe with stirring. The mixture was kept at 100 °C for 1 h. The solvent was removed by oil pump vacuum. Water (100 mL) and $CH_2Cl_2$ (100 mL) were added and the phases separated. The aqueous phase was extracted with $CH_2Cl_2$ (2 × 100 mL). The combined $CH_2Cl_2$ layers were dried ($MgSO_4$). The solvent was removed by oil pump vacuum. The residue was chromatographed on a silica column (37 × 4 cm, 1/1 v/v ethyl acetate/$CH_2Cl_2$). The solvent was removed from the product-containing fraction by rotary evaporation to give **8** as a colorless solid (0.2902 g, 0.6369 mmol, 32%). Mp (capillary): 151−154 °C. NMR ($\delta$, $CDCl_3$): $^1$H 8.73 (br s, 2H, *o*-$HC_{2,6pyr}$), 7.97 (t, 1H, $^4J_{HH}$ = 2.3 Hz, *p*-$HC_{4pyr}$), 7.56 and 7.01 (2 m, 2 × 4H, pyr-CC*H* and pyr-CCHC*H*), 5.87−5.79 (ddt, 2H, $^3J_{HHtrans}$ = 17.3 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.4 Hz, C*H*=), 5.05−4.94 (m, 4H, =$CH_2$), 4.02 (t, 4H, $^3J_{HH}$ = 6.7 Hz, O$CH_2$), 2.10 (m, 4H, $CH_2$CH=$CH_2$), 1.83 (m, 4H, O$CH_2CH_2$), 1.52−1.47 (m, 8H, $CH_2$); $^{13}C\{^1H\}$ 159.6 (s, $COCH_2$), 145.8 (s, *o*-$C_{2,6pyr}$), 139.0 (s, CH=), 136.6 (s, *m*-$C_{3,5pyr}$), 132.3 (s, *p*-$C_{4pyr}$), 130.1 (s, pyr-C(CH)$_2$), 128.5 (s, pyr-C(CH)$_2$), 115.4 (s, (CH)$_2$CO), 114.7 (s, =$CH_2$), 68.3 (s, $C_6H_4OCH_2$), 33.9, 29.3, 28.8, and 25.8 (4 s, 4$CH_2$). IR (cm$^{-1}$, powder film): 2936 (m), 2864 (w), 1715 (w), 1605 (m), 1510 (m), 1287 (m), 1246 (s), 1180 (m), 910 (m), 824 (s), 716 (m).

***trans*-$PtCl_2$(2-$NC_5H_4$($CH_2OCH_2CH$=$CH_2$))$_2$ (*trans*-10a).** A round-bottom flask was charged with $PtCl_2$ (0.8468 g, 3.183 mmol) and benzene (50 mL) and fitted with a condenser. Then **1a** (1.2956 g, 8.6841 mmol) was added with stirring. The mixture was refluxed (oil bath). After 14 h, the solvent removed by oil pump vacuum. The residue was chromatographed on a silica column (32 × 2.5 cm, 1/4 v/v ethyl acetate/$CH_2Cl_2$). The solvent was removed from the product-containing fraction by oil pump vacuum to give *trans*-**10a** (0.7258 g, 1.286 mmol, 40%) as a light yellow solid and a mixture of atropisomers (ca. 50:50; see text). Mp (capillary): 160−162 °C. Anal. Calcd for $C_{18}H_{22}Cl_2N_2O_2Pt$: C, 38.31; H, 3.93; N, 4.96. Found: C, 38.35; H, 3.93; N, 4.97. NMR ($\delta$, $CDCl_3$): $^1$H 8.92 (m, 2H, *o*-$HC_{6pyr}$), 7.77 (m, 2H, *m*-$HC_{4pyr}$), 7.69 (m, 2H, *p*-$HC_{3pyr}$), 7.24 (m, 2H, *m*-$HC_{5pyr}$), 6.13−5.98 (m, 2H, C*H*=), 5.65 and 5.63 (2 s, 4H, atropisomers, $NC_5H_4CH_2O$), 5.50−5.26 (m, 4H, =$CH_2$), 4.27 (m, 4H, O$CH_2$CH). VT-NMR data ($NC_5H_4CH_2O$ signal): −50 °C, 5.605 and 5.584 ($\Delta$ = 6.2 Hz); −30 °C, 5.617 and 5.597 ($\Delta$ = 6.0 Hz); −10 °C, 5.624 and 5.606 ($\Delta$ = 5.9 Hz); 0 °C, 5.631 and 5.613 ($\Delta$ = 5.4 Hz); 10 °C, 5.638 and 5.620 ($\Delta$ = 5.2 Hz); 30 °C, 5.650 and 5.636 ($\Delta$ = 4.1 Hz); 35 °C,

5.650 and 5.642 (Δ = 3.0 Hz); 40 °C, 5.648 (Δ = 0 Hz). On the basis of the visual appearance of the spectra at 35 and 40 °C, the coalescence temperature ($T_c$) was extrapolated as 311 K. The $\Delta G^{\ddagger}(T_c)$ value was calculated by standard methods[44] as detailed elsewhere.[14b] IR (cm$^{-1}$, powder film): 3073 (w), 2868 (w), 2837 (w), 1611 (m), 1483 (m), 1431 (m), 1340 (m), 1123 (s), 1094 (s), 926 (m), 768 (s), 719 (s).

***trans*-PtCl$_2$(2-NC$_5$H$_4$(CH$_2$O(CH$_2$)$_2$CH=CH$_2$))$_2$ (*trans*-10b).** Pyridine **1b** (1.4989 g, 9.1833 mmol) and PtCl$_2$ (1.1470 g, 4.3120 mmol) were combined in a procedure similar to that for *trans*-**10a**. An analogous workup gave *trans*-**10b** as a light yellow solid (0.3065 g, 0.5174 mmol, 12.0%). Mp (capillary): 188−191 °C dec. The broadened CH$_2$O $^1$H NMR signal suggested a mixture of atropisomers. Anal. Calcd for C$_{20}$H$_{26}$Cl$_2$N$_2$O$_2$Pt: C, 40.55; H, 4.42; N, 4.73. Found: C, 40.27; H, 4.35; N, 4.49. NMR ($\delta$, CDCl$_3$): $^1$H 8.92 (m, 2H, *o*-*HC*$_{6pyr}$), 7.77 (m, 2H, *m*-*HC*$_{4pyr}$), 7.67 (m, 2H, *p*-*HC*$_{3pyr}$), 7.24 (m, 2H, *m*-*HC*$_{5pyr}$), 5.96−5.87 (m, 2H, C*H*=), 5.64 (br s, 4H, C*H*$_2$O), 5.20−5.09 (m, 4H, =C*H*$_2$), 3.80 (t, 4H, $^3J_{HH}$ = 6.4 Hz, OC*H*$_2$CH$_2$), 2.50 (m, 4H, OCH$_2$C*H*$_2$). IR (cm$^{-1}$, powder film): 2164 (w), 2012 (w), 1981 (w), 1611 (w), 1477 (w), 1439 (w), 1356 (m), 1130 (s), 1099 (s), 1001 (m), 924 (m), 773 (s), 721 (m).

***trans*-PtCl$_2$[2,2′-(NC$_5$H$_4$(CH$_2$O(CH$_2$)$_4$OCH$_2$)H$_4$C$_5$N)] (*trans*-11a).** A two-necked round-bottom flask was charged with *trans*-**10a** (0.4344 g, 0.7697 mmol) and CH$_2$Cl$_2$ (382 mL), fitted with a condenser, and flushed with N$_2$ (5 min). A solution of Grubbs' catalyst (0.0251 g, 0.0305 mmol, 4.0 mol %) in CH$_2$Cl$_2$ (5 mL) was added dropwise with stirring (the resulting solution is 0.002 01 M in *trans*-**10a**). The mixture was refluxed (24 h) and cooled to room temperature. The solvent was removed by rotary evaporation. The residue was chromatographed on a silica column (15.5 × 1.5 cm, 1/4 v/v ethyl acetate/CH$_2$Cl$_2$). The solvent was removed by rotary evaporation and oil pump vacuum. A round-bottom flask was charged with the residue (metathesis product), 10% Pd/C (0.0325 g of 10% w/w, 0.0305 mmol Pd, 4.0 mol %), toluene (30 mL), and ethanol (30 mL), flushed with H$_2$, and fitted with a balloon of H$_2$ (1.0 atm). After 23 h, CHCl$_3$ (40 mL) was added and the mixture filtered through a Celite column (5 × 2 cm). The column was washed with CHCl$_3$ (2 × 40 mL). The solvent was removed from the filtrate by oil pump vacuum, and the residue was chromatographed on a silica column (29 × 1.5 cm, 1/4 v/v ethyl acetate/CH$_2$Cl$_2$) to give *trans*-**11a** as a light yellow solid (0.2593 g, 0.4187 mmol, 63%). Mp (capillary): 227−229 °C dec. Anal. Calcd for C$_{16}$H$_{20}$Cl$_2$N$_2$O$_2$Pt: C, 35.70; H, 3.74; N, 5.20. Found: C, 35.39; H, 3.81; N, 5.12. NMR ($\delta$, CDCl$_3$): $^1$H 9.01 (m, 2H, *o*-*HC*$_{6pyr}$), 7.76 (m, 2H, *p*-*HC*$_{4pyr}$), 7.54 (m, 2H, *m*-*HC*$_{3pyr}$), 7.28 (m, 2H, *m*-*HC*$_{5pyr}$), 5.63 (s, 4H, C*H*$_2$O), 3.90 (m, 4H, OC*H*$_2$CH$_2$), 2.10 (m, 4H, OCH$_2$C*H*$_2$); $^{13}$C{$^1$H} 160.4 (s, *o*-*C*$_{2pyr}$), 154.7 (s, *o*-*C*$_{6pyr}$), 138.6 (s, *p*-*C*$_{4pyr}$), 126.7 (s, *m*-*C*$_{3pyr}$), 124.8 (s, *m*-*C*$_{5pyr}$), 72.2 (s, *C*H$_2$O), 69.8 (s, OCH$_2$CH$_2$), 24.6 (s, *C*H$_2$). IR (cm$^{-1}$, powder film): 2966 (w), 2911 (w), 2851 (w), 2149 (w), 1981 (w), 1607 (m), 1437 (m), 1225 (m), 1109 (s), 930 (m), 789 (s), 772 (s).

***trans*-PtCl$_2$[2,2′-(NC$_5$H$_4$(CH$_2$O(CH$_2$)$_6$OCH$_2$)H$_4$C$_5$N)] (*trans*-11b).** Grubbs' catalyst (two charges 24 h apart, 0.0132 and 0.0126 g, 0.0314 mmol, 8.0 mol %), CH$_2$Cl$_2$ (197 mL), *trans*-**10b** (0.2334 g, 0.3940 mmol), and Pd/C (0.0174 g of 10% w/w, 0.0164 mmol Pd, 4.2 mol %) were combined in a procedure similar to that for *trans*-**11a**. An analogous workup gave *trans*-**11b** as an off-white solid (0.1761 g, 0.3109 mmol, 79%). Mp (capillary): 242−244 °C dec. Anal. Calcd for C$_{18}$H$_{24}$Cl$_2$N$_2$O$_2$Pt: C, 38.17; H, 4.27; N, 4.95. Found: C, 38.57; H, 4.29; N, 4.96. NMR ($\delta$, CDCl$_3$): $^1$H 8.91 (m, 2H, *o*-*HC*$_{6pyr}$), 7.76 (m, 2H, *p*-*HC*$_{4pyr}$), 7.63 (m, 2H, *m*-*HC*$_{3pyr}$), 7.24 (m, 2H, *m*-*HC*$_{5pyr}$), 5.77 (s, 4H, C*H*$_2$O), 3.87 (t, 4H, $^3J_{HH}$ = 6.4 Hz, OC*H*$_2$CH$_2$), 1.89 (m, 4H, OCH$_2$C*H*$_2$), 1.68 (m, 4H, OCH$_2$CH$_2$C*H*$_2$); $^{13}$C{$^1$H} 161.7 (s, *o*-*C*$_{2pyr}$), 153.5 (s, *o*-*C*$_{6pyr}$), 138.5 (s, *p*-*C*$_{4pyr}$), 124.1 (s, *m*-*C*$_{3pyr}$), 124.0 (s, *m*-*C*$_{5pyr}$), 71.8 (s, *C*H$_2$O), 70.2 (s, OCH$_2$CH$_2$), 27.3 (s, *C*H$_2$), 23.9 (s, *C*H$_2$). IR (cm$^{-1}$, powder film): 3061 (w), 2941 (m), 2859 (m), 1607 (m), 1570 (m), 1477 (m), 1229 (m), 1126 (s), 1101 (s), 787 (s), 768 (s), 719 (s).

***trans*-PtCl$_2$(3-NC$_5$H$_4$(CH$_2$OCH$_2$CH=CH$_2$))$_2$ (*trans*-12a).** Pyridine **2a** (1.2028 g, 8.0620 mmol) and PtCl$_2$ (1.0038 g, 3.7738 mmol) were combined in a procedure similar to that for *trans*-**10a**. An analogous workup gave *trans*-**12a** as a yellow solid (1.8265 g, 3.236 mmol, 86%). Mp (capillary): 120−121 °C. Anal. Calcd for C$_{18}$H$_{22}$Cl$_2$N$_2$O$_2$Pt: C, 38.31; H, 3.93; N, 4.96. Found: C, 38.28; H, 3.81; N, 4.96. NMR ($\delta$, CDCl$_3$): $^1$H 8.84 (m, 2H, *o*-*HC*$_{2pyr}$), 8.80 (m, 2H, *o*-*HC*$_{6pyr}$), 7.80 (m, 2H, *p*-*HC*$_{4pyr}$), 7.29 (m, 2H, *m*-*HC*$_{5pyr}$), 6.00−5.87 (ddt, 2H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.4 Hz, $^3J_{HH}$ = 6.8 Hz, C*H*=), 5.32−5.18 (m, 4H, =C*H*$_2$), 4.54 (s, 4H, C*H*$_2$O), 4.07 (m, 4H, OC*H*$_2$CH); $^{13}$C{$^1$H} 152.8 and 152.6 (2 s, *o*-*C*$_{2pyr}$ and *o*-*C*$_{6pyr}$), 137.6 (s, *C*H=), 136.6 (s, *p*-*C*$_{4pyr}$), 134.1 (s, *m*-*C*$_{3pyr}$), 125.1 (s, *m*-*C*$_{5pyr}$), 118.3 (s, =*C*H$_2$), 72.0 (s, *C*H$_2$O), 68.4 (s, OCH$_2$*C*H$_2$). IR (cm$^{-1}$, powder film): 2924 (w), 2857 (w), 1609 (w), 1423 (m), 1096 (s), 924 (s), 800 (s), 696 (s).

**PtCl$_2$(3-NC$_5$H$_4$(CH$_2$O(CH$_2$)$_2$CH=CH$_2$))$_2$ (12b).** Pyridine **2b** (1.3203 g, 8.0891 mmol) and PtCl$_2$ (1.0233 g, 3.8471 mmol) were combined in a procedure similar to that for *trans*-**10a**. An analogous workup gave *trans*-**12b** (1.1204 g, 1.8912 mmol, 49%; mp (capillary) 118−119 °C) and *cis*-**12b** (0.9764 g, 1.648 mmol, 43%; mp (capillary) 54−56 °C) as yellow solids. Anal. Calcd for C$_{20}$H$_{26}$Cl$_2$N$_2$O$_2$Pt: C, 40.55; H, 4.42; N, 4.73. Found (*trans*-**12b**): C, 40.50; H, 4.37; N, 4.71.

Data for *trans*-**12b** are as follows. NMR ($\delta$, CDCl$_3$): $^1$H 8.83 (m, 2H, *o*-*HC*$_{2pyr}$), 8.80 (m, 2H, *o*-*HC*$_{6pyr}$), 7.78 (m, 2H, *p*-*HC*$_{4pyr}$), 7.29 (m, 2H, *m*-*HC*$_{5pyr}$), 5.91−5.76 (ddt, 2H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.4 Hz, $^3J_{HH}$ = 6.8 Hz, C*H*=), 5.16−5.04 (m, 4H, =C*H*$_2$), 4.53 (s, 4H, C*H*$_2$O), 3.56 (t, 4H, $^3J_{HH}$ = 6.6 Hz, OC*H*$_2$CH$_2$), 2.39 (apparent qt, 4H, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH}$ = 1.4 Hz, C*H*$_2$CH=CH$_2$); $^{13}$C{$^1$H} 152.8 and 152.5 (2 s, *o*-*C*$_{2pyr}$ and *o*-*C*$_{6pyr}$), 137.5 (s, *C*H=), 136.7 (s, *p*-*C*$_{4pyr}$), 135.0 (s, *m*-*C*$_{3pyr}$), 125.1 (s, *m*-*C*$_{5pyr}$), 117.0 (s, =*C*H$_2$), 70.5 (s, *C*H$_2$O), 69.3 (s, OCH$_2$*C*H$_2$), 34.3 (s, *C*H$_2$). IR (cm$^{-1}$, powder film): 2943 (w), 2870 (m), 1641 (m), 1477 (m), 1436 (s), 1364 (m), 1101 (s), 927 (s), 799 (s).

Data for *cis*-**12b** are as follows. NMR ($\delta$, CDCl$_3$): $^1$H 8.85 (m, 4H, *o*-*HC*$_{2,6pyr}$), 7.75 (m, 2H, *p*-*HC*$_{4pyr}$), 7.27 (m, 2H, *m*-*HC*$_{5pyr}$), 5.84−5.70 (ddt, 2H, $^3J_{HHtrans}$ = 17.3 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*=), 5.12−5.01 (m, 4H, =C*H*$_2$), 4.47 (s, 4H, C*H*$_2$O), 3.50 (t, 4H, $^3J_{HH}$ = 6.6 Hz, OC*H*$_2$CH$_2$), 2.32 (apparent qt, 4H, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH}$ = 1.4 Hz, C*H*$_2$CH=CH$_2$); $^{13}$C{$^1$H} 152.1 and 151.7 (2 s, *o*-*C*$_{2pyr}$ and *o*-*C*$_{6pyr}$), 137.9 (s, *C*H=), 137.5 (s, *p*-*C*$_{4pyr}$), 134.9 (s, *m*-*C*$_{3pyr}$), 126.2 (s, *m*-*C*$_{5pyr}$), 117.0 (s, =*C*H$_2$), 70.6 (s, *C*H$_2$O), 69.0 (s, OCH$_2$*C*H$_2$), 34.2 (s, *C*H$_2$). IR (cm$^{-1}$, powder film): 3068 (w), 2904 (w), 2860 (w), 1608 (m), 1479 (m), 1437 (m), 1098 (s), 912 (s), 702 (s).

***trans*-PtCl$_2$(3-NC$_5$H$_4$(CH$_2$O(CH$_2$)$_3$CH=CH$_2$))$_2$ (*trans*-12c).** Pyridine **2c** (1.6721 g, 9.4338 mmol) and PtCl$_2$ (1.1893 g, 4.4711 mmol) were combined in a procedure similar to that for *trans*-**10a**. An analogous workup gave *trans*-**12c** as a yellow solid (2.3537 g, 3.793 mmol, 85%). Mp (capillary): 77−79 °C. Anal. Calcd for C$_{22}$H$_{30}$Cl$_2$N$_2$O$_2$Pt: C, 42.59; H, 4.87; N, 4.51. Found: C, 43.00; H, 4.78; N, 4.10. NMR ($\delta$, CDCl$_3$): $^1$H 8.84 (m, 2H, *o*-*HC*$_{2pyr}$), 8.81 (m, 2H, *o*-*HC*$_{6pyr}$), 7.78 (m, 2H, *p*-*HC*$_{4pyr}$), 7.29 (m, 2H, *m*-*HC*$_{5pyr}$), 5.86−5.78 (ddt, 2H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.1 Hz, $^3J_{HH}$ = 6.4 Hz, C*H*=), 5.07−4.97 (m, 4H, =C*H*$_2$), 4.52 (s, 4H, C*H*$_2$O), 3.52 (t, 4H, $^3J_{HH}$ = 6.4 Hz, OC*H*$_2$CH$_2$), 2.16 (m, 4H, C*H*$_2$CH=CH$_2$), 1.74 (m, 4H, OCH$_2$C*H*$_2$); $^{13}$C{$^1$H} 152.8 and 152.6 (2 s, *o*-*C*$_{2pyr}$ and *o*-*C*$_{6pyr}$), 138.2 (s, *C*H=), 137.4 (s, *p*-*C*$_{4pyr}$), 136.8 (s, *m*-*C*$_{3pyr}$), 125.1 (s, *m*-*C*$_{5pyr}$), 115.2 (s, =*C*H$_2$), 70.7 (s, *C*H$_2$O), 69.3 (s, OCH$_2$*C*H$_2$), 30.4 (s, *C*H$_2$), 29.0 (s, *C*H$_2$). IR (cm$^{-1}$, powder film): 2938 (m), 2872 (m), 1643 (m), 1611 (m), 1441 (m), 1366 (m), 1096 (s), 1078 (s), 988 (m), 926 (m), 816 (s), 698 (s), 638 (m).

***trans*-PtCl$_2$(3-NC$_5$H$_4$(CH$_2$O(CH$_2$)$_4$CH=CH$_2$))$_2$ (*trans*-12d).** Pyridine **2d** (2.2421 g, 11.722 mmol) and PtCl$_2$ (1.4588 g, 5.4844 mmol) were combined in a procedure similar to that for *trans*-**10a**. An analogous workup gave *trans*-**12d** as a yellow solid (2.9313 g, 4.5199 mmol, 82%). Mp (capillary): 85−87 °C. Anal. Calcd for C$_{24}$H$_{34}$Cl$_2$N$_2$O$_2$Pt: C, 44.45; H, 5.28; N, 4.32. Found: C, 44.71; H, 4.97; N, 4.24. NMR ($\delta$, CDCl$_3$): $^1$H 8.83 (m, 2H, *o*-*HC*$_{2pyr}$), 8.80 (m, 2H, *o*-*HC*$_{6pyr}$), 7.78 (m, 2H, *p*-*HC*$_{4pyr}$), 7.29 (m, 2H, *m*-*HC*$_{5pyr}$), 5.88−5.74 (ddt, 2H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*=), 5.06−4.93 (m, 4H, =C*H*$_2$), 4.51 (s, 4H, C*H*$_2$O), 3.50 (t, 4H, $^3J_{HH}$ = 6.4 Hz, OC*H*$_2$CH$_2$), 2.08 (m, 4H, C*H*$_2$CH=CH$_2$), 1.65 (m, 4H, OCH$_2$C*H*$_2$),


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1.48 (m, 4H, $OCH_2CH_2CH_2$); $^{13}C\{^1H\}$ 152.7 and 152.5 (2 s, *o*-$C_{2pyr}$ and *o*-$C_{6pyr}$), 138.8 (s, CH═), 137.4 (s, *p*-$C_{4pyr}$), 136.8 (s, *m*-$C_{3pyr}$), 125.1 (s, *m*-$C_{5pyr}$), 114.9 (s, ═$CH_2$), 71.2 (s, $CH_2O$), 69.3 (s, $OCH_2CH_2$), 33.7, 29.2, and 25.6 (3 s, $3CH_2$). IR ($cm^{-1}$, powder film): 2934 (m), 2872 (m), 1641 (w), 1611 (w), 1483 (w), 1439 (m), 1369 (m), 1084 (s), 995 (m), 920 (s), 808 (s), 698 (s), 650 (m).

***trans*-$PtCl_2$(3-$NC_5H_4(CH_2O(CH_2)_5CH═CH_2)$)$_2$ (*trans*-12e).** Pyridine **2e** (1.5794 g, 7.6913 mmol) and $PtCl_2$ (0.9657 g, 3.630 mmol) were combined in a procedure similar to that for *trans*-**10a**. An analogous workup gave *trans*-**12e** as a yellow solid (2.2861 g, 3.3789 mmol, 93%). Mp (capillary): 86−88 °C. Anal. Calcd for $C_{26}H_{38}Cl_2N_2O_2Pt$: C, 46.16; H, 4.91; N, 4.14. Found: C, 46.21; H, 4.91; N, 4.11. NMR (*δ*, $CDCl_3$): $^1H$ 8.83 (m, 2H, *o*-$HC_{2pyr}$), 8.80 (m, 2H, *o*-$HC_{6pyr}$), 7.78 (m, 2H, *p*-$HC_{4pyr}$), 7.28 (m, 2H, *m*-$HC_{5pyr}$), 5.85−5.77 (ddt, 2H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.1 Hz, $^3J_{HH}$ = 6.9 Hz, CH═), 5.02−4.92 (m, 4H, ═$CH_2$), 4.51 (s, 4H, $CH_2O$), 3.49 (t, 4H, $^3J_{HH}$ = 6.4 Hz, $OCH_2CH_2$), 2.06 (m, 4H, $CH_2CH═CH_2$), 1.63 (m, 4H, $OCH_2CH_2$), 1.44−1.36 (m, 8H, $CH_2$); $^{13}C\{^1H\}$ 152.7 and 152.5 (2 s, *o*-$C_{2pyr}$ and *o*-$C_{6pyr}$), 139.1 (s, CH═), 137.4 (s, *p*-$C_{4pyr}$), 136.9 (s, *m*-$C_{3pyr}$), 125.0 (s, *m*-$C_{5pyr}$), 114.6 (s, ═$CH_2$), 71.4 (s, $CH_2O$), 69.3 (s, $OCH_2CH_2$), 33.9, 29.7, 28.9, and 25.8 (4 s, $4CH_2$). IR ($cm^{-1}$, powder film): 2931 (m), 2872 (m), 2851 (m), 1643 (w), 1610 (w), 1440 (m), 1089 (s), 986 (m), 924 (s), 816 (s), 698 (s), 648 (m).

**$PtCl_2$(3-$NC_5H_4(CH_2O(CH_2)_8CH═CH_2)$)$_2$ (12h).** Pyridine **2h** (1.0658 g, 4.3084 mmol) and $PtCl_2$ (0.5188 g, 1.950 mmol) were combined in a procedure similar to that for *trans*-**10a**. An analogous workup gave *trans*-**12h** (0.6785 g, 0.8919 mmol, 46%; mp (capillary) 101−102 °C) and *cis*-**5h** (0.6558 g, 0.8621 mmol, 44%) as yellow solids. Anal. Calcd for $C_{32}H_{50}Cl_2N_2O_2Pt$: C, 50.52; H, 6.62; N, 3.68. Found (*trans*-**12h**): C, 50.64; H, 5.78; N, 3.53.[45]

Data for *trans*-**12h** are as follows. NMR (*δ*, $CDCl_3$): $^1H$ 8.83 (m, 2H, *o*-$HC_{2pyr}$), 8.80 (m, 2H, *o*-$HC_{6pyr}$), 7.79 (m, 2H, *p*-$HC_{4pyr}$), 7.29 (m, 2H, *m*-$HC_{5pyr}$), 5.88−5.74 (ddt, 2H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.4 Hz, $^3J_{HH}$ = 6.6 Hz, CH═), 5.03−4.89 (m, 4H, ═$CH_2$), 4.51 (s, 4H, $CH_2O$), 3.49 (t, 4H, $^3J_{HH}$ = 6.6 Hz, $OCH_2CH_2$), 2.04 (m, 4H, $CH_2CH═CH_2$), 1.62 (m, 4H, $OCH_2CH_2$), 1.44−1.25 (m, 24H, $CH_2$); $^{13}C\{^1H\}$ 152.7 and 152.5 (2 s, *o*-$C_{2pyr}$ and *o*-$C_{6pyr}$), 139.4 (s, CH═), 137.5 (s, *p*-$C_{4pyr}$), 136.9 (s, *m*-$C_{3pyr}$), 125.1 (s, *m*-$C_{5pyr}$), 114.3 (s, ═$CH_2$), 71.5 (s, $CH_2O$), 69.3 (s, $OCH_2CH_2$), 34.0, 29.8, 29.6 (2×), 29.3, 29.1, and 26.3 (6 s, $7CH_2$). IR ($cm^{-1}$, powder film): 2918 (m), 2849 (m), 2357 (w), 1641 (w), 1464 (w), 1439 (w), 1369 (m), 1258 (w), 1227 (w), 1093 (s), 926 (s), 810 (s), 698 (s), 644 (m).

Data for *cis*-**12h** are as follows. NMR (*δ*, $CDCl_3$): $^1H$ 8.89 (m, 2H, *o*-$HC_{2pyr}$), 8.86 (m, 2H, *o*-$HC_{6pyr}$), 7.73 (m, 2H, *p*-$HC_{4pyr}$), 7.26 (m, 2H, *m*-$HC_{5pyr}$), 5.85−5.71 (ddt, 2H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.2 Hz, $^3J_{HH}$ = 6.6 Hz, CH═), 5.00−4.87 (m, 4H, ═$CH_2$), 4.42 (s, 4H, $CH_2O$), 3.41 (t, 4H, $^3J_{HH}$ = 6.6 Hz, $OCH_2CH_2$), 2.06−1.97 (m, 4H, $CH_2CH═CH_2$), 1.59−1.48 (m, 4H, $OCH_2CH_2$), 1.40−1.22 (m, 24H, $CH_2$); $^{13}C\{^1H\}$ 152.1 and 151.7 (2 s, *o*-$C_{2pyr}$ and *o*-$C_{6pyr}$), 139.3 (s, CH═), 138.0 (s, *p*-$C_{4pyr}$), 137.4 (s, *m*-$C_{3pyr}$), 126.1 (s, *m*-$C_{5pyr}$), 114.3 (s, ═$CH_2$), 71.5 (s, $CH_2O$), 68.9 (s, $OCH_2CH_2$), 33.9, 29.7, 29.5 (2×), 29.2, 29.0, and 26.2 (6 s, $7CH_2$).

***trans*-$PtCl_2$(3-$NC_5H_4(CH_2O(CH_2)_9CH═CH_2)$)$_2$ (*trans*-12i).** Pyridine **2i** (1.4690 g, 5.6196 mmol) and $PtCl_2$ (0.7101 g, 2.670 mmol) were combined in a procedure similar to that for *trans*-**10a**. An analogous workup gave *trans*-**12i** as a yellow solid (1.8760 g, 2.3783 mmol, 89%). Mp (capillary): 102−103 °C. Anal. Calcd for $C_{34}H_{54}Cl_2N_2O_2Pt$: C, 51.77; H, 6.90; N, 3.55. Found: C, 51.71; H, 6.00; N, 3.40.[45] NMR (*δ*, $CDCl_3$): $^1H$ 8.83 (m, 2H, *o*-$HC_{2pyr}$), 8.80 (m, 2H, *o*-$HC_{6pyr}$), 7.79 (m, 2H, *p*-$HC_{4pyr}$), 7.29 (m, 2H, *m*-$HC_{5pyr}$), 5.85−5.77 (ddt, 2H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.1 Hz, $^3J_{HH}$ = 6.9 Hz, CH═), 5.01−4.91 (m, 4H, ═$CH_2$), 4.51 (s, 4H, $CH_2O$), 3.49 (t, 4H, $^3J_{HH}$ = 6.4 Hz, $OCH_2CH_2$), 2.03 (m, 4H, $CH_2CH═CH_2$), 1.62 (m, 4H, $OCH_2CH_2$), 1.40−1.26 (m, 24H, $CH_2$); $^{13}C\{^1H\}$ 152.7 and 152.5 (2 s, *o*-$C_{2pyr}$ and *o*-$C_{6pyr}$), 139.5 (s, CH═), 137.4 (s, *p*-$C_{4pyr}$), 136.9 (s, *m*-$C_{3pyr}$), 125.1 (s, *m*-$C_{5pyr}$), 114.3 (s, ═$CH_2$), 71.5 (s, $CH_2O$), 69.3 (s, $OCH_2CH_2$), 34.0, 29.8, 29.7, 29.6 (2×), 29.3, 29.1, and 26.3 (7 s, $8CH_2$). IR ($cm^{-1}$, powder film): 2920 (s), 2847 (s), 2324 (w), 1641 (w), 1611 (w), 1462 (m), 1366 (m), 1096 (s), 920 (s), 810 (s), 700 (s).

***trans*-$PtCl_2$[3,3′-($NC_5H_4(CH_2O(CH_2)_{10}OCH_2)H_4C_5N$)] (*trans*-13d).** Grubbs' catalyst (0.0254 g, 0.0306 mmol, 3.9 mol %), $CH_2Cl_2$ (398 mL), *trans*-**12d** (0.5158 g, 0.7953 mmol), and Pd/C (0.0423 g of 10% w/w, 0.0398 mmol Pd, 5.0 mol %) were combined in a procedure similar to that for *trans*-**11a**. An analogous workup gave *trans*-**13d** as a light yellow solid (0.4615 g, 0.7414 mmol, 93%). Mp (capillary): 204−208 °C. Anal. Calcd for $C_{22}H_{32}Cl_2N_2O_2Pt$: C, 42.45; H, 5.18; N, 4.50. Found: C, 42.52; H, 4.78; N, 4.45. NMR (*δ*, $CDCl_3$): $^1H$ 9.05 (m, 2H, *o*-$HC_{2pyr}$), 8.82 (m, 2H, *o*-$HC_{6pyr}$), 7.54 (m, 2H, *p*-$HC_{4pyr}$), 7.23 (m, 2H, *m*-$HC_{5pyr}$), 4.53 (s, 4H, $CH_2O$), 3.54 (t, 4H, $^3J_{HH}$ = 5.7 Hz, $OCH_2CH_2$), 1.64 (m, 4H, $OCH_2CH_2$), 1.56 (m, 4H, $O(CH_2)_2CH_2$), 1.45−1.35 (m, 8H, $CH_2$); $^{13}C\{^1H\}$ 153.1 and 152.5 (2 s, *o*-$C_{2pyr}$ and *o*-$C_{6pyr}$), 136.8 (s, *p*-$C_{4pyr}$), 136.5 (s, *m*-$C_{3pyr}$), 124.5 (s, *m*-$C_{5pyr}$), 71.3 (s, $CH_2O$), 69.6 (s, $OCH_2CH_2$), 30.1, 29.8, 29.4, and 26.5 (4 s, $4CH_2$). IR ($cm^{-1}$, powder film): 2922 (m), 2853 (m), 1609 (w), 1439 (m), 1358 (m), 1315 (m), 1103 (s), 802 (s), 698 (s).

***trans*-$PtCl_2$[3,3′-($NC_5H_4(CH_2O(CH_2)_{18}OCH_2)H_4C_5N$)] (*trans*-13h).** Grubbs' catalyst (0.0237 g, 0.0288 mmol, 5.0 mol %), $CH_2Cl_2$ (290 mL), *trans*-**12h** (0.4409 g, 0.5796 mmol), and Pd/C (0.0316 g of 10% w/w, 0.0297 mmol Pd, 5.1 mol %) were combined in a procedure similar to that for *trans*-**11a**. An analogous workup gave *trans*-**13h** as a yellow solid (0.3398 g, 0.4625 mmol, 80%). Mp (capillary): 131−134 °C. Anal. Calcd for $C_{30}H_{48}Cl_2N_2O_2Pt$: C, 49.04; H, 6.59; N, 3.81. Found: C, 49.16; H, 5.82; N, 3.75.[45] NMR (*δ*, $CDCl_3$): $^1H$ 8.93 (m, 2H, *o*-$HC_{2pyr}$), 8.82 (m, 2H, *o*-$HC_{6pyr}$), 7.71 (m, 2H, *p*-$HC_{4pyr}$), 7.28 (m, 2H, *m*-$HC_{5pyr}$), 4.51 (s, 4H, $CH_2O$), 3.50 (t, 4H, $^3J_{HH}$ = 6.7 Hz, $OCH_2CH_2$), 1.63 (m, 4H, $OCH_2CH_2$), 1.41−1.24 (m, 28H, $CH_2$); $^{13}C\{^1H\}$ 153.1 and 152.8 (2 s, *o*-$C_{2pyr}$ and *o*-$C_{6pyr}$), 137.5 (s, *p*-$C_{4pyr}$), 136.8 (s, *m*-$C_{3pyr}$), 124.9 (s, *m*-$C_{5pyr}$), 71.4 (s, $CH_2O$), 69.5 (s, $OCH_2CH_2$), 29.7, 29.4 (5 × ), 29.3, and 26.1 (4 s, $8CH_2$). IR ($cm^{-1}$, powder film): 2924 (s), 2851 (s), 1611 (w), 1435 (m), 1364 (m), 1103 (s), 800 (s), 692 (s).

***trans*-$PtCl_2$[3,3′-($NC_5H_4(CH_2O(CH_2)_{20}OCH_2)H_4C_5N$)] (*trans*-13i).** Grubbs' catalyst (two charges 24 h apart, 0.0219 and 0.0196 g, 0.0505 mmol, 7.6 mol %), $CH_2Cl_2$ (334 mL), *trans*-**12i** (0.5273 g. 0.6685 mmol), and Pd/C (0.0363 g of 10% w/w, 0.0341 mmol Pd, 5.1 mol %) were combined in a procedure similar to that for *trans*-**11a**. An analogous workup gave *trans*-**13i** as an off-white solid (0.4581 g, 0.6006 mmol, 90%). Mp (capillary): 134−136 °C. Anal. Calcd for $C_{32}H_{52}Cl_2N_2O_2Pt$: C, 50.39; H, 6.87; N, 3.67. Found: C, 50.40; H, 6.75; N, 3.55. NMR (*δ*, $CDCl_3$): $^1H$ 8.91 (m, 2H, *o*-$HC_{2pyr}$), 8.81 (m, 2H, *o*-$HC_{6pyr}$), 7.72 (m, 2H, *p*-$HC_{4pyr}$), 7.28 (m, 2H, *m*-$HC_{5pyr}$), 4.52 (s, 4H, $CH_2O$), 3.49 (t, 4H, $^3J_{HH}$ = 6.4 Hz, $OCH_2CH_2$), 1.63 (m, 4H, $OCH_2CH_2$), 1.40−1.22 (m, 32H, $CH_2$); $^{13}C\{^1H\}$ 153.0 and 152.8 (2 s, *o*-$C_{2pyr}$ and *o*-$C_{6pyr}$), 137.5 (s, *p*-$C_{4pyr}$), 136.8 (s, *m*-$C_{3pyr}$), 124.9 (s, *m*-$C_{5pyr}$), 71.3 (s, $CH_2O$), 69.4 (s, $OCH_2CH_2$), 29.7, 29.5 (5 × ), 29.4, 29.3, and 26.1 (5 s, $9CH_2$). IR ($cm^{-1}$, powder film): 2922 (s), 2851 (s), 2341 (w), 2160 (w), 2039 (w), 1981 (w), 1476 (w), 1458 (w), 1435 (m), 1103 (s), 800 (s), 692 (s).

***trans*-$PdCl_2$[2,6-$NC_5H_3(CH_2CH_2CH═CH_2)_2]_2$ (*trans*-14).**[8] A Schlenk flask was charged with *trans*-$(PhCN)_2PdCl_2$ (0.527 g, 1.37 mmol), benzene (15 mL), and **3** (0.565 g, 3.02 mmol) and fitted with a condenser. The solution was refluxed (40 min). A black precipitate formed after 5 min. The mixture was cooled to room temperature and filtered. The solvent was removed by rotary evaporation. The residue was chromatographed on a silica column (30 × 1 cm, 3/1 v/v hexanes/$CH_2Cl_2$). The solvents were removed from the product-containing fractions by rotary evaporation and oil pump vacuum to give *trans*-**14** as a yellow solid (0.112 g, 0.203 mmol, 15%). NMR (*δ*, $CDCl_3$): $^1H$ 7.61 (t, 2H, $^3J_{HH}$ = 7.7 Hz, *p*-$HC_{4pyr}$), 7.12 (d, 4H, $^3J_{HH}$ = 7.7 Hz, *m*-$HC_{3,5pyr}$), 6.05 (ddt, 4H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.4 Hz, $^3J_{HH}$ = 6.5 Hz, CH═), 5.23 (dd, 4H, $^3J_{HHtrans}$ = 17.1 Hz, $^2J_{HH}$ = 1.6 Hz, ═$CH_EH_Z$), 5.14 (dd, 4H, $^3J_{HHcis}$ = 10.2 Hz, $^2J_{HH}$ = 1.1 Hz, ═$CH_EH_Z$), 4.42 (t, 8H, $^3J_{HH}$ = 7.5 Hz, $CH_2$), 2.85 (q, 8H, $^3J_{HH}$ = 7.2 Hz, $CH_2$); $^{13}C\{^1H\}$ 163.3 (s, *o*-$C_{2,6pyr}$), 138.2 (s, *p*-$C_{4pyr}$), 136.8 (s, CH═), 122.2 (s, *m*-$C_{3,5pyr}$), 116.4 (s, ═$CH_2$), 38.7 (s, $CH_2$), 32.1 (s, $CH_2$). IR ($cm^{-1}$, powder film): 3080 (m), 2964 (m), 2868 (m), 2934 (m), 2856 (m), 1644 (m), 1606 (m), 1575 (m), 1471 (s), 1262 (s), 1096 (s),


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915 (s), 807 (s). MS:[41] 517 ([**14** − Cl]$^+$, 30%), 292 (unknown, 100%), 188 ([**3** + H]$^+$, 80%).

***trans*-PdCl$_2$[2,6,2′,6′-(NC$_5$H$_3$((CH$_2$)$_2$CH═CH(CH$_2$)$_2$)$_2$H$_3$C$_5$N)] (*trans*-15).**[8] A two-necked round-bottom flask was charged with *trans*-**14** (0.108 g, 0.196 mmol) and $CH_2Cl_2$ (5 mL). A solution of Grubbs' catalyst (0.0081 g, 0.098 mmol, 5.0 mol %) in $CH_2Cl_2$ (1.5 mL) was added dropwise over 10 min with stirring (the resulting solution is 0.0301 M in *trans*-**14**). A precipitate formed after 20 min. After 6 h, a second charge of Grubbs' catalyst (0.0081 g, 5.0 mol %) was added as a solid. After 18 h, a final charge of Grubbs' catalyst (0.0081 g, 5.0 mol %) was added. The mixture was stirred for an additional 6 h. Water (15 mL) and $CH_2Cl_2$ (15 mL) were added. After 30 min, the organic layer was separated. The aqueous layer was extracted with $CH_2Cl_2$ (3 × 15 mL). The organic layer and the extracts were combined, dried ($MgSO_4$), and concentrated by rotary evaporation. The residue was chromatographed on a silica column (25 × 1 cm, 7/3 v/v hexanes/ethyl acetate). The solvents were removed from the product-containing fractions by rotary evaporation and oil pump vacuum to give *trans*-**15** as a light yellow solid (0.0563 g, 0.114 mmol, 58%). $^1$H NMR ($\delta$, $CDCl_3$): 7.62 (t, 2H, $^3J_{HH}$ = 7.7 Hz, *p*-$HC_{4pyr}$), 7.12 (d, 4H, $^3J_{HH}$ = 7.7 Hz, *m*-$HC_{3,5pyr}$), 6.05−5.97 (m, 4H, C*H*═), 4.00 (t, 8H, $^3J_{HH}$ = 7.5 Hz, $CH_2$), 3.28−3.18 (m, 8H, $CH_2$).

***trans*-PdCl$_2$[2,6,2′,6′-(NC$_5$H$_3$((CH$_2$)$_6$)$_2$H$_3$C$_5$N)] (*trans*-16).** A round-bottom flask was charged with **15** (0.0702 g, 0.142 mmol), $PtO_2$ (0.0048 g, 0.021 mmol, 15 mol %), and $CH_2Cl_2$ (14 mL), flushed with $H_2$, and fitted with a balloon of $H_2$ (1.0 atm). The mixture was stirred (3 days). The solvent was removed by rotary evaporation. The residue was chromatographed on alumina (10 × 2 cm column, $CH_2Cl_2$). The solvent was removed from the product-containing fractions by rotary evaporation and oil pump vacuum to give *trans*-**16** as a light yellow solid (0.044 g, 0.088 mmol, 62%). The sample slightly darkened at 150 °C. TGA: onset of mass loss, 159.6 °C. Anal. Calcd for $C_{22}H_{30}Cl_2N_2Pd$: C, 52.87; H 6.05; N 5.60. Found: C, 52.42; H, 6.60; N, 4.88. NMR ($\delta$, $CDCl_3$): $^1$H 7.54 (t, 2H, $^3J_{HH}$ = 7.7 Hz, *p*-$HC_{4pyr}$), 7.11 (d, 4H, $^3J_{HH}$ = 7.7 Hz, *m*-$HC_{3,5pyr}$), 3.94−3.89 (m, 8H, $CH_2$), 2.72−2.55 (m, 8H, $CH_2$), 2.02−1.85 (m, 8H, $CH_2$); $^{13}$C{$^1$H} 165.1 (s, *o*-$C_{2,6pyr}$), 139.0 (s, *p*-$C_{4pyr}$), 123.8 (s, *m*-$C_{3,5pyr}$), 40.6 (s, $CH_2$), 26.3 (s, $CH_2$), 25.2 (s, $CH_2$). IR (cm$^{-1}$, powder film): 3069 (w), 2961 (m), 2926 (m), 2868 (m), 1644 (m), 1606 (m), 1575 (m), 1463 (s), 1262 (m), 1092 (s), 1019 (s), 915 (s), 791 (s), 757 (s). MS:[41] 501 (**16**$^+$, 60%), 486 (unknown, 100%), 428 ([**16** − 2Cl]$^+$, 20%).

***trans*-PtCl$_2$[2,6-NC$_5$H$_3$(CH$_2$OCH$_2$CH═CH$_2$)$_2$]$_2$ (*trans*-17a).** A Schlenk flask was charged with $PtCl_2$ (0.513 g, 1.93 mmol), benzene (19 mL), and **4a** (0.930 g, 4.24 mmol) and fitted with a condenser. The mixture was refluxed with stirring (5 days; after 2 days, a yellow solution had formed) and cooled to room temperature. The solvent was removed by rotary evaporation and the residue chromatographed on a silica column (10 × 2 cm, $CH_2Cl_2$). A single yellow band was collected. The solvent was removed by rotary evaporation. Hexanes was added (10 mL). The residue was collected by filtration, washed with hexanes (10 × 3 mL), and dried overnight by oil pump vacuum to give *trans*-**17a** as a yellow solid (1.196 g, 1.698 mmol, 88%). Mp (capillary): 148−150 °C. DSC ($T_i$/$T_e$/$T_p$/$T_c$/$T_f$): 107.5/152.0/154.9/156.5/168.3 °C (endotherm). TGA: onset of mass loss, 163.1 °C. Anal. Calcd for $C_{26}H_{34}Cl_2N_2O_4Pt$: C, 44.32; H, 4.86; N, 3.98. Found: C, 43.39; H, 4.86; N, 3.79.[45] NMR ($\delta$, $CDCl_3$): $^1$H 7.78 (t, 2H, $^3J_{HH}$ = 7.9 Hz, *p*-$HC_{4pyr}$), 7.58 (d, 4H, $^3J_{HH}$ = 7.9 Hz, *m*-$HC_{3,5pyr}$), 6.04 (ddt, 2H, $^3J_{HHtrans}$ = 17.2 Hz, $^3J_{HHcis}$ = 10.6 Hz, $^3J_{HH}$ = 5.4 Hz, C*H*═), 5.82 (s, 8H, $CH_2O$), 5.44 (dd, 4H, $^3J_{HHtrans}$ = 17.2 Hz, $^2J_{HH}$ = 1.6 Hz, ═$CH_EH_Z$), 5.30 (dd, 4H, $^3J_{HHcis}$ = 10.4 Hz, $^2J_{HH}$ = 1.5 Hz, ═$CH_EH_Z$), 4.27 (dt, 8H, $^3J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 1.5 Hz, $OCH_2$); $^{13}$C{$^1$H} 161.5 (s, *o*-$C_{2,6pyr}$), 139.0 (s, *p*-$C_{4pyr}$), 134.0 (s, CH═), 121.5 (s, *m*-$C_{3,5pyr}$), 117.9 (s, ═$CH_2$), 72.2 and 71.3 (2 s, $CH_2OCH_2$). IR (cm$^{-1}$, powder film): 3092 (w), 3015 (w), 2868 (m), 2837 (m), 1613 (m), 1471 (m), 1332 (m), 1239 (w), 1123 (s), 1107 (s), 911 (s), 787 (s). MS:[41] 705 (**17a**$^+$, 10%), 669 ([**17a** − Cl]$^+$, 40%), 220 ([**4a** + H]$^+$, 100%).

***trans*-PtCl$_2$[2,6-NC$_5$H$_3$(CH$_2$O(CH$_2$)$_2$CH═CH$_2$)$_2$]$_2$ (*trans*-17b).** A Schlenk flask was charged with $PtCl_2$ (0.477 g, 1.79 mmol), benzene (15 mL), and **4b** (0.914 g, 3.70 mmol) and fitted with a condenser. The mixture was refluxed with stirring (7 days; after 4 days, a yellow solution had formed) and cooled to room temperature. The solvent was removed by rotary evaporation, and the residue was chromatographed on a silica column (20 × 2 cm, 4/1 v/v hexanes/ethyl acetate). The solvents were removed by rotary evaporation from the product-containing fractions. Hexanes was added (15 mL). The residue was collected by filtration, washed with hexanes (10 × 3 mL), and dried overnight by oil pump vacuum to give *trans*-**17b** as a yellow solid (0.354 g, 0.465 mmol, 26%). Mp (capillary): 106−108 °C. DSC ($T_i$/$T_e$/$T_p$/$T_c$/$T_f$): 90.7/109.9/110.8/112.1/135.3 °C (endotherm). TGA: onset of mass loss, 167.9 °C. Anal. Calcd for $C_{30}H_{42}Cl_2N_2O_4Pt$: C, 47.37; H, 5.57; N, 3.68. Found: C, 47.25; H, 5.55; N, 3.62. NMR ($\delta$, $CDCl_3$): $^1$H 7.78 (t, 2H, $^3J_{HH}$ = 7.9 Hz, *p*-$HC_{4pyr}$), 7.58 (d, 4H, $^3J_{HH}$ = 7.9 Hz, *m*-$HC_{3,5pyr}$), 5.94 (ddt, 4H, $^3J_{HHtrans}$ = 17.1 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.8 Hz, C*H*═), 5.81 (s, 8H, $CH_2O$), 5.19 (dd, 4H, $^3J_{HHtrans}$ = 17.2 Hz, $^2J_{HH}$ = 1.8 Hz, ═$CH_EH_Z$), 5.12 (dd, 4H, $^3J_{HHcis}$ = 10.2 Hz, $^2J_{HH}$ = 1.8 Hz, ═$CH_EH_Z$), 3.84 (t, 8H, $^3J_{HH}$ = 6.6 Hz, $OCH_2$), 2.55−2.50 (m, 8H, $CH_2$); $^{13}$C{$^1$H} 161.3 (s, *o*-$C_{2,6pyr}$), 138.9 (s, *p*-$C_{4pyr}$), 134.8 (s, CH═), 121.5 (s, *m*-$C_{3,5pyr}$), 116.9 (s, ═$CH_2$), 71.9 (s, $CH_2O$), 70.9 (s, $OCH_2CH_2$), 34.2 (s, $CH_2$). IR (cm$^{-1}$, powder film): 3074 (w), 2981 (w), 2866 (m), 1613 (m), 1475 (m), 1352 (m), 1120 (s), 1027 (m), 911 (s), 796 (s). MS:[41] 760 (**17b**$^+$, 5%), 725 ([**17b** − Cl]$^+$, 30%), 248 ([**4b** + H]$^+$, 100%).

***trans*-PtCl$_2$[2,6,2′,6′-(NC$_5$H$_3$(CH$_2$O(CH$_2$)$_4$OCH$_2$)$_2$H$_3$C$_5$N)] (*trans*-18a).** A two-necked round-bottom flask was charged with *trans*-**17a** (0.250 g, 0.355 mmol) and $CH_2Cl_2$ (173 mL), fitted with a condenser, and flushed with $N_2$. A solution of Grubbs' catalyst (0.0292 g, 0.0355 mmol, 10 mol %) in $CH_2Cl_2$ (5 mL) was added dropwise over 30 min with stirring (the resulting solution is 0.001 99 M in *trans*-**17a**). The mixture was refluxed (24 h). A precipitate formed after 30 min. The mixture was cooled to room temperature, and the solvent was removed by rotary evaporation. The residue was chromatographed on alumina (15 × 2 cm column, $CH_2Cl_2$). A single light yellow band was collected. The solvent was removed by rotary evaporation and oil pump vacuum. A round-bottom flask was charged with the crude metathesis product, 10% Pd/C (0.0263 g, 0.0246 mmol of Pd), toluene (10 mL), and ethanol (10 mL), flushed with $H_2$, and fitted with a balloon of $H_2$ (1.0 atm). The mixture was stirred (3 days) and passed through a pad of Celite (7 × 2 cm, rinsed with $CH_2Cl_2$). The filtrate was concentrated by oil pump vacuum (to ca. 1 mL), carefully layered with hexanes (20 mL), and kept at −4 °C. After 24 h, the supernatant was carefully decanted, and the precipitate was dried by oil pump vacuum to give *trans*-**18a** as an off-white solid (0.0221 g, 0.0338 mmol, 10%). The sample slightly darkened at 150 °C. TGA: onset of mass loss, 160.0 °C. Anal. Calcd for $C_{22}H_{30}Cl_2N_2O_4Pt$: C, 40.50; H, 4.63; N, 4.29. Found: C, 41.08; H, 4.95; N, 4.04. NMR ($\delta$, $CDCl_3$): $^1$H 7.80 (t, 2H, $^3J_{HH}$ = 7.7 Hz, *p*-$HC_{4pyr}$), 7.53 (d, 4H, $^3J_{HH}$ = 7.7 Hz, *m*-$HC_{3,5pyr}$), 5.95 (s, 8H, $CH_2O$), 3.97−3.94 (m, 8H, $OCH_2CH_2$), 2.08−2.13 (m, 8H, $CH_2$); $^{13}$C{$^1$H} 161.0 (s, *o*-$C_{2,6pyr}$), 139.5 (s, *p*-$C_{4pyr}$), 125.6 (s, *m*-$C_{3,5pyr}$), 72.5 and 69.9 (2 s, $CH_2OCH_2$), 24.5 (s, $CH_2$). IR (cm$^{-1}$, powder film): 2941 (w), 2914 (w), 2856 (m), 1610 (m), 1471 (m), 1370 (m), 1212 (m), 1123 (s), 1108 (s), 984 (s), 803 (s). MS:[41] 617 ([**18a** − Cl]$^+$, 30%), 580 (unknown, 100%).

***trans*-PtCl$_2$[2,6,2′,6′-(NC$_5$H$_3$(CH$_2$O(CH$_2$)$_6$OCH$_2$)$_2$H$_3$C$_5$N)] (*trans*-18b).** Solutions of *trans*-**17b** (0.250 g, 0.328 mmol) in $CH_2Cl_2$ (160 mL) and of Grubbs' catalyst (0.027 g, 0.0328 mmol, 10 mol %) in $CH_2Cl_2$ (4 mL) were combined in a procedure similar to that for *trans*-**18a** (the resulting solution is 0.002 01 M in *trans*-**17b**). After hydrogenation, an analogous workup gave *trans*-**18b** as a white solid (0.0501 g, 0.0706 mmol, 22% overall). The sample slightly darkened at 200 °C. DSC ($T_i$/$T_e$/$T_p$/$T_c$/$T_f$): 126.7/166.3/170.1/174.7/182.0 °C (endotherm). TGA: onset of mass loss, 231.6 °C. Anal. Calcd for $C_{26}H_{38}Cl_2N_2O_4Pt$: C, 44.07; H, 5.41; N, 3.95. Found: C, 43.51; H, 5.31; N, 3.66. NMR ($\delta$, $CDCl_3$): $^1$H 7.79 (t, 2H, $^3J_{HH}$ = 7.8 Hz, *p*-$HC_{4pyr}$), 7.56 (d, 4H, $^3J_{HH}$ = 7.8 Hz, *m*-$HC_{3,5pyr}$), 5.90 (s, 8H, $CH_2O$), 3.89 (t, 8H, $^3J_{HH}$ = 6.5 Hz, $OCH_2$), 1.92−1.89 (m, 8H, $CH_2$), 1.70−1.68 (m, 8H, $CH_2$); $^{13}$C{$^1$H} 161.5 (s, *o*-$C_{2,6pyr}$), 138.9 (s, *p*-$C_{4pyr}$), 121.5 (s, *m*-$C_{3,5pyr}$), 70.7 and 69.6 (2 s, $CH_2OCH_2$), 26.1 (s, $CH_2$), 23.0 (s, $CH_2$). IR (cm$^{-1}$, powder film): 2943 (w), 2866 (w),

1614 (m), 1468 (m), 1367 (m), 1213 (w), 1112 (s), 1012 (m), 965 (m), 811 (s). MS:[41] 709 (**18b**$^+$, 60%), 673 ([**18b** − Cl]$^+$, 50%), 636 (unknown, 100%).

***trans*-PtCl$_2$[3,5-NC$_5$H$_3$(COOCH$_2$CH=CH$_2$)$_2$]$_2$ (*trans*-19a).** A Schlenk flask was charged with **5a** (0.790 g, 3.198 mmol), PtCl$_2$ (0.4051 g, 1.523 mmol), and benzene (15 mL) and fitted with a condenser. The mixture was refluxed with stirring (12 h; after 1 h, a yellow solution had formed) and cooled to room temperature. The solvent was removed by rotary evaporation. The residue was chromatographed on a silica column (20 × 2 cm, 4/1 v/v hexanes/ethyl acetate). A single yellow band was collected. The solvent was removed by rotary evaporation. Hexanes was added (15 mL). The residue was collected by filtration, washed with hexanes (7 × 2 mL), and dried by oil pump vacuum to give *trans*-**19a** as a yellow solid (1.004 g, 1.321 mmol, 87%). Mp (capillary): 178−180 °C. TGA: onset of mass loss, 145.3 °C. Anal. Calcd for $C_{26}H_{26}Cl_2N_2O_8Pt$: C, 41.06; H, 3.45; N, 3.68. Found: C, 40.65; H, 3.18; N, 3.53. NMR ($\delta$, $CDCl_3$): $^1$H 9.68 (d, 4H, $^4J_{HH}$ = 1.8 Hz, *o*-$HC_{2,6pyr}$), 9.02 (t, 2H, $^4J_{HH}$ = 1.8 Hz, *p*-$HC_{4pyr}$), 6.05 (ddt, 4H, $^3J_{HHtrans}$ = 16.9 Hz, $^3J_{HHcis}$ = 10.6 Hz, $^3J_{HH}$ = 6.2 Hz, C*H*=), 5.47 (dd, 4H, $^3J_{HHtrans}$ = 17.2 Hz, $^2J_{HH}$ = 1.3 Hz, =C$H_EH_Z$), 5.39 (dd, 4H, $^3J_{HHcis}$ = 10.3 Hz, $^2J_{HH}$ = 1.1 Hz, =C$H_EH_Z$), 4.92 (dt, 8H, $^3J_{HH}$ = 5.9 Hz, $^4J_{HH}$ = 1.2 Hz, OC$H_2$); $^{13}$C{$^1$H} 162.1 (s, CO), 157.6 (*o*-$C_{2,6pyr}$), 140.1 (s, *p*-$C_{4pyr}$), 130.8 (s, CH=), 128.4 (s, *m*-$C_{3,5pyr}$), 120.0 (s, =$CH_2$), 67.1 (s, O$CH_2$). IR (cm$^{-1}$, powder film): 3082 (w), 2968 (m), 2895 (m), 1733 (s), 1652 (m), 1598 (m), 1447 (m), 1301 (s), 1251 (s), 1135 (s), 1112 (s), 980 (s), 911 (s), 745 (s). MS:[41] 760 (**19a**$^+$, 20%), 725 ([**19a** − Cl]$^+$, 18%).

***trans*-PtCl$_2$[3,5-NC$_5$H$_3$(COO(CH$_2$)$_3$CH=CH$_2$)$_2$]$_2$ (*trans*-19c).** Pyridine **5c** (1.000 g, 3.297 mmol), PtCl$_2$ (0.400 g, 1.50 mmol), and benzene (33 mL) were combined in a procedure similar to that for *trans*-**19a**. An analogous workup gave *trans*-**19c** as a yellow solid (1.098 g, 1.258 mmol, 84%). Mp (capillary): 92−94 °C. DSC ($T_i$/$T_e$/$T_p$/$T_c$/$T_f$): 72.5/95.5/97.6/99.9/133.3 °C (endotherm). TGA: onset of mass loss, 176.3 °C. Anal. Calcd for $C_{34}H_{42}Cl_2N_2O_8Pt$: C, 46.79; H, 4.85; N, 3.21. Found: C, 46.23; H, 4.56; N, 3.04. NMR ($\delta$, $CDCl_3$): $^1$H 9.68 (d, 4H, $^4J_{HH}$ = 1.8 Hz, *o*-$HC_{2,6pyr}$), 8.99 (t, 2H, $^4J_{HH}$ = 1.8 Hz, *p*-$HC_{4pyr}$), 5.86 (ddt, 4H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.7 Hz, C*H*=), 5.12 (dd, 4H, $^3J_{HHtrans}$ = 17.2 Hz, $^2J_{HH}$ = 1.3 Hz, =C$H_EH_Z$), 5.06 (dd, 4H, $^3J_{HHcis}$ = 10.3 Hz, $^2J_{HH}$ = 1.1 Hz, =C$H_EH_Z$), 4.46 (t, 8H, $^3J_{HH}$ = 6.7 Hz, OC$H_2$), 2.28−2.23 (m, 8H, C$H_2$), 1.98−1.91 (m, 8H, C$H_2$); $^{13}$C{$^1$H} 162.0 (s, CO), 157.6 (s, *o*-$C_{2,6pyr}$), 140.1 (s, *p*-$C_{4pyr}$), 137.0 (s, CH=), 128.5 (s, *m*-$C_{3,5pyr}$), 115.8 (s, =$CH_2$), 66.1 (s, O$CH_2$), 30.0 (s, $CH_2$), 27.6 (s, $CH_2$). IR (cm$^{-1}$, powder film): 3128 (w), 3082 (w), 2958 (m), 2926 (m), 1722 (s), 1645 (m), 1607 (m), 1447 (s), 1305 (s), 1251 (s), 1112 (s), 981 (s), 911 (s), 742 (s). MS:[41] 872 (**19c**$^+$, 30%), 836 ([**19c** − Cl]$^+$, 10%), 304 (**5c**$^+$, 100%).

***trans*-PtCl$_2$[3,5-NC$_5$H$_3$(COO(CH$_2$)$_4$CH=CH$_2$)$_2$]$_2$ (*trans*-19d).** Pyridine **5d** (1.002 g, 3.018 mmol), PtCl$_2$ (0.382 g, 1.437 mmol), and benzene (14 mL) were combined in a procedure similar to that for *trans*-**19a**. An analogous workup gave *trans*-**19d** as a yellow solid (1.234 g, 1.329 mmol, 92%). Mp (capillary): 74−76 °C. DSC ($T_i$/$T_e$/$T_p$/$T_c$/$T_f$): 49.4/56.6/58.6/61.8/62.6 °C (endotherm); 63.0/65.7/67.3/68.5/68.5 °C (endotherm); 75.5/76.7/79.3/80.8/83.2 °C (endotherm). TGA: onset mass loss, 165.3 °C. Anal. Calcd for $C_{38}H_{50}Cl_2N_2O_8Pt$: C, 49.14; H, 5.43; N, 3.02. Found: C, 48.69; H, 5.42; N, 2.73. NMR ($\delta$, $CDCl_3$): $^1$H 9.67 (d, 4H, $^4J_{HH}$ = 1.8 Hz, *o*-$HC_{2,6pyr}$), 8.99 (t, 2H, $^4J_{HH}$ = 1.8 Hz, *p*-$HC_{4pyr}$), 5.83 (ddt, 4H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.7 Hz, C*H*=), 5.07 (dd, 4H, $^3J_{HHtrans}$ = 17.1 Hz, $^2J_{HH}$ = 1.9 Hz, =C$H_EH_Z$), 5.01 (dd, 4H, $^3J_{HHcis}$ = 10.2 Hz, $^2J_{HH}$ = 1.9 Hz, =C$H_EH_Z$), 4.44 (t, 8H, $^3J_{HH}$ = 6.7 Hz, OC$H_2$), 2.19−2.13 (m, 8H, C$H_2$), 1.89−1.81 (m, 8H, C$H_2$), 1.61−1.53 (m, 8H, C$H_2$); $^{13}$C{$^1$H} 162.1 (s, CO), 157.5 (s, *o*-$C_{2,6pyr}$), 140.0 (s, *p*-$C_{4pyr}$), 138.0 (s, CH=), 128.5 (s, *m*-$C_{3,5pyr}$), 115.2 (s, =$CH_2$), 66.6 (s, O$CH_2$), 33.2, 27.9, and 25.1 (3 s, 3$CH_2$). IR (cm$^{-1}$, powder film): 3113 (w), 3075 (w), 2950 (m), 2920 (m), 1730 (s), 1645 (m), 1607 (m), 1452 (s), 1267 (s), 1112 (s), 966 (s), 911 (s), 742 (s). MS:[41] 928 (**19d**$^+$, 30%), 893 ([**19d** − Cl]$^+$, 30%), 332 ([**5d** + H]$^+$, 100%).

***trans*-PtCl$_2$[3,5-NC$_5$H$_3$(COO(CH$_2$)$_5$CH=CH$_2$)$_2$]$_2$ (*trans*-19e).** Pyridine **5e** (0.853 g, 2.373 mmol), PtCl$_2$ (0.300 g, 1.128 mmol), and benzene (11 mL) were combined in a procedure similar to that for *trans*-**19a**. An analogous workup gave *trans*-**19e** as a yellow solid (1.042 g, 1.058 mmol, 94%). Mp (capillary): 74−76 °C. DSC ($T_i$/$T_e$/$T_p$/$T_c$/$T_f$): 48.5/52.1/53.6/55.6/57.3 °C (endotherm); 70.4/79.3/81.1/82.9/99.8 °C (endotherm). TGA: onset of mass loss, 165.7 °C. Anal. Calcd for $C_{42}H_{58}Cl_2N_2O_8Pt$: C, 51.22; H, 5.94; N, 2.84. Found: C, 51.71; H, 6.19; N, 2.93. NMR ($\delta$, $CDCl_3$): $^1$H 9.67 (d, 4H, $^4J_{HH}$ = 1.8 Hz, *o*-$HC_{2,6pyr}$), 8.98 (t, 2H, $^4J_{HH}$ = 1.8 Hz, *p*-$HC_{4pyr}$), 5.83 (ddt, 4H, $^3J_{HHtrans}$ = 17.1 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.7 Hz, C*H*=), 5.04 (dd, 4H, $^3J_{HHtrans}$ = 18.1 Hz, $^2J_{HH}$ = 2.5 Hz, =C$H_EH_Z$), 4.99 (dd, 4H, $^3J_{HHcis}$ = 10.2 Hz, $^2J_{HH}$ = 1.2 Hz, =C$H_EH_Z$), 4.43 (t, 8H, $^3J_{HH}$ = 6.7 Hz, OC$H_2$), 2.13−2.09 (m, 8H, C$H_2$), 1.88−1.81 (m, 8H, C$H_2$), 1.47−1.50 (m, 16H, C$H_2$); $^{13}$C{$^1$H} 162.1 (s, CO), 157.5 (s, *o*-$C_{2,6pyr}$), 140.0 (s, *p*-$C_{4pyr}$), 138.5 (s, CH=), 128.6 (s, *m*-$C_{3,5pyr}$), 114.7 (s, =$CH_2$), 66.8 (s, O$CH_2$), 33.5, 28.4, 28.3, and 25.3 (4 s, 4$CH_2$). IR (cm$^{-1}$, powder film): 3130 (w), 3080 (w), 2926 (m), 2856 (m), 1722 (s), 1447 (m), 1305 (s), 1247 (s), 1127 (s), 984 (s), 907 (s), 741 (s). MS:[41] 984 (**19e**$^+$, 4%), 949 ([**19e** − Cl]$^+$, 14%), 360 (**5e**$^+$, 100%).

***trans*-PtCl$_2$[3,5-NC$_5$H$_3$(COO(CH$_2$)$_6$CH=CH$_2$)$_2$]$_2$ (*trans*-19f).** Pyridine **5f** (1.410 g, 3.641 mmol), PtCl$_2$ (0.440 g, 1.66 mmol), and benzene (15 mL) were combined in a procedure similar to that for *trans*-**19a**. An analogous workup gave *trans*-**19f** as a yellow solid (0.906 g, 0.870 mmol, 63%). Mp (capillary): 66−68 °C. DSC ($T_i$/$T_e$/$T_p$/$T_c$/$T_f$): 60.8/68.5/70.7/72.3/82.7 °C (endotherm). TGA: onset of mass loss, 171.8 °C. Anal. Calcd for $C_{46}H_{66}Cl_2N_2O_8Pt$: C, 53.07; H, 6.39; N, 2.69. Found: C, 52.62; H, 6.44; N, 2.63. NMR ($\delta$, $CDCl_3$): $^1$H 9.66 (d, 4H, $^4J_{HH}$ = 1.8 Hz, *o*-$HC_{2,6pyr}$), 8.98 (t, 2H, $^4J_{HH}$ = 1.8 Hz, *p*-$HC_{4pyr}$), 5.82 (ddt, 4H, $^3J_{HHtrans}$ = 17.1 Hz, $^3J_{HHcis}$ = 10.2 Hz, $^3J_{HH}$ = 6.8 Hz, C*H*=), 5.01 (dd, 4H, $^3J_{HHtrans}$ = 17.0 Hz, $^2J_{HH}$ = 2.3 Hz, =C$H_EH_Z$), 4.95 (dd, 4H, $^3J_{HHcis}$ = 10.1 Hz, $^2J_{HH}$ = 1.1 Hz, =C$H_EH_Z$), 4.43 (t, 8H, $^3J_{HH}$ = 6.7 Hz, OC$H_2$), 2.09−2.03 (m, 8H, C$H_2$), 1.83−1.81 (m, 8H, C$H_2$), 1.45−1.42 (m, 24H, C$H_2$); $^{13}$C{$^1$H} 162.1 (s, CO), 157.5 (s, *o*-$C_{2,6pyr}$), 140.0 (s, *p*-$C_{4pyr}$), 138.8 (s, CH=), 128.6 (s, *m*-$C_{3,5pyr}$), 114.4 (s, =$CH_2$), 66.8 (s, O$CH_2$), 33.6, 28.7, 28.6, 28.5, and 25.7 (5 s, 5$CH_2$). IR (cm$^{-1}$, powder film): 3127 (w), 3080 (w), 2926 (s), 2856 (m), 1718 (s), 1606 (m), 1447 (s), 1305 (s), 1225 (s), 1127 (s), 968 (s), 911 (s), 741 (s). MS:[41] 1040 (**19f**$^+$, 2%), 1005 ([**19f** − Cl]$^+$, 20%), 388 ([**5f** + H]$^+$, 100%).

***trans*-PtCl$_2$[3,5-NC$_5$H$_3$(COO(CH$_2$)$_8$CH=CH$_2$)$_2$]$_2$ (*trans*-19h).** Pyridine **5h** (0.652 g, 1.47 mmol), PtCl$_2$ (0.178 g, 0.668 mmol), and benzene (7 mL) were combined in a procedure similar to that for *trans*-**19a**. An analogous workup gave *trans*-**19h** as a yellow solid (0.600 g, 0.520 mmol, 78%). Mp (capillary): 68−70 °C. DSC ($T_i$/$T_e$/$T_p$/$T_c$/$T_f$): 34.5/39.5/41.6/43.6/47.0 °C (endotherm); 50.6/68.3/70.3/72.1/87.2 °C (endotherm). TGA: onset of mass loss, 177.5 °C. Anal. Calcd for $C_{54}H_{82}Cl_2N_2O_8Pt$: C, 56.24; H, 7.17; N, 2.43. Found: C, 55.93; H, 7.12; N, 2.38. NMR ($\delta$, $CDCl_3$): $^1$H 9.66 (d, 4H, $^4J_{HH}$ = 1.8 Hz, *o*-$HC_{2,6pyr}$), 8.98 (t, 2H, $^4J_{HH}$ = 1.8 Hz, *p*-$HC_{4pyr}$), 5.82 (ddt, 4H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.7 Hz, C*H*=), 5.00 (dd, 4H, $^3J_{HHtrans}$ = 17.1 Hz, $^2J_{HH}$ = 2.1 Hz, =C$H_EH_Z$), 4.95 (dd, 4H, $^3J_{HHcis}$ = 10.2 Hz, $^2J_{HH}$ = 2.1 Hz, =C$H_EH_Z$), 4.42 (t, 8H, $^3J_{HH}$ = 6.7 Hz, OC$H_2$), 2.08−2.04 (m, 8H, C$H_2$), 1.86−1.79 (m, 8H, C$H_2$), 1.45−1.34 (m, 40H, C$H_2$); $^{13}$C{$^1$H} 162.1 (s, CO), 157.4 (s, *o*-$C_{2,6pyr}$), 140.1 (s, *p*-$C_{4pyr}$), 139.6 (s, CH=), 128.6 (s, *m*-$C_{3,5pyr}$), 114.6 (s, =$CH_2$), 67.3 (s, O$CH_2$), 34.2, 29.9, 29.7, 29.6, 29.4, 28.9, and 26.2 (7 s, 7$CH_2$). IR (cm$^{-1}$, powder film): 3127 (w), 3080 (w), 2922 (s), 2853 (m), 1733 (s), 1718 (s), 1606 (m), 1447 (m), 1305 (s), 1262 (s), 1127 (s), 1108 (s), 992 (s), 911 (s), 741 (s). MS:[41] 1152 (**19h**$^+$, 5%), 1117 ([**19h** − Cl]$^+$, 50%), 444 ([**5h** + H]$^+$, 100%).

***trans*-PtCl$_2$[3,5,3′,5′-(NC$_5$H$_3$(COO(CH$_2$)$_{10}$OCO)$_2$H$_2$C$_5$N)] (*trans*-20d).** A round-bottom flask was charged with *trans*-**19d** (0.250 g, 0.269 mmol) and $CH_2Cl_2$ (130 mL), fitted with a condenser, and flushed with $N_2$. A solution of Grubbs' catalyst (0.0220 g, 0.0269 mmol, 10 mol %) in $CH_2Cl_2$ (4 mL) was added dropwise over 30 min with stirring (the resulting solution is 0.002 01 M in *trans*-**19d**). The mixture was refluxed (24 h) and cooled to room temperature. The solvent was removed by rotary evaporation. The residue was chromatographed on an alumina column (20 × 2 cm, $CH_2Cl_2$). A single yellow band was collected. The solvent was removed by rotary


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evaporation and oil pump vacuum. A round-bottom flask was charged with the crude metathesis product, 10% Pd/C (0.0343 g, 0.0322 mmol of Pd), toluene (10 mL), and ethanol (10 mL), flushed with $H_2$, and fitted with a balloon of $H_2$ (1.0 atm). The mixture was stirred (3 days) and passed through a pad of Celite (7 × 2 cm, $CH_2Cl_2$). The filtrate was concentrated by oil pump vacuum (to ca. 1 mL), carefully layered with hexanes (20 mL), and kept at −4 °C. After 24 h, the supernatant was carefully decanted, and the precipitate was dried by oil pump vacuum to give *trans*-**20d** as a pale yellow solid (0.0469 g, 0.0535 mmol, 20%). The sample slightly darkened at 190 °C. DSC ($T_i/T_e/T_p/T_c/T_f$): 159.5/167.8/194.6/201.7/209.4 °C (endotherm). TGA: onset of mass loss, 253.2 °C. Anal. Calcd for $C_{34}H_{46}Cl_2N_2O_8Pt$: C, 46.58; H, 5.29; N, 3.20. Found: C, 45.75; H, 5.41; N, 3.09.[45] NMR ($\delta$, $CDCl_3$): $^1$H 9.68 (d, 4H, $^4J_{HH}$ = 1.8 Hz, *o*-$HC_{2,6pyr}$), 9.12 (t, 2H, $^4J_{HH}$ = 1.8 Hz, *p*-$HC_{4pyr}$), 4.44 (t, 8H, $^3J_{HH}$ = 5.8 Hz, $OCH_2$), 1.87−1.81 (m, 8H, $CH_2$), 1.71−1.63 (m, 8H, $CH_2$), 1.54−1.47 (m, 16H, $CH_2$); $^{13}C\{^1H\}$ 162.1 (s, *C*O), 157.1 (s, *o*-$C_{2,6pyr}$), 141.0 (s, *p*-$C_{4pyr}$), 128.6 (s, $C_{3,5pyr}$), 67.2 (s, $OCH_2$), 29.3, 28.6, 28.5, and 26.5 (4 s, 4$CH_2$). IR ($cm^{-1}$, powder film): 3074 (w), 2935 (m), 2850 (m), 1738 (s), 1599 (w), 1460 (w), 1390 (w), 1267 (s), 1104 (m), 1004 (m), 958 (s), 749 (s). MS:[41] 876 (**20d**$^+$, 30%), 840 ([**20d** − Cl]$^+$, 60%), 817 (unknown, 100%).

***trans*-PtCl$_2$[3,5,3′,5′-(NC$_5$H$_3$(COO(CH$_2$)$_{12}$OCO)$_2$H$_3$C$_5$N)] (*trans*-20e).** Solutions of *trans*-**19e** (0.250 g, 0.253 mmol) in $CH_2Cl_2$ (120 mL) and of Grubbs' catalyst (0.021 g, 0.0253 mmol, 10 mol %) in $CH_2Cl_2$ (5 mL) were combined in a procedure similar to that for *trans*-**20d** (the resulting solution is 0.002 02 M in *trans*-**19e**). After hydrogenation, an analogous workup gave *trans*-**20e** as a light yellow solid (0.105 g, 0.113 mmol, 45%). Mp (capillary): 214−216 °C. DSC ($T_i/T_e/T_p/T_c/T_f$): 63.5/63.5/69.8/74.0/74.0 °C (endotherm); 75.0/80.4/86.8/91.8/101.0 °C (endotherm); 208.8/213.9/223.9/229.5/229.5 °C (endotherm). TGA: onset of mass loss, 220.3 °C. Anal. Calcd for $C_{38}H_{54}Cl_2N_2O_8Pt$: C, 48.92; H, 5.84; N, 3.00. Found: C, 48.52; H, 5.83; N, 3.00. NMR ($\delta$, $CDCl_3$): $^1$H 9.66 (d, 4H, $^4J_{HH}$ = 1.8 Hz, *o*-$HC_{2,6pyr}$), 9.12 (t, 2H, $^4J_{HH}$ = 1.8 Hz, *p*-$HC_{4pyr}$), 4.45 (t, 8H, $^3J_{HH}$ = 5.9 Hz, $OCH_2$), 1.82−1.89 (m, 8H, $CH_2$), 1.60−1.53 (m, 8H, $CH_2$), 1.48−1.40 (m, 24H, $CH_2$); $^{13}C\{^1H\}$ 162.1 (s, *C*O), 157.0 (s, *o*-$C_{2,6pyr}$), 141.2 (s, *p*-$C_{4pyr}$), 128.9 (s, *m*-$C_{3,5pyr}$), 67.1 (s, $OCH_2$), 29.0, 28.6, 28.4, 28.3, and 26.3 (5 s, 5$CH_2$). IR ($cm^{-1}$, powder film): 3084 (w), 3061(w), 2926 (m), 2853 (m), 1737 (s), 1463 (w), 1444 (w), 1266 (s), 1243 (s), 1112 (m), 1046 (m), 965 (m), 748 (s), 687 (m). MS:[41] 932 (**20e**$^+$, 100%), 897 ([**20e** − Cl]$^+$, 80%), 859 (unknown, 70%).

***trans*-PtCl$_2$[3,5,3′,5′-(NC$_5$H$_3$(COO(CH$_2$)$_{14}$OCO)$_2$H$_3$C$_5$N)] (*trans*-20f).** Solutions of *trans*-**19f** (0.250 g, 0.240 mmol) in $CH_2Cl_2$ (115 mL) and of Grubbs' catalyst (0.0197 g, 0.024 mmol, 10 mol %) in $CH_2Cl_2$ (5 mL) were combined in a procedure similar to that for *trans*-**20d** (the resulting solution is 0.002 00 M in *trans*-**19f**). After hydrogenation, an analogous workup gave *trans*-**20f** as a light yellow solid (0.0420 g, 0.0425 mmol, 18% overall). Mp (capillary): 150−152 °C. DSC ($T_i/T_e/T_p/T_c/T_f$): 137.1/146.0/152.4/154.3/154.3 °C (endotherm). TGA: onset of mass loss, 217.6 °C. Anal. Calcd for $C_{42}H_{62}Cl_2N_2O_8Pt$: C, 51.01; H, 6.32; N, 2.83. Found: C, 49.52, H, 5.78; N, 2.74. NMR ($\delta$, $CDCl_3$): $^1$H 9.65 (d, 4H, $^4J_{HH}$ = 1.8 Hz, *o*-$HC_{2,6pyr}$), 9.10 (t, 2H, $^4J_{HH}$ = 1.8 Hz, *p*-$HC_{4pyr}$), 4.46 (t, 8H, $^3J_{HH}$ = 5.9 Hz, $OCH_2$), 1.83−1.81 (m, 8H, $CH_2$), 1.45−1.40 (m, 40H, $CH_2$); $^{13}C\{^1H\}$ 162.1 (s, *C*O), 157.2 (s, *o*-$C_{2,6pyr}$), 141.0 (s, *p*-$C_{4pyr}$), 128.9 (s, *m*-$C_{3,5pyr}$), 66.9 (s, $OCH_2$), 28.9, 28.8, 28.7, 28.6, 28.4, and 25.8 (6 s, 6$CH_2$). IR ($cm^{-1}$, powder film): 3127 (w), 3107 (w), 2922 (s), 2853 (m), 1718 (s), 1606 (m), 1447 (m), 1305 (s), 1258 (s), 1108 (s), 799 (s), 741 (s), 683 (s). MS:[41] 988 (**20f**$^+$, 50%), 953 ([**20f** − Cl]$^+$, 30%), 915 (unknown, 100%).

***trans*-PtCl$_2$[3,5,3′,5′-(NC$_5$H$_3$(COO(CH$_2$)$_{18}$OCO)$_2$H$_3$C$_5$N)] (*trans*-20h).** Solutions of *trans*-**19h** (0.230 g, 0.20 mmol) in $CH_2Cl_2$ (95 mL) and of Grubbs' catalyst (0.0248 g, 0.0301 mmol, 15 mol %) in $CH_2Cl_2$ (5 mL) were combined in a procedure similar to that for *trans*-**19d** (the resulting solution is 0.002 00 M in *trans*-**19h**). After hydrogenation, an analogous workup gave *trans*-**20h** as a light yellow solid (0.0301 g, 0.0272 mmol, 14% overall). Mp (capillary): 182−184 °C. DSC ($T_i/T_e/T_p/T_c/T_f$): 143.5/178.9/187.0/190.3/192.2 °C (endotherm). TGA: onset of mass loss, 202 °C. Anal. Calcd for $C_{50}H_{78}Cl_2N_2O_8Pt$: C, 54.54; H, 7.14; N, 2.54. Found: C, 54.13; H, 7.08; N, 2.33. NMR ($\delta$, $CDCl_3$): $^1$H 9.65 (d, 4H, $^4J_{HH}$ = 1.8 Hz, *o*-$HC_{2,6pyr}$), 9.10 (t, 2H, $^4J_{HH}$ = 1.8 Hz, *p*-$HC_{4pyr}$), 4.45 (t, 8H, $^3J_{HH}$ = 5.9 Hz, $OCH_2$), 1.85−1.82 (m, 8H, $CH_2$), 1.45−1.29 (m, 56H, $CH_2$); $^{13}C\{^1H\}$ 162.2 (s, *C*O), 157.1 (s, *o*-$C_{2,6pyr}$), 141.6 (s, *p*-$C_{4pyr}$), 128.8 (s, *m*-$C_{3,5pyr}$), 66.9 (s, $OCH_2$), 29.2, 29.0, 28.9, 28.7, 28.5, 27.8, 26.8, and 25.6 (8 s, 8$CH_2$). IR ($cm^{-1}$, powder film): 3080 (w), 2926 (s), 2853 (m), 1737 (s), 1598 (m), 1459 (m), 1266 (s), 1243 (s), 1162 (s), 1112 (s), 973 (s), 930 (s), 749 (s), 683 (s). MS:[41] 1101 (**20h**$^+$, 25%), 1066 ([**20h** − Cl]$^+$, 35%), 1027 (unknown, 10%).

***trans*-PtCl$_2$(3,5-NC$_5$H$_3$(4-C$_6$H$_4$O(CH$_2$)$_5$CH=CH$_2$)$_2$)$_2$ (*trans*-22).** $PtCl_2$ (0.0162 g, 0.0609 mmol) and **8** (0.0570 g, 0.125 mmol) were combined in a procedure similar to that for *trans*-**10a**. An analogous workup gave *trans*-**22** as a light yellow solid (0.0687 g, 0.0584 mmol, 96%). Mp (capillary): 190−192 °C. Anal. Calcd for $C_{62}H_{74}Cl_2N_2O_4Pt$: C, 63.25; H, 6.34; N, 2.38. Found: C, 62.59; H, 6.31; N, 2.30.[45] NMR ($\delta$, $CDCl_3$): $^1$H 9.01 (d, 4H, $^4J_{HH}$ = 1.8 Hz, *o*-$HC_{2,6pyr}$), 8.00 (t, 2H, $^4J_{HH}$ = 1.8 Hz, *p*-$HC_{4pyr}$), 7.57 and 7.01 (2 m, 2 × 8H, pyr-C*CH* and $C_{pyr}$CCHC*H*), 5.88−5.79 (ddt, 4H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.1 Hz, $^3J_{HH}$ = 6.4 Hz, C*H*=), 5.06−4.94 (m, 8H, =C$H_2$), 4.02 (t, 8H, $^3J_{HH}$ = 6.4 Hz, $OCH_2$), 2.11 (m, 8H, $CH_2CH$=$CH_2$), 1.83 (m, 8H, $OCH_2CH_2$), 1.50 (m, 16H, $CH_2$); $^{13}C\{^1H\}$ 160.2 (s, $COCH_2$), 149.6 (s, *o*-$C_{2,6pyr}$), 139.0 (s, =*C*H$_2$), 138.4 (s, *m*-$C_{3,5pyr}$), 133.9 (s, *p*-$C_{4pyr}$), 128.7 (s, pyr-*C*(CH)$_2$), 128.0 (s, pyr-C(*C*H)$_2$), 115.5 (s, (*C*H)$_2$CO), 114.7 (s, *C*H=), 68.3 (s, $C_6H_4OCH_2$), 33.9, 29.3, 28.8, 25.7 (4 s, 4$CH_2$). IR ($cm^{-1}$, powder film): 3074 (w), 2930 (m), 2857 (m), 1607 (s), 1512 (s), 1449 (s), 1287 (s), 1240 (s), 1180 (s), 995 (m), 908 (s), 823 (s), 696 (m).

***trans*-PtCl$_2$[3,5,3′,5′-(NC$_5$H$_3$(4-C$_6$H$_4$O(CH$_2$)$_{12}$O-4-C$_6$H$_4$)$_2$H$_3$C$_5$N)] (*trans*-23).** Grubbs' catalyst (0.0287 g, 0.0349 mmol, 15 mol %), *trans*-**22** (0.2737 g. 0.2325 mmol), and Pd/C (10% w/w; three hydrogenation cycles using 0.0203, 0.0217, and 0.0217 g or 0.0599 mmol of Pd, 26 mol %) were combined in a procedure similar to that for *trans*-**11a**. An analogous workup gave *trans*-**23** as a yellow solid (0.1036 g, 0.09207 mmol, 40%). Mp (capillary): 198−204 °C dec. Anal. Calcd for $C_{58}H_{70}Cl_2N_2O_4Pt$: C, 61.91; H, 6.27; N, 2.49. Found: C, 60.58; H, 6.07; N, 2.42.[45] NMR ($\delta$, $CDCl_3$): $^1$H 8.83 (d, 4H, $^4J_{HH}$ = 2.0 Hz, *o*-$HC_{2,6pyr}$), 7.96 (t, 2H, $^4J_{HH}$ = 2.0 Hz, *p*-$HC_{4pyr}$), 7.48 and 6.97 (2 m, 2 × 8H, pyr-C*CH* and $C_{pyr}$CCHC*H*), 4.05 (t, 8H, $^3J_{HH}$ = 6.9 Hz, $OCH_2$), 1.86−1.76 (m, 8H, $OCH_2CH_2$), 1.54−1.44 (m, 8H, $CH_2$), 1.44−1.28 (m, 24H, $CH_2$); $^{13}C\{^1H\}$ 160.1 (s, $COCH_2$), 149.2 (s, *o*-$C_{2,6pyr}$), 137.7 (s, *m*-$C_{3,5pyr}$), 133.1 (s, *p*-$C_{4pyr}$), 128.7 (s, pyr-*C*(CH)$_2$), 127.5 (s, pyr-C(*C*H)$_2$), 115.4 (s, (*C*H)$_2$CO), 68.2 (s, $C_6H_4OCH_2$), 29.2, 29.1, 29.0 (2×), and 25.8 (4 s, 5$CH_2$). IR ($cm^{-1}$, powder film): 2924 (s), 2853 (m), 2359 (w), 1607 (s), 1512 (s), 1449 (s), 1287 (s), 1240 (s), 1180 (s), 1028 (m), 824 (s), 698 (m).

***trans*-PtCl(CH$_3$)[3-NC$_5$H$_4$(CH$_2$O(CH$_2$)$_2$CH=CH$_2$)]$_2$ (*trans*-24b).** A round-bottom flask was charged with *trans*-**12b** (0.6121 g, 1.033 mmol) and diethyl ether (15 mL) in an argon glovebox. Then $CH_3MgBr$ (2.94 M in ether; 0.86 mL, 2.5 mmol) was added with stirring. After 2 h, saturated aqueous $NH_4Cl$ (5 mL), water (45 mL), and diethyl ether (35 mL) were added, and the phases were separated. The water layer was extracted with diethyl ether (2 × 50 mL). The combined ethereal layers were dried ($MgSO_4$). The solvent was removed by oil pump vacuum. The residue was chromatographed on a silica column (39 × 2.5 cm, 1/4 v/v ethyl acetate/$CH_2Cl_2$) to give *trans*-**24b** as a white solid (0.5549 g, 0.9701 mmol, 94%). NMR ($\delta$, $CDCl_3$): $^1$H 8.89 (m, 2H, *o*-$HC_{2pyr}$), 8.85 (m, 2H, *o*-$HC_{6pyr}$), 7.74 (m, 2H, *p*-$HC_{4pyr}$), 7.23 (m, 2H, *m*-$HC_{5pyr}$), 5.90−5.76 (ddt, 2H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.2 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*=), 5.15−5.03 (m, 4H, =C$H_2$), 4.52 (s, 4H, $CH_2O$), 3.56 (t, 4H, $^3J_{HH}$ = 6.6 Hz, $OCH_2CH_2$), 2.39 (apparent qt, 4H, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.4 Hz, $CH_2CH$=$CH_2$), 0.87 (s, 3H, Pt$CH_3$); $^{13}C\{^1H\}$ NMR 153.1 and 152.9 (2 s, *o*-$C_{2pyr}$ and *o*-$C_{6pyr}$), 136.5 (s, CH=), 136.1 (s, *p*-$C_{4pyr}$), 135.0 (s, *m*-$C_{3pyr}$), 125.2 (s, *m*-$C_{5pyr}$), 117.0 (s, =$CH_2$), 70.5 (s, $CH_2O$), 69.4 (s, $OCH_2CH_2$), 34.3 (s, $CH_2$), −6.6 (s, Pt$CH_3$).

***trans*-PtCl(CH$_3$)[3-NC$_5$H$_4$(CH$_2$O(CH$_2$)$_8$CH=CH$_2$)]$_2$ (*trans*-24h).** $CH_3MgBr$ (2.94 M in diethyl ether; 1.50 mL, 4.41 mmol) and


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*trans*-**12h** (0.9494 g, 1.248 mmol) were combined in a procedure similar to that for *trans*-**24b**. An analogous workup gave *trans*-**24h** as a white waxy solid (0.6175 g, 0.8341 mmol, 67%). NMR ($\delta$, $CDCl_3$): $^1H$ 8.89 (m, 2H, *o*-$HC_{2pyr}$), 8.86 (m, 2H, *o*-$HC_{6pyr}$), 7.75 (m, 2H, *p*-$HC_{4pyr}$), 7.24 (m, 2H, *m*-$HC_{5pyr}$), 5.87−5.74 (ddt, 2H, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.4 Hz, $^3J_{HH}$ = 6.6 Hz, C*H*═), 4.94 (m, 4H, ═C$H_2$), 4.50 (s, 4H, C$H_2$O), 3.49 (t, 4H, $^3J_{HH}$ = 6.6 Hz, OC$H_2$CH$_2$), 2.03 (m, 4H, C$H_2$CH═CH$_2$), 1.62 (m, 4H, OCH$_2$C$H_2$), 1.42−1.26 (m, 20H, C$H_2$), 0.88 (s, 3H, PtC$H_3$); $^{13}C\{^1H\}$ 153.0 and 152.9 (2 s, *o*-$C_{2pyr}$ and *o*-$C_{6pyr}$), 139.4 (s, *C*H═), 136.7 (s, *p*-$C_{4pyr}$), 136.1 (s, *m*-$C_{3pyr}$), 125.1 (s, *m*-$C_{5pyr}$), 114.3 (s, ═$CH_2$), 71.5 (s, $CH_2$O), 69.4 (s, O$CH_2$CH$_2$), 34.0, 29.8, 29.6 (2×), 29.3, 29.1, and 26.3 (6 s, 7$CH_2$), −6.6 (s, PtC$H_3$).

***trans*-PtCl(CH$_3$)[3,3′-(NC$_5$H$_4$(CH$_2$O(CH$_2$)$_{10}$OCH$_2$)H$_4$C$_5$N)] (*trans*-25d).** $CH_3MgBr$ (2.94 M in diethyl ether; 0.33 mL, 0.97 mmol) and *trans*-**13d** (0.2038 m, 0.3274 mmol) were combined in a procedure similar to that for *trans*-**24b**. An analogous workup gave *trans*-**25d** as a white solid (0.1273 g, 0.2114 mmol, 65%). NMR ($\delta$, $CDCl_3$): $^1H$ 9.06 (m, 2H, *o*-$HC_{2pyr}$), 8.94 (m, 2H, *o*-$HC_{6pyr}$), 7.51 (m, 2H, *p*-$HC_{4pyr}$), 7.19 (m, 2H, *m*-$HC_{5pyr}$), 4.52 (s, 4H, C$H_2$O), 3.55 (t, 4H, $^3J_{HH}$ = 5.5 Hz, OC$H_2$CH$_2$), 1.64 (m, 4H, OCH$_2$C$H_2$), 1.54 (m, 4H, C$H_2$), 1.39 (m, 8H, C$H_2$), 0.93 (s, 3H, PtC$H_3$); $^{13}C\{^1H\}$ 153.6 and 152.7 (2 s, *o*-$C_{2pyr}$ and *o*-$C_{6pyr}$), 136.7 (s, *p*-$C_{4pyr}$), 135.2 (s, *m*-$C_{3pyr}$), 124.5 (s, *m*-$C_{5pyr}$), 71.2 (s, $CH_2$O), 69.8 (s, O$CH_2$CH$_2$), 30.2, 29.9, 29.6, 26.7 (4 s, 4$CH_2$), −6.4 (s, PtC$H_3$).

***trans*-PtCl(CH$_3$)[3,3′-(NC$_5$H$_4$(CH$_2$O(CH$_2$)$_{18}$OCH$_2$)H$_4$C$_5$N)] (*trans*-25h).** $CH_3MgBr$ (2.94 M in ether; 0.28 mL, 0.82 mmol) and *trans*-**13h** (0.2034 g, 0.2768 mmol) were combined in a procedure similar to that for *trans*-**24b**. An analogous workup gave *trans*-**25h** as an off-white solid (0.0815 g, 0.114 mmol, 41%). NMR ($\delta$, $CDCl_3$): $^1H$ 8.97 (m, 2H, *o*-$HC_{2pyr}$), 8.91 (m, 2H, *o*-$HC_{6pyr}$), 7.68 (m, 2H, *p*-$HC_{4pyr}$), 7.22 (m, 2H, *m*-$HC_{5pyr}$), 4.50 (s, 4H, C$H_2$O), 3.50 (t, 4H, $^3J_{HH}$ = 6.4 Hz, OC$H_2$CH$_2$), 1.63 (m, 4H, OCH$_2$C$H_2$), 1.40−1.22 (m, 28H, C$H_2$), 0.91 (s, 3H, PtC$H_3$); $^{13}C\{^1H\}$ 153.3 and 153.2 (2 s, *o*-$C_{2pyr}$ and *o*-$C_{6pyr}$), 136.6 (s, *p*-$C_{4pyr}$), 136.2 (s, *m*-$C_{3pyr}$), 125.0 (s, *m*-$C_{5pyr}$), 71.3 (s, $CH_2$O), 69.7 (s, O$CH_2$CH$_2$), 29.6, 29.45, 29.44, 29.41, 29.38, 29.37, 29.25, 26.1 (8 s, 8$CH_2$), −6.5 (PtC$H_3$).

***trans*-Pt(Cl)(C≡CPh)[3,5-NC$_5$H$_3$(COO(CH$_2$)$_3$CH═CH$_2$)$_2$]$_2$ (*trans*-26c).** A round-bottom flask was charged with *trans*-**19c** (0.124 g, 0.142 mmol), CuI (0.0027 g, 0.014 mmol), and $CH_2Cl_2$/*i*-$Pr_2NH$ (10/1 v/v, 12 mL) with stirring. Then PhC≡CH (0.0207 g, 0.199 mmol) in $CH_2Cl_2$/*i*-$Pr_2NH$ (2 mL) was added dropwise over 5 min. The flask was fitted with a condenser. The solution was refluxed (3 days) and cooled to room temperature. The solvents were removed by rotary evaporation and oil pump vacuum. The residue was chromatographed on a silica column (25 × 2 cm, gradient elution, 8/2 to 0/10 v/v hexanes/ethyl acetate). The solvents were removed from the product-containing fractions by rotary evaporation and oil pump vacuum. The residue was dissolved in $CH_2Cl_2$ (ca. 1 mL) and carefully layered with hexanes (20 mL). The sample was kept at −4 °C. After 24 h, the supernatant was decanted and the precipitate dried by oil pump vacuum to give *trans*-**26c** as a pale yellow solid (0.0245 g, 0.0261 mmol, 18%). NMR ($\delta$, $CDCl_3$): $^1H$ 9.96 (d, 4H, $^4J_{HH}$ = 1.9 Hz, *o*-$HC_{2,6pyr}$), 9.01 (t, 2H, $^4J_{HH}$ = 1.9 Hz, *p*-$HC_{4pyr}$), 7.24−7.13 (m, 5H, Ph), 5.85 (ddt, 4H, $^3J_{HHtrans}$ = 17.1 Hz, $^3J_{HHcis}$ = 10.3 Hz, $^3J_{HH}$ = 6.7 Hz, C*H*═), 5.08 (dd, 4H, $^3J_{HHtrans}$ = 17.1 Hz, $^2J_{HH}$ = 1.9 Hz, ═C$H_EH_Z$), 5.02 (dd, 4H, $^3J_{HHcis}$ = 10.3 Hz, $^2J_{HH}$ = 1.9 Hz, ═C$H_EH_Z$), 4.43 (t, 8H, $^3J_{HH}$ = 6.6 Hz, OC$H_2$), 2.25−2.20 (m, 8H, C$H_2$), 1.94−1.87 (m, 8H, C$H_2$); $^{13}C\{^1H\}$ 162.7 (s, CO), 158.6 (s, *o*-$C_{2,6pyr}$), 140.1 (s, *p*-$C_{4pyr}$), 137.7 (s, *C*H═), 132.1 (s, *o*-$C_{Ph}$), 128.9 (s, $C_{3,5pyr}$), 128.3 (s, *p*-$C_{Ph}$), 127.2 (s, *m*-$C_{Ph}$), 126.5 (s, *i*-$C_{Ph}$), 115.7 (s, ═$CH_2$), 94.0 and 85.0 (2 s, C≡C), 66.4 (s, O$CH_2$), 30.4 (s, $CH_2$), 28.1 (s, $CH_2$). IR ($cm^{-1}$, powder film): 3076 (w), 2961 (w), 2907 (w), 2351 (m), 2131 (m, $\nu_{C\equiv C}$), 1725 (s), 1640 (m), 1598 (m), 1444 (m), 1305 (s), 1262 (s), 1239 (s), 1112 (s), 984 (s), 911 (s), 741 (s). MS:[41] 938 (**26c**$^+$, 100%)

***trans*-Rh(Cl)(CO)[2,6-NC$_5$H$_3$(CH$_2$OCH$_2$CH═CH$_2$)$_2$]$_2$ (*trans*-27a).** A Schlenk flask was charged with [RhCl(coe)$_2$]$_2$ (0.430 g, 0.599 mmol) and methanol/toluene (1/1 v/v, 22 mL). A solution of **4a** (0.564 g, 2.58 mmol) in methanol/toluene (1/1 v/v, 4 mL) was added dropwise over 10 min with stirring. The flask was fitted with a condenser. The mixture was refluxed (2 h), cooled to room temperature, and filtered under $N_2$. The orange solution was aspirated with CO (1 h). The solvents were removed by oil pump vacuum, and the residue was chromatographed on a silica column (10 × 2 cm, 4/1 v/v hexanes/ethyl acetate). An orange band was collected. The solvents were removed by rotary evaporation and oil pump vacuum. The residue was dissolved in $CH_2Cl_2$ (ca. 1 mL). The solution was layered with pentane (20 mL) and kept at −4 °C. After 24 h, the supernatant was carefully decanted, and the precipitate was dried by oil pump vacuum to give *trans*-**27a** as a light orange solid (0.090 g, 0.149 mmol, 26%). Mp (capillary): 106−108 °C. DSC ($T_i/T_e/T_p/T_c/T_f$): 79.2/102.6/106.5/109.1/114.8 °C (endotherm). TGA: onset of mass loss, 114.7 °C. NMR ($\delta$, $CDCl_3$): $^1H$ 7.81 (t, 2H, $^3J_{HH}$ = 7.8 Hz, *p*-$HC_{4pyr}$), 7.59 (d, 4H, $^3J_{HH}$ = 7.8 Hz, *m*-$HC_{3,5pyr}$), 6.08 (ddt, 4H, $^3J_{HHtrans}$ = 17.2 Hz, $^3J_{HHcis}$ = 10.6 Hz, $^3J_{HH}$ = 5.4 Hz, CH═), 5.76 (d, 4H, $^4J_{RhH}$ = 15.0 Hz, 4CH*H*′O), 5.64 (d, 4H, $^4J_{RhH}$ = 15.0 Hz, 4C*H*H′O), 5.46 (dd, 4H, $^3J_{HHtrans}$ = 17.2 Hz, $^2J_{HH}$ = 1.6 Hz, ═C$H_EH_Z$), 5.33 (dd, 4H, $^3J_{HHcis}$ = 10.4 Hz, $^2J_{HH}$ = 1.5 Hz, ═C$H_EH_Z$), 4.29 (dt, 8H, $^3J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 1.4 Hz, OC$H_2$); $^{13}C\{^1H\}$ 183.6 (d, $^1J_{RhC}$ = 70.3 Hz, CO), 162.2 (s, *o*-$C_{2,6pyr}$), 138.0 (s, *p*-$C_{4pyr}$), 134.1 (s, *C*H═), 121.5 (s, *m*-$C_{3pyr}$), 117.7 (s, ═$CH_2$), 73.4 and 72.1 (2 s, $CH_2$OC$H_2$). IR ($cm^{-1}$, powder film): 3088 (w), 3015 (w), 2860 (m), 2837 (w), 1945 (s, $\nu_{CO}$), 1610 (m), 1583 (w), 1471 (m), 1332 (m), 1239 (w), 1116 (s), 1007 (s), 988 (m), 787 (s). MS:[41] 576 ([**27a** − CO]$^+$, 40%), 569 ([**27a** − Cl]$^+$, 20%), 321 ([**27a** − **4a** − 2Cl]$^+$, 100%), 220 ([**4a** + H]$^+$, 30%).

**Crystallography.** *A. trans-11b.* A saturated $CH_2Cl_2$ solution was layered with ethyl acetate. After one day, the yellow plates were taken to a Bruker APEX2 X-ray diffractometer for data collection as outlined in Table S1 (Supporting Information). Cell parameters were obtained from 36 frames using a 0.5° scan and refined with 17 016 reflections. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program suite APEX2.[46] Lorentz, polarization, and absorption corrections[47] were applied. The space group was determined from systematic reflection conditions and statistical tests. The structure was solved by direct methods using SHELXTL (SHELXS).[48] Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in idealized positions. The parameters were refined by weighted least-squares refinement on $F^2$ to convergence.[48]

*B. trans-13d.* A saturated $CH_2Cl_2$ solution was layered with ethyl acetate. After 1 day, the yellow plates were analyzed as described for *trans*-**11b** (cell parameters from 36 frames using a 0.5° scan; refined with 24 911 reflections). The structure was solved and refined as for *trans*-**11b**. Two independent molecules were found in the unit cell. Both exhibited disordered methylene groups (two in one molecule, 80:20 occupancies; six in the other, (70−50):(30−50) occupancies), which were treated by restraining the bond lengths and angles to idealized values. In the final stages of refinement, additional electron density not associated with either molecule was observed and tentatively assigned to a disordered $CH_2Cl_2$ molecule (occupancy ca. 50%). After many attempts to model the disorder, the electron density contribution was extracted with the program PLATON/SQUEEZE.[49]

*C. trans-13h.* A saturated $CH_2Cl_2$ solution was layered with ethyl acetate. After 1 day, yellow plates of the solvate *trans*-**13h**·$CH_2Cl_2$ were analyzed as described for *trans*-**11b** (cell parameters from 36 frames using a 0.5° scan; refined with 14 813 reflections). The structure was solved and refined as for *trans*-**11b**.

*D. trans-17a.* A concentrated $CH_2Cl_2$ solution was layered with hexanes. After 7 days, the yellow blocks were taken directly to a Nonius KappaCCD area detector for data collection as outlined in Table S2 (Supporting Information). Cell parameters were obtained from 10 frames using a 10° scan and refined with 1788 reflections. Lorentz, polarization, and absorption corrections[50] were applied. The space group was determined from systematic absences and subsequent least-squares refinement. The structure was solved by


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direct methods. The parameters were refined with all data by full-matrix least squares on $F^2$ using SHELXL-97.[51] Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were fixed in idealized positions using a riding model. The complex exhibited a 2-fold symmetry axis containing the N−Pt−N vector and an orthogonal mirror plane containing the Cl−Pt−Cl vector. The data indicated some disorder at C3, but this could not be resolved. Scattering factors were taken from the literature.[52]

*E. trans-**18a**.* A concentrated $CHCl_3$ solution was layered with hexanes. After 3 days, the pale yellow blocks were analyzed as described for *trans*-**17a** (cell parameters from 10 frames using a 10° scan; refined with 2487 reflections). The structure was solved and refined as for *trans*-**17a**. The structure exhibited an inversion center at platinum.

*F. trans-**18b**.* A concentrated $CHCl_3$ solution was layered with hexanes. The sample was kept at −4 °C. After 3 days, the yellow needles were analyzed as described for *trans*-**17a** (cell parameters from 10 frames using a 10° scan; refined with 2898 reflections). The structure was solved and refined as for *trans*-**17a**. Three atoms were disordered, which were refined to an 81:19 occupancy ratio (C7/C8/O9 and C7′/C8′/O9′). The structure exhibited an inversion center at platinum.

*G. trans-**20e**.* A concentrated $CHCl_3$ solution was layered with hexanes. The sample was kept at −20 °C. After 7 days, the light yellow blocks of the solvate *trans*-**20e**·2$CHCl_3$ were analyzed as described for *trans*-**17a** (cell parameters from 10 frames using a 10° scan; refined with 10 662 reflections). The structure was solved and refined as for *trans*-**17a**. Several sets of atoms were disordered, which were refined to 66:34 (C44/C44′), 65:35 (C53/C53′), and 73:27 (C65/C65′) occupancy ratios. Large atomic displacement factors for C46−C52 indicated additional disorder, which could not be resolved.

*H. trans-**16**.* A concentrated $CHCl_3$ solution of *trans*-**16** was layered with hexanes. After 7 days, the yellow blocks were analyzed as described for *trans*-**17a** (cell parameters from 10 frames using a 10° scan; refined with 2337 reflections). The structure was solved and refined as for *trans*-**17a**. The structure exhibited an inversion center at palladium.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Text giving details of the reactions with Grubbs' second-generation catalyst and tables of crystallographic data and CIF files for the complexes in Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Author Contributions

[§]Both co-workers contributed equally to the experimental work.


### Notes

The authors declare no competing financial interest.

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## ■ DEDICATION

This article is dedicated with admiration and affection to the memory of our Texas neighbor, Professor F. G. A. Stone.

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