FULL PAPER

Alkene metatheses in transition metal coordination spheres: dimacrocyclizations that join *trans* positions of square-planar platinum complexes to give topologically novel diphosphine ligands

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The alkene-containing phosphines $PPh((CH_2)_nCH=CH_2)_2$ (4) are prepared from $PPhH_2$, n-BuLi, and the corresponding bromoalkenes (1:2:2), and combined with the platinum tetrahydrothiophene complex $[Pt(\mu-Cl)(C_6F_5)(S(CH_2CH_2-)_2)]_2$ (12) to give the square-planar adducts trans- $(Cl)(C_6F_5)Pt(PPh((CH_2)_nCH=CH_2)_2)_2$ (11, 93-73%; n = a, 2; b, 3; c, 4; d, 5; e, 6; f, 8). Ring-closing metatheses with Grubbs' catalyst (2) are studied. With 11e, two isomers of trans-(Cl)(C₆F₅)Pt(PPh(CH₂)₁₄P(CH₂)₁₄Ph) (15e) are isolated after hydrogenation. Both form via dimacrocyclization between the trans-phosphine ligands, but differ in the dispositions of the PPh rings (syn, 31%; anti, 7%). The alternative intraligand metathesis product trans-(Cl)($C_{s}F_{s}$)Pt(PPh(CH₂)₁₄)₂ (16e) is independently prepared by (i) protecting 4e as a borane adduct, H₃B·PPh((CH₂)₆CH=CH₂)₂, (ii) cyclization with 2 and hydrogenation to give $H_3B \cdot PPh(CH_2)_{14}$, (iii) deprotection and reaction with 12. The sample derived from 11e contains $\leq 2\%$ 16e; mass spectra suggest that the other products are dimers or oligomers. The structures of *syn*-15e, *anti*-15e and **16e** are verified crystallographically, and the macrocycle conformations analyzed. As expected from the $(CH_2)_{\mu}$ segment length, **11a** undergoes intraligand metathesis to give (Z,Z)-trans-(Cl)(C₆F₅)Pt(PPh(CH₂)₂CH=CH(CH₂)₂)₂ (86%), as confirmed by a crystal structure of the hydrogenation product. Although 11b does not yield tractable products, 11c gives syn(E,E)-trans-(Cl)(C₆F₅)Pt(PPh(CH₂)₄CH=CH(CH₂)₄P(CH₂)₄CH=CH(CH₂)₄Ph) (21%). This structure, and that of the hydrogenation product (syn-15c; 95%), are verified crystallographically. Analogous sequences with 11d,f give syn-15d,f (5 and 14% overall).

Introduction

Alkene metathesis is seeing increasing use in syntheses of metal-containing molecules.¹ Among many applications, the generation of topologically novel metall*o*- and metall*a*macrocycles has attracted particular interest. This rapidly growing theme has its origins in Sauvage's elegant syntheses of catenanes,² and has been further developed by ourselves^{3,4} and others.⁵ In our previous full paper,^{3d} we studied the series of square-planar sixteen-valence-electron platinum complexes *trans*-(Cl)(C₆F₅)Pt(PPh₂(CH₂)_nCH=CH₂)₂ (1) shown in Scheme 1. These feature monophosphine ligands with a polymethylene bridge to a terminal alkenyl group. Ring-closing metatheses



n	Yield, metathesis (%)	^a Yield, hydrogenation (%) ^b	Overall yield (%)
4, c	95	70	67
6, e	96	72	69
8, f	90	59	53
9, g	85	50	43
^a Inclu	ides minor amounts of	dimeric or oligomeric byproc	ducts.
^b Afte	r chromatographic puri	fication that removes dimerio	c or
oligo	meric byproducts.		

Scheme 1 Monomacrocyclizations involving *trans* phosphine ligands with one alkene-containing substituent.

with Grubbs' catalyst (2) gave high yields of thirteen to twentythree membered macrocycles featuring unusual *trans*-spanning diphosphine ligands.⁶ Mixtures of E/Z C=C isomers were obtained, but were easily hydrogenated to the saturated analogs 3, which were robust and readily crystallized.

We established the feasibility of analogous reaction sequences with substituted polymethylene bridges^{3d} and related square-planar rhodium complexes.^{3c} However, we wondered whether this chemistry could be extended to topologically more complicated substrates. In particular, what might occur with similar complexes of phosphines containing *two* polymethylene bridges to terminal alkenyl groups – *e.g.*, PPh((CH₂)_nCH=CH₂)₂ (4)? As generalized in Scheme 2, two cyclization modes would be possible: (a) reaction between the *trans* phosphine ligands (interligand metathesis) to give an adduct of a macrocyclic *di*phosphine, also a metalladimacrocycle (II), or (b) reaction within the phosphine ligands (intraligand metathesis) to give a bis(adduct) of a cyclic monophosphine (III).



Scheme 2 Possible ring-closing metathesis modes for *trans* donor ligands with two alkene-containing substituents.

The feasibility of the second pathway had been explicitly demonstrated for the rhenium complexes **5h**,**i** shown in Scheme 3, which feature *one* ligand of the type **4** (n = 6). The

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Scheme 3 Monomacrocyclizations involving phosphine ligands with two alkene-containing substituents.

metallomacrocycles **6h**,**i** could be isolated in 94–81% yields. The tungsten complex **7** in Scheme 4, which features *three* such ligands, is also relevant. It gave a complicated and nearly intractable mixture of all possible cyclization products (**8**, **9**, **10**), as established by mass spectrometric, HPLC, and crystallographic data. Although no attempt was made to vary the lengths of the $(CH_2)_n$ segments, it was evident that a simpler type of test substrate was needed. Accordingly, platinum complexes of **4**, *trans*-(Cl)(C₆F₅)Pt(PPh((CH₂)_nCH=CH₂)₂)₂ (**11**), were selected for intensive study.

In this paper, we describe the partitioning of **11** between the cyclization modes in Scheme 2 as a function of the number of methylene groups. Depending upon the chain length, either can dominate. However, dimeric or oligomeric species derived from intermolecular metathesis are generally the major products. Nonetheless, significant quantities of topologically novel diphosphine complexes of the type **II** can be accessed from several substrates. These would require lengthy syntheses *via* conventional methodologies. The crystal structures of four such compounds are determined, and their conformational features analyzed in detail. A small portion of this work has been communicated.³⁶

Results

PPhH₂

1 Starting phosphines and complexes

1) 2.0-2.1 *n*-BuLi

2) 2.0-2.1 Br(CH₂)_nCH=CH₂

As shown in eqn. (1), commercial PPhH₂ was successively treated at 0 °C with *n*-BuLi (2.0–2.1 equiv.) and then an α,ω -bromoalkene Br(CH₂)_nCH=CH₂ ($n = \mathbf{a}, 2; \mathbf{b}, 3; \mathbf{c}, 4; \mathbf{d}, 5;$ $\mathbf{e}, 6; \mathbf{f}, 8; 2.0–2.1$ equiv.). Workups gave the requisite tertiary phosphines **4a**–**f** as colorless oils in 98–89% yields. The bromoalkenes were either commercially available or prepared from the corresponding alcohols as reported earlier.^{3d} Other syntheses of **4a**,**b** have been published,^{7,8} and the preparation of **4e** by this procedure has been described previously.^{3c}

PPh((CH₂)_nCH=CH₂)₂

4

n = 2, **a**, 90%

3, **b**, 92% 4, **c**, 89%

5, d, 93%

6, **e**, 78%

8. f. 98%





Scheme 5 Synthesis of substrates for alkene metatheses.

2 Ring-closing metathesis of 11e

Alkene metatheses were conducted under conditions similar to those used in Scheme 1. As shown in Scheme 6, **11e** (*ca*. 0.0034 M) and **2** (10 mol%, added in two portions) were reacted in refluxing CH_2Cl_2 . Although the catalyst loading might appear somewhat high, it should be divided by two to normalize to the number of ring closures. The mixture was filtered through alumina to separate the catalyst residue. The metathesis products, for which **13e** and **14e** are the only possible monomeric structures, were obtained in 97% yield. The sample was characterized as described for **11a–f**.

The ¹H NMR spectrum showed no terminal alkene residues, indicating metathesis to be \geq 98% complete. Accordingly, new CH=CH signals were detected between 5.20 and 5.35 ppm, presumably due to both *E* and *Z* isomers. The ³¹P NMR spectrum exhibited a multitude of peaks, the dominant one of which represented 44% of the total area. The ¹³C NMR spectrum exhibited an even more complex mixture of peaks. These were not tabulated, but only signals in the aromatic/alkene (132–126.5 ppm) and aliphatic (32.8–23.0 ppm) regions were observed.

The microanalysis fit the formulae of 13e, 14e, or related species derived from intermolecular metathesis. The mass spectrum showed a significant ion with a mass corresponding to $[13e - Cl]^+$ or $[14e - Cl]^+$ (m/z 966, 45% relative intensity). Another ion had the formal composition $[2 \cdot 13e - Cl]^+$ or $[2 \cdot 14e - Cl]^+$ (m/z 1969, 30%), indicating the presence of dimeric or oligomeric byproducts. Analogous ions were *not* observed for the macrocyclizations in Scheme 1. In order to simplify further analysis and product isolation, a hydrogenation was conducted.

The metathesis mixture was treated with H_2 (1 atm) in the presence of 10% Pd/C (Scheme 6). Filtration through alumina



(1)

Scheme 4 Polymacrocyclizations involving phosphine ligands with two alkene-containing substituents.



Scheme 6 Ring-closing metathesis/hydrogenation sequence for 11e.

gave the crude saturated macrocycles (77%), for which **15e** and **16e** are the only possible monomeric structures. The ¹H NMR spectrum showed that all double bonds had been reduced, but the ³¹P NMR spectrum still exhibited many signals. The dominant peak represented 52% of the total area, and matched the chemical shift of *syn*-**15e** (see below). The mass spectrum showed significant ions with masses corresponding to **15e**⁺ or **16e**⁺ (*m*/*z* 1006, 40%) and [**15e** - Cl]⁺ or [**16e** - Cl]⁺ (*m*/*z* 970, 100%). Diplatinum ions of the formal composition [2·**15e** - Cl]⁺ or [**2·16e** - Cl]⁺ (*m*/*z* 1977, 20%) were also evident.

The sample was chromatographed on alumina. The two least polar products were isolated as white powders in 31 and 7% yields, and characterized analogously to **11a–f**. The mass spectra indicated that both were monoplatinum species. The first product exhibited a single ³¹P NMR signal, and seven methylene ¹³C NMR signals, whereas the second exhibited two mutually coupled ³¹P NMR signals and several additional methylene ¹³C NMR signals. Complexes of the type **15e** can exist as two stereoisomers, differing in the relative orientations of the phenyl groups (*syn* or *anti*). Accordingly, crystal structures described below showed the products to be *syn*-**15e** and *anti*-**15e**, respectively. The contrasting NMR properties are further analyzed below.

3 Independent synthesis of an intraligand metathesis product

We wanted to be certain that the workups in Scheme 6 did not overlook products derived from intraligand metathesis (14e, 16e). Thus, an independent synthesis was sought. An initial ring-closing metathesis of the free phosphine 4e was considered. However, Grubbs' catalyst 2 is not normally effective with alkenes that contain phosphines,¹² and there are only scattered successes with Schrock-type catalysts.^{12b,13} In contrast, phosphines in which the lone pairs are protected with borane are reliable substrates for alkene metatheses.¹² Hence, the sequence summarized in Scheme 7 was investigated.

A potential problem was obvious at the outset. Reactions of alkene-containing phosphines with borane sources can lead either to protected phosphines or alkene hydroboration. In some cases, the latter event can be circumvented by introducing the alkene moieties subsequent to phosphorus protection.^{12*a*} Fortunately, the reaction of H₃B·SMe₂ and **4e** at -20 °C gave the target compound **17e** in 65% yield. The ³¹P NMR spectrum showed coupling to boron (¹*J*(³¹P,¹¹B) 75 Hz), and the ¹H NMR spectrum exhibited a broad BH₃ signal (1.0–0.2 ppm).

As illustrated in Scheme 7, ring-closing metathesis of 17e with 2 gave the crude 15-membered cyclic phosphine derivative 18e in 62–91% yields. Unlike the monomacrocyclizations in Scheme 1, the mass spectrum exhibited ions corresponding both to intramolecular and intermolecular metathesis products (18e⁺, m/z 315, 80%; formal composition [2·18e]⁺, m/z 629, 20%). The ¹H NMR spectrum showed three closely spaced multiplets in the CH=CH region (ca. 1 : 1 : 1), consistent with a mixture of E/Z isomers and/or intra/intermolecular products.

When 18e was subjected to the hydrogenation conditions in Schemes 1 and 6 (10% Pd/C, 1 atm H₂), as well as higher H₂ pressures (6 atm), no reaction occurred. Thus, 18e and H₂ (6 atm) were combined in the presence of Wilkinson's catalyst. Chromatography gave the saturated cyclic phosphine derivative 19e in 77–74% yields. The ³¹P NMR spectrum showed one signal (¹J(³¹P,¹¹B) 70 Hz), and the ¹³C NMR spectrum was much simpler than that of 19e. However, besides the seven expected methylene signals, several minor peaks were evident (<10%). The mass spectrum also showed, in addition to ions derived from 19e, some diphosphorus species. Hence, the chromatography conditions did not completely remove the material derived from intermolecular metathesis.

As shown in Scheme 7, **19e** was deprotected by a standard procedure using HNEt₂.¹⁴ The crude cyclic phosphine $PPh(CH_2)_{14}$ (**20e**) was directly reacted with the tetrahydro-thiophene complex **12**. Chromatography gave the target complex **16e** in 24% overall yield from **19e**. The mass spectrum exhibited only monoplatinum ions. The most intense peaks involved phosphine ligand loss, in contrast to *syn*-**15e** and *anti*-**15e** where no such fragments were observed. NMR spectra showed no traces of any byproducts. The ³¹P signal (7.2 ppm)



Scheme 7 Synthesis of an authentic sample of 16e.



Fig. 1 Molecular structure of syn-15e.

was considerably upfield from those of *syn*-**15e** (11.8 ppm) and *anti*-**15e** (15.8, 11.2 ppm).

The ³¹P NMR spectrum of the crude hydrogenation product in Scheme 6 was reinvestigated. A small peak with a chemical shift close to that of **16e** was apparent. Integration allowed an upper limit of 2% to be placed upon the yield of **16e** from **11e**. The NMR tube was doped with a small amount of the independently synthesized **16e** to confirm that the chemical shifts were identical. Finally, *syn*-**15e**, *anti*-**15e**, and **16e** were compared by alumina TLC (1 : 3 v/v CH₂Cl₂-hexanes). $R_{\rm f}$ values of 0.56, 0.44, and 0.20 were found. Those of the various byproducts from Scheme 6 were much lower.

4 Structural and dynamic properties of syn-15e, anti-15e and 16e

The crystal structures of *syn*-**15e** and *anti*-**15e** were determined as summarized in Table 1 and the experimental section. Key bond lengths, bond angles, and torsion angles are listed in Table 2.¹⁵ The two macrocycles in each compound are given primed and unprimed atom labels so that their features are more easily compared. The molecular structure of *syn*-**15e** is depicted in Fig. 1 and that of *anti*-**15e** in Fig. 2. The left views in Figs. 1 and 2 highlight the contrasting orientations of the phenyl rings with respect to the platinum square planes. The isomers also exhibit markedly different macrocycle conformations.

A $C_6H_5/C_6F_5/C_6H_5$ π stacking interaction is evident in *syn*-15e (Fig. 1). This feature is also found in the crystal structures of 3c,e-g, (Scheme 1).^{3d} It is now well established that $C_6H_5/C_6F_5 \pi$ interactions are attractive and a driving force

in many crystallizations.¹⁶ The average of the two centroid– centroid distances in *syn*-**15e** is 4.05 Å. This is somewhat greater than in **3e** (3.60 Å), the related complex with only one $P(CH_2)_{14}P$ bridge. In contrast, *anti*-**15e** exhibits a single C₆H₅/ C₆F₅ π interaction (Fig. 2). It is not as pronounced, with a centroid–centroid distance of 4.26 Å.

The crystal structure of **16e** was similarly determined. Views that highlight the *trans* relationship of the macrocyclic monophosphine ligands are given in Fig. 3. Selected metrical parameters are listed in Table 3. Like *anti*-**15e**, **16e** exhibits a single, somewhat weak $C_6H_5/C_6F_5 \pi$ interaction, with a centroid–centroid distance of 4.49 Å.

The symmetry properties of *syn*-15e and *anti*-15e are relevant to several observations. As illustrated in Fig. 4, *syn*-15e has idealized C_{2v} symmetry. The phosphorus atoms and phenyl rings are homotopic; they can be exchanged by a rotation around the Cl-Pt-C₆F₅ axis. Each carbon atom of a given macrocycle has a homotopic counterpart in the other macrocycle. In addition, the carbon atoms labeled C_a in Fig. 4 are enantiotopic with the carbon atoms labeled C_b. However, the geminal protons of each methylene group are diastereotopic.

In contrast, *anti*-15e has C_1 symmetry. As illustrated in Fig. 4, both phosphorus atoms and phenyl rings are diastereotopic. The same holds for all carbon atoms of the macrocycles, as well as the geminal protons of the methylene groups. Hence, the NMR spectra of *anti*-15e should be more complicated than those of *syn*-15e, in accord with observations above and additional details provided in the experimental section. For example, the ³¹P NMR spectrum of *anti*-15e shows an AB spin system, with distinct ¹J_{PtP} values for each signal.

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# Table 1 General crystallographic data^a

Complex	syn-(E,E)-13c	syn-15c	syn-15e	anti-15e	16a	16e
Formula	C ₃₈ H ₄₆ ClF ₅ P ₂ Pt	C ₃₈ H ₅₀ ClF ₅ P ₂ Pt	C46H66ClF5P2Pt	C46H66ClF5P2Pt	C ₃₀ H ₃₄ ClF ₅ P ₂ Pt	C46H66ClF5P2Pt
Formula weight	890.23	894.26	1006.47	1006.47	782.05	1006.47
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P\overline{1}$	Pbcn	$P\overline{1}$
aĺÅ	13.64790(10)	23.5432(11)	24.8121(3)	11.69470(10)	18.5572(3)	10.57500(10)
b/Å	19.0165(3)	15.7182(6)	10.5438(2)	13.29450(10)	10.9033(2)	12.2670(2)
c/Å	15.0138(2)	21.5805(6)	18.0730(4)	14.9666(2)	28.7856(5)	18.1630(3)
a/°	90	90	90	88.3340(10)	90	72.9290(9)
βl°	106.7190(10)	112.273(2)	104.6070(10)	81.1850(10)	90	84.6100(8)
y/°	90	90	90	76.1950(10)	90	82.4310(8)
V/Å ³	3731.89(8)	7390.2(5)	4575.32(14)	2232.96(4)	5824.33(17)	2228.93(6)
Ζ	4	8	4	2	8	2
$D_{\rm c}/{\rm Mg}~{\rm m}^{-3}$	1.584	1.607	1.461	1.495	1.784	1.500
$\mu/\mathrm{mm}^{-1}$	3.968	4.008	3.246	3.325	5.071	3.331
F(000)	1776	3584	2048	1022	3072	1024
Crystal size/mm	$0.35 \times 0.20 \times 0.20$	$0.10 \times 0.10 \times 0.10$	$0.30 \times 0.20 \times 0.10$	$0.1 \times 0.1 \times 0.1$	$0.30 \times 0.20 \times 0.20$	$0.20 \times 0.20 \times 0.10$
$\theta$ Limit/°	1.89-27.48	1.60-25.02	2.11-27.51	1.38-25.05	1.41-27.48	2.21-27.52
Index ranges hkl	-17 to 17, $-24$ to 24,	-27 to 28, $-18$ to 18,	-31 to 32, $-12$ to 13,	-13 to 13, -15 to 15,	-24 to 24, $-14$ to 14,	-13 to 13, $-15$ to 15,
-	-19 to 19	-24 to 25	-23 to 23	-17 to 17	-37 to 37	-23 to 23
Reflections collected	16508	43886	17699	15379	12286	19533
Independent reflections	8549	13024	10322	7900	6642	10238
Reflections $[I > 2\sigma(I)]$	7851	6875	7022	7011	5538	9428
Data/restraints/parameters	8549/0/424	13024/0/847	10322/0/496	7900/0/496	6642/0/352	10238/0/496
Goodness-of-fit on $F^2$	1.061	0.930	0.998	1.152	1.116	1.029
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0199, wR2 = 0.0491	R1 = 0.0449, wR2 = 0.0958	R1 = 0.0404, wR2 = 0.0695	R1 = 0.0247, wR2 = 0.0601	R1 = 0.0240, wR2 = 0.0602	R1 = 0.0268, wR2 = 0.0621
R Indices (all data)	R1 = 0.0233, wR2 = 0.0505	R1 = 0.1156, wR2 = 0.1319	R1 = 0.0860, wR2 = 0.0796	R1 = 0.0324, wR2 = 0.0751	R1 = 0.0334, wR2 = 0.0751	R1 = 0.0305, wR2 = 0.0636
Largest diff. peak and hole $\Delta \rho / e \text{ Å}^{-3}$	0.997 and -0.966	0.894 and -1.307	2.621 and -1.408	1.371 and -0.978	0.893 and -0.996	1.431 and -0.920

^a Data common to all structures: diffractometer, Nonius Kappa CCD; wavelength, 0.71073 Å; temperature, 173(2) K.

		syn-15c			
Complex	<i>syn</i> -( <i>E</i> , <i>E</i> )-13c	First molecule ^{<i>a</i>}	Second molecule ^{<i>a</i>}	syn-15e	anti-15e
Bond lengths (Å)					
$\begin{array}{l} Pt-P(1)/Pt-P(2) \\ Pt-Cl \\ Pt-C(30) \\ C(1)-C(2)/C(1')-C(2') \\ C(2)-C(3)/C(2')-C(3') \\ C(3)-C(4)/C(3')-C(4') \\ C(4)-C(5)/C(4')-C(5') \\ C(5)-C(6)/C(5')-C(6') \\ C(5)-C(6)/C(5')-C(6') \\ C(6)-C(7)/C(6')-C(7') \\ C(7)-C(8)/C(7')-C(8') \\ C(8)-C(9)/C(8')-C(9') \\ C(9)-C(10)/C(9')-C(10') \\ C(10)-C(11)/C(10')-C(11') \\ C(11)-C(12)/C(11')-C(12') \\ C(12)-C(13)/C(12')-C(13') \\ C(13)-C(14)/C(13')-C(14') \end{array}$	2.3064(6)/2.2984(6) 2.3671(5) 2.015(2) 1.531(3)/1.533(3) 1.523(3)/1.528(3) 1.530(3)/1.530(4) 1.493(4)/1.502(4) 1.316(4)/1.314(4) 1.492(4)/1.502(4) 1.526(4)/1.529(4) 1.525(3)/1.521(3) 1.524(3)/1.530(3)	2.313(2)/2.303(2) 2.377(2) 1.989(10) 1.526(14)/1.522(14) 1.532(14)/1.569(18) 1.508(15)/1.345(19) 1.505(14)/1.471(16) 1.523(13)/1.526(16) 1.502(13)/1.490(15) 1.525(15)/1.509(16) 1.504(14)/1.456(16) 1.533(14)/1.500(15)	2.323(2)/2.318(3) 2.380(3) 2.005(11) 1.529(13)/1.520(17) 1.517(13)/1.533(17) 1.491(14)/1.536(18) 1.558(15)/1.497(17) 1.430(17)/1.513(17) 1.565(15)/1.497(15) 1.519(14)/1.497(15) 1.515(15)/1.484(16)	$\begin{array}{c} 2.3139(11)/2.3075(11)\\ 2.3778(11)\\ 2.002(4)\\ 1.515(6)/1.540(5)\\ 1.518(6)/1.514(6)\\ 1.518(6)/1.504(6)\\ 1.520(6)/1.516(6)\\ 1.518(7)/1.521(6)\\ 1.509(7)/1.534(6)\\ 1.515(7)/1.505(7)\\ 1.547(6)/1.545(7)\\ 1.515(6)/1.531(7)\\ 1.520(6)/1.508(6)\\ 1.518(6)/1.508(6)\\ 1.513(6)/1.528(6)\\ 1.512(6)/1.525(6)\\ \end{array}$	$\begin{array}{c} 2.2970(10)/2.2986(9)\\ 2.3560(10)\\ 2.017(4)\\ 1.522(6)/1.522(5)\\ 1.533(7)/1.532(6)\\ 1.503(8)/1.513(7)\\ 1.508(7)/1.520(6)\\ 1.519(8)/1.522(7)\\ 1.489(8)/1.513(6)\\ 1.530(8)/1.525(6)\\ 1.548(7)/1.521(6)\\ 1.524(7)/1.523(6)\\ 1.509(7)/1.513(6)\\ 1.511(7)/1.515(6)\\ 1.521(6)/1.517(6)\\ 1.527(6)/1.529(5)\end{array}$
Bond angles (°) C(30)-Pt-P(1) C(30)-Pt-P(2) P(1)-Pt-P(2) C(30)-Pt-Cl P(1)-Pt-Cl P(2)-Pt-Cl	94.00(6) 91.50(6) 174.41(2) 178.06(6) 84.062(19) 90.44(2)	94.6(3) 91.3(3) 172.21(10) 178.3(3) 86.83(9) 87.37(9)	89.4(3) 93.1(3) 173.96(11) 179.3(3) 90.42(10) 86.94(9)	90.47(12) 91.51(12) 177.99(4) 178.89(13) 88.89(4) 89.14(4)	93.31(10) 87.42(10) 173.33(3) 175.18(11) 86.71(3) 93.12(3)
Torsion angles (°) P(2)-Pt-P(1)-C(1)/P(2)-Pt-P(1)-C(1') Pt-P(1)-C(1)-C(2)/Pt-P(1)-C(1')-C(2') P(1)-C(1)-C(2)-C(3)/P(1)-C(1')-C(2')-C(3') C(1)-C(2)-C(3)-C(4)/C(1')-C(2')-C(3')-C(4') C(2)-C(3)-C(4)-C(5)/C(2')-C(3')-C(4')-C(5') C(3)-C(4)-C(5)-C(6)/C(3')-C(4')-C(5')-C(6') C(4)-C(5)-C(6)-C(7)/C(4')-C(5')-C(6')-C(7') C(5)-C(6)-C(7)-C(8)/C(5')-C(6')-C(7')-C(8') C(6)-C(7)-C(8)-C(9)/C(6')-C(7')-C(8')-C(9') C(7)-C(8)-C(9)-C(10)/C(7')-C(8')-C(9')-C(10') C(8)-C(9)-C(10)-C(11)/C(8')-C(9')-C(10')-C(11') C(9)-C(10)-C(11)/C(8')-C(9')-C(10')-C(11') C(9)-C(10)-C(11)/C(12)-C(13)/C(10')-C(11')-C(12')-C(13') C(11)-C(12)-C(13)-C(14)/C(11')-C(12')-C(13')-C(14') C(n - 2)-C(n - 1)-C(n)-P(2)/C(n' - 2)-C(n' - 1)-C(n')-P(2)^{b} C(n)-P(2)-Pt-P(1)/C(n')-P(2)-Pt-P(1)^{b} C(n)-P(2)-Pt-P(1)/C(n')-P(2)-Pt-P(1)^{b}	$\begin{array}{c} 45.2(2)/-70.5(2)\\ 35.56(19)/-50.42(19)\\ -176.85(17)/179.15(18)\\ 172.4(2)/-75.0(3)\\ -64.2(3)/-67.6(3)\\ 131.5(3)/129.7(3)\\ -175.2(2)/179.4(2)\\ 118.4(3)/132.5(3)\\ -66.7(3)/-68.5(3)\\ 179.6(2)/166.0(2)\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\ -\\$	$\begin{array}{c} 19.8(9)/-95.2(8)\\ 59.0(8)/-70.8(9)\\ 176.6(7)/69.1(12)\\ 60.8(12)/156.7(16)\\ 53.5(13)/174.3(13)\\ 52.8(14)/83.8(19)\\ 170.5(9)/-157.9(13)\\ 56.0(13)/97.0(14)\\ 53.6(14)/-58.9(15)\\ -179.1(8)/176.0(11)\\ -\\ 154.6(7)/-168.0(9)\\ -44.2(8)/36.9(11)\\ -11.6(9)/102.2(8)\\ \end{array}$	$\begin{array}{c} -22.4(11)/-139.9(10)\\ 47.8(9)/51.5(11)\\ -157.9(8)/-94.5(13)\\ 179.6(9)/172.6(11)\\ -67.6(14)/172.8(12)\\ 107.7(13)/45.1(16)\\ 177.0(10)/60.4(15)\\ 59.4(15)/-169.9(11)\\ 57.9(15)/-166.1(11)\\ -174.7(10)/-61.8(15)\\ -\\ -\\ -\\ 169.8(7)/-69.7(13)\\ -48.2(9)/82.7(9)\\ 8.6(12)/121.2(10)\\ \end{array}$	$\begin{array}{c} -69.1(12)/49.8(12)\\ 46.5(4)/56.5(3)\\ -175.3(3)/-164.6(3)\\ 178.8(4)/-180.0(4)\\ -176.7(4)/-177.4(4)\\ -170.2(4)/-176.5(4)\\ -51.7(6)/-60.6(7)\\ -62.1(6)/-67.0(7)\\ -179.6(4)/-176.7(4)\\ -61.9(6)/-60.5(7)\\ -59.7(6)/-50.4(7)\\ -178.6(4)/-171.3(4)\\ 176.3(4)/-171.3(4)\\ 176.3(4)/-172.2(3)\\ 56.0(4)/39.2(4)\\ 28.1(12)/-91.9(12)\end{array}$	$\begin{array}{c} 90.3(3)/-145.5(3)\\ -160.1(3)/-44.7(3)\\ 172.5(3)/161.9(3)\\ -54.1(5)/-174.3(3)\\ -59.0(5)/60.7(5)\\ 178.1(4)/56.0(5)\\ 179.6(4)/169.1(4)\\ 71.5(6)/-175.8(4)\\ 75.9(6)/-179.1(4)\\ -167.7(4)/72.4(5)\\ -173.7(4)/72.9(5)\\ -167.2(4)/-177.4(3)\\ 73.8(5)/62.0(5)\\ 75.0(5)/51.8(5)\\ 177.4(3)/-179.7(3)\\ 53.6(3)/167.6(3)\\ -23.4(3)/96.9(3)\\ \end{array}$



# $\begin{array}{c|c} IV & V \\ (syn-15) & (anti-15) \\ C_{2v} & C_1 \\ homotopic: \\ P_i/P_i, Ph_A/Ph_A, C_a/C_a, C_b/C_b \\ enantiotopic: \\ enantiotopic: \\ \end{array}$

Fig. 4 Idealized structures and stereochemical relationships in 15.

A toluene-d₈ solution of *anti*-15e was warmed to 95 °C while ³¹P NMR spectra were periodically recorded. No coalescence or significant broadening of the ³¹P NMR signals was noted, and no new peaks derived from *syn*-15e or other species

appeared. Application of the coalescence formula,¹⁷ using the  $\Delta v$  and J values for the phosphorus atoms from the low temperature limit (618.2 and 426.8 Hz, 25 °C), allowed a lower limit of 16.4 kcal mol⁻¹ (95 °C) to be placed on any process capable of rendering the phosphorus atoms of *anti*-**15e** equivalent. One such possibility, which should become accessible with longer P(CH₂)_nP bridges, is analyzed in the discussion section.

16a

Ph

64%

# 5 Ring-closing metatheses of 11a,b,c,d,f

Complex 11a, which features short  $(CH_2)_2$  segments between the phosphorus and terminal alkenyl moieties, would be a very unlikely candidate for interligand metathesis, or cyclization mode II in Scheme 2. The *trans* phosphorus atoms would be bridged by only six carbon atoms, resulting in a highly strained nine-membered ring. The shortest known saturated bridge between *trans* phosphorus atoms in a square planar complex consists of nine methylene groups, giving a twelve-membered ring.^{6,18}

As shown in Scheme 8, 11a (0.0093 M) and 2 were combined under conditions analogous to those in Schemes 1 and 6. Workup gave the expected intraligand metathesis product, bis(monophosphine) complex (Z,Z)-14a, in 86% yield.

 $C_a/C_b$ 

Table 3 Key bond lengths, bond angles, and torsion angles for intraligand metathesis products

Complex	16a	16e
Bond lengths (Å)		
Pt-P(1)/Pt-P(2)	2.3129(9)/2.3056(9)	2.2972(7)/2.3049(7)
Pt-Cl	2.3660(8)	2.3554(7)
Pt-C(30)	2.017(3)	2.017(3)
C(1) = C(2)/C(1') = C(2')	1.527(6)/1.537(5)	1.535(4)/1.533(4)
C(2) - C(3)/C(2') - C(3')	1.510(7)/1.516(6)	1.520(4)/1.515(5)
C(3)-C(4)/C(3')-C(4')	1 513(7)/1 533(6)	1.520(1)/1.512(6)
C(4)-C(5)/C(4')-C(5')	1 523(5)/1 527(6)	1.519(5)/1.564(9)
C(5) - C(6)/C(5') - C(6')	1.525(5)/1.527(6) 1.540(5)/1.530(5)	$1.519(5)/1.291(11)^{b}$
C(6) - C(7) + C(7)		$1.524(5)/1.251(11)^{b}$
C(7) - C(8)/C(7') - C(8')		1.522(5)/1.420(11) $1.517(6)/1.388(9)^{b}$
C(8) - C(9)/C(8') - C(9')		1.562(6)/1.578(8)
C(9) - C(10)/C(9') - C(10')		1.502(0)/1.576(0) 1.504(5)/1.487(7)
C(10), C(11)/C(10'), C(11')	—	1.504(5)/1.407(7) 1.513(6)/1.554(8)
C(11) = C(11)/C(11') = C(12')	—	1.513(6)/1.534(6) 1.503(5)/1.531(6)
C(11) - C(12)/C(11) - C(12) C(12) - C(13)/C(12') - C(13')	—	1.505(5)/1.551(6) 1.528(5)/1.524(5)
C(12) - C(13)/C(12) - C(13) C(13) - C(14)/C(13') - C(14')	—	1.526(5)/1.524(5) 1.541(4)/1.532(4)
C(13) - C(14)/C(13) - C(14)	_	1.341(4)/1.332(4)
Bond angles (°)		
C(30)-Pt-P(1)/C(30)-Pt-P(2)	91.23(9)/93.41(9)	93.69(7)/87.72(7)
P(1)-Pt-P(2)	174.84(3)	175.54(3)
C(30)–Pt–Cl	177.99(10)	177.52(8)
P(1)-Pt-Cl/P(2)-Pt-Cl	86.85(3)/88.53(3)	86.39(3)/92.38(3)
Torsion angles (°)		
$P(2) = P_t = P(1) = C(1)/P(1) = P_t = P(2) = C(1')$	32.9(4)/-170.9(4)	-104 1(3)/77 9(3)
$P_{t-P(1)-C(1)-C(2)/P_{t-P(2)-C(1')-C(2')}$	-1525(3)/-497(3)	-17624(18)/-1706(2)
P(1)-C(1)-C(2)-C(3)/P(2)-C(1')-C(2')-C(3')	63 4(5)/-33 1(4)	-1667(2)/-1731(3)
C(1) = C(2) = C(3) = C(4)/C(1') = C(2') = C(3') = C(4')	-94.9(5)/-49.2(5)	-177 8(3)/-57 8(5)
C(2) = C(3) = C(4) = C(5)/C(2') = C(3') = C(4') = C(5')	39 1(5)/94 8(4)	-543(4)/-555(5)
C(3)-C(4)-C(5)-C(6)/C(3')-C(4')-C(5')-C(6')	50.0(5)/-72.3(4)	-54.9(4)/-148.0(9)
C(4)-C(5)-C(6)-C(7)/C(4')-C(5')-C(6')-C(7')	-	178 3(3)/-162 0(2)
C(5) - C(6) - C(7) - C(8)/C(5') - C(6') - C(7') - C(8')	_	-169 2(3)/-60 6(14)
C(6)-C(7)-C(8)-C(9)/C(6')-C(7')-C(8')-C(9')	_	60.5(5)/77.8(11)
C(7) - C(8) - C(9) - C(10)/C(7') - C(8') - C(9') - C(10')	_	52 3(5)/56 7(9)
C(8)-C(9)-C(10)-C(11)/C(8')-C(9')-C(10')-C(11')	_	170.6(3)/171.8(5)
C(9) - C(10) - C(11) - C(12)/C(9') - C(10') - C(11') - C(12')	_	57 5(4)/61 9(5)
C(10) - C(11) - C(12) - C(13)/C(10') - C(11') - C(12') - C(13')	_	53 5(5)/58 1(5)
C(11)-C(12)-C(13)-C(14)/C(11')-C(12')-C(13')	_	52.9(4)/-179.9(3)
$C(n-2) = C(n-1) = C(n) = P(1)/C(n-2') = C(n-1') = D(2)^{a}$	-92.7(4)/59.1(4)	161 3(2)/171 4(2)
$C(n - 1) - C(n) - P(1) - C(n) - C(n) - P(2) - C(n') - P(2) - C(1')^{a}$	$54 1(3)/_70 6(3)$	50.3(2)/-46.1(3)
C(n) = P(1) = C(1) = C(1) = C(n) = P(1) = C(1) =	-30.9(4)/79.2(3)	57.0(3)/-63.1(3)
$D_{1} = (1) - C(1) - C(2) - C(n') - 1 - (2) - C(n') $	174 5(2)/61 5(3)	-79.9(2)/63.0(2)
$P(2)_Pt_P(1)_C(n)/P(1)_Pt_P(2)_C(n')^a$	-86 A(4)/65 5(4)	-1330(3)/-423(4)
1(2) - 1(-1)(1) - C(n)/1(1) - 1(-1)(2) - C(n)	00.4(4)/03.3(4)	155.0(5)/-42.5(4)

^{*a*} n = Number of methylene groups in macrocycle. ^{*b*} The thermal ellipsoids for C(5') to C(8') are very elongated.



Fig. 5 Molecular structure of 16a.

Hydrogenation as in Schemes 1 and 6 gave 16a in 64% yield after workup. The crystal structure was determined as summarized in Table 1 and the experimental section. Metrical parameters are listed in Table 3. The molecular structure is depicted in Fig. 5. There is a single  $C_6H_5/C_6F_5 \pi$  interaction, with a centroid-centroid distance of 3.58 Å.

Complex 11b, which could cyclize to an eleven-membered interligand metathesis product or a nine-membered intraligand metathesis product, was similarly combined with 2. However, no tractable products could be isolated, even when reactions were conducted at higher dilution (0.0033 M). Complex 11c gave similar results in comparable concentration ranges. How-



Scheme 9 Ring-closing metathesis/hydrogenation sequence for 11c.



Fig. 6 Molecular structure of syn-(E,E)-13c (top left and right) and syn-15c (bottom left, first independent molecule; bottom right, second independent molecule).

ever, when 0.00067 M solutions were used as shown in Scheme 9, a monoplatinum product could be isolated in 21% yield. A crystal structure established the formation of the intraligand metathesis product syn-(E,E)-13c.¹⁹ The molecular structure is depicted in Fig. 6 (top), and metrical parameters are listed in Table 2.

Hydrogenation of syn(E,E)-13c gave the saturated analog syn-15c in 95% yield. The crystal structure of this compound, a lower homolog of syn-15e (Fig. 1), was similarly determined. The unit cell contained two independent molecules. As illustrated in Fig. 6 (bottom), they differ in the macrocycle conformations. Both syn-(E,E)-13c and syn-15cexhibit  $C_6H_5/C_6F_5/C_6H_5 \pi$  stacking interactions, with average centroid-centroid distances of 4.16 and 3.85-3.94 Å, respectively. They also give a single ³¹P NMR signal, as expected for syn isomers from the analysis in Fig. 4. The ring-closing metathesis of 1c (Scheme 1), which yields a P(CH₂)₄CH=  $CH(CH_2)_4P$  bridge as in syn-(E,E)-13c, gives a 93 : 7 mixture of E/Z isomers.

Since 11d contains a longer methylene segment and interligand metathesis would generate a presumably less strained fifteen-membered ring, enhanced selectivity for cyclization mode II was expected. However, only very small amounts of non-oligomeric products could be isolated, even when 0.0019 M solutions of 11d were treated with 2. As shown in Scheme 10, the crude reaction mixture was directly hydro-

the mass spectrum.

(0.0033 M)



derived from loss of a monophosphine ligand were evident in



Fig. 7 Some representative conformations of 11 for interligand metathesis.

Given the yield trends in Scheme 1, it was thought that **11f** and **11e** might give comparable amounts of interligand metathesis products. As shown in Scheme 10, the reaction of **11f** (0.0033 M) and **2** was followed by hydrogenation. Chromatography gave *syn*-**15f** in 14% overall yield.¹⁹ Other fractions gave material with ³¹P NMR signal patterns suggestive of *anti*-**15f**, but samples could not be purified. Since it has not yet been possible to crystallographically characterize *syn*-**15f**, a remote possibility remains that it might be the intraligand metathesis product **16f**. However, the complexes assigned as *syn*-**15c**, **d**, **e**, **f** exhibit several monotonic trends (*e.g.*, ³¹P NMR 16.2, 12.5, 11.8, 10.8 ppm; *J*_{PPt} 2612, 2590, 2560, 2551 Hz), in accord with a homologous series.

### Discussion

#### 1 Scope and efficiency of macrocyclizations

Schemes 6, 9 and 10 establish that complexes of doubly *trans*spanning diphosphine ligands are easily accessed by alkene metatheses. Although the yields are modest, advanced generation metathesis catalysts may help in certain cases,¹⁹ and other routes would require many additional steps. Such complexes are to our knowledge unknown. However, as shown in Scheme 11, a conceptually related doubly *trans*-spanning bis(pyridine) complex has also been accessed by alkene metathesis.²⁰ In the educt **21**, each pyridine nitrogen is flanked by two *ortho* homoallyl groups. These would be expected to extend above and below the palladium square plane, preorganizing the alkenyl moieties for interligand metathesis. Accordingly, **22** is isolated in 80% yield. Hence, alkene metathesis may prove to be a general route to metalladimacrocycles of the type **II** (Scheme 2), albeit in variable yields.



Scheme 11 A doubly *trans*-spanning bis(pyridine) complex.

In earlier papers, we have argued that alkene metatheses in metal coordination spheres are often aided by some analog of the "geminal dialkyl effect".²¹ A PPh₂, MPPh, or similar group might play a role analogous to a CR₂ group in making *gauche* conformations of four-atom segments energetically more competitive with *anti* conformations. When only *anti* linkages are present, the termini of  $\alpha$ , $\omega$ -difunctionalized systems cannot approach one another. Shaw and co-workers have furthermore studied reactions of diphosphines R₂P(CH₂)_nPR₂ and square planar complexes that lead to *trans* substitution products.¹⁸ They find that the ratio of monometallic to di- and polymetallic

products dramatically increases with the size of the phosphorus substituent.

The PPh₂ and PPhR units in our platinum complexes promote gauche conformations in the solid state, as described below. However, for the monomacrocyclizations of 1 in Scheme 1, we see no obvious factor that should direct the alkenyl moieties on the same sides of the platinum square plane. Also, no axial bonding interactions involving pendant or bridging C=C (or C=C)²² moieties have ever been observed (e.g., syn-(E,E)-13c, Fig. 6). Nonetheless, the yields of intramolecular metathesis products are not much lower than with 21, which as noted above is geometrically predisposed to cyclization. The new data in this paper do not offer additional insight on this point, and pose several further questions, such as: (i) why is intraligand metathesis (III, Scheme 2) disfavored in Schemes 6, 9 and 10? (ii) why do the yields of monoplatinum interligand metathesis products drop relative to Scheme 1, despite comparable dilution levels? In analyzing these issues, we presume that our product mixtures are under kinetic control.¹⁹

Appreciable quantities of intraligand metathesis products are found only with **11a** (Scheme 8), for which interligand metathesis is impossible. Complex **11b**, for which interligand metathesis would also be unlikely, gives exclusively *intermolecular* metathesis. Perhaps intraligand metathesis, which would give a nine-membered cyclic phosphine ligand, is kinetically less favorable than with **11a**, allowing bimolecular condensations to compete. However, with **11c**,d,e,f, all of which give at least some intramolecular metathesis, we have no rationale for the absence of intraligand cyclization. Note that high yields of fifteen-membered cyclic phosphine complexes are obtained by intraligand metathesis in Scheme 3.

Given that intraligand metathesis is not very rapid with **11c,d,e,f**, why are the yields of interligand metathesis products lower than in Scheme 1? Fig. 7 shows two representative conformations of **11 (VI, VII)** as viewed down the phosphorus-carbon bond axes, the energies of which should be nearly equal. The chlorine and  $C_6F_5$  ligands can be visualized as directly behind and in front of the "Pt". In both cases, *gauche* Pt–PPhR–CH₂–CH₂ conformations are used to direct two (CH₂)_nCH=CH₂ moieties on the same side of the platinum square plane, and in orientations that are favorable for interligand metathesis. Many other conformations are possible that are to varying degrees less favorable for macrocyclization, as analyzed elsewhere.²³

Importantly, VI can only lead to *syn* isomers of 13, whereas VII can only lead to *anti* isomers. Hence, the *synlanti* stereochemistry is set by the first metathesis. Furthermore, in the macrocycle resulting from VII, the two remaining  $(CH_2)_n$ -CH=CH₂ moieties will be directed on opposite sides of the platinum square plane, an orientation unfavorable for intramolecular metathesis. Thus, bimolecular condensations should be more competitive, and more oligomeric products should arise from this manifold. This would result in lower yields of monoplatinum interligand metathesis products. Accordingly, only in the case of 15e is an *anti* isomer isolated. Finally, we note in passing that it might be easier to incorporate a C₆H₃/  $C_6F_5/C_6H_5 \pi$  stacking interaction into the transition state derived from VI.

### 2 Macrocycle structures

Various crystallographic features are relevant to phenomena analyzed above. First, the interligand metathesis products in Table 2 have bond lengths and angles about platinum similar to those of the intraligand metathesis products in Table 3. The P–Pt–P bond angles  $(177.99(4)-172.21(10)^{\circ} vs. 175.54(3)-174.84(3)^{\circ})$  might have contracted if the ring strain associated with the *trans*-spanning ligands were significant.

Consider the torsion angle patterns of the complexes in Table 2 next. With syn-15e, the macrocycles are homologous. All four Pt-PPh-CH₂-CH₂ segments (Pt-P(1)-C(1)-C(2), C(13)-C(14)-P(2)-Pt, and primed analogs) exhibit gauche conformations with torsion angles of 46.5/56.5° and 56.0/39.2°. This is in accord with an analog of a "germinal dialkyl effect" as discussed in the previous section, and as exploited in the cyclization-favorable conformations in Fig. 7. All of the macrocycles in Scheme 1 (3c,e,f,g) crystallize similarly. The four PPh-CH₂-CH2-CH2 segments in syn-15e exhibit anti conformations, with torsion angles of -175.3/-164.6° and -169.7/-172.2°. The three subsequent four-carbon sequences in each ring also show anti conformations. However, of the five remaining four-carbon sequences, four exhibit gauche conformations, with torsion angles of -51.7/-60.6°, -62.1/-67.0°, -61.9/-60.5°, and  $-59.7/-50.4^{\circ}$ .

The torsion angle patterns of the macrocycles in anti-15e are not homologous, and differ significantly from those of syn-15e. One of the two Pt-PPh-CH₂-CH₂ segments in each ring now exhibits a gauche conformation (C(13)–C(14)–P(2)–Pt  $-53.6^{\circ}$ ; Pt-P(1)-C(1')-C(2') -44.7°), while the other remains anti (-160.1°, 167.6°). All PPh-CH₂-CH₂-CH₂ sequences again show anti conformations. However, now there are six fourcarbon gauche segments in each ring, for a total of seven gauche moieties – one more than in each ring of syn-15e. Although an ensemble of accessible conformations would be expected in solution, this suggests (in the absence of non-bonded interactions) that anti-15e is more highly strained. As summarized in Table 3, each fifteen-membered ring in the constitutional isomer 16e exhibits seven four-carbon gauche segments. Furthermore, all C(13)-C(14)-P-C(1) and C(14)-P-C(1)-C(2) sequences have gauche conformations (50.3/-46.1°, 57.0/  $-63.1^{\circ}$ ), consistent with a PPhPt-based "geminal dialkyl effect".

Complex syn-15c, with two thirteen-membered rings, crystallizes with two independent molecules in the unit cell. Although none of the torsion angle patterns are homologous, all eight Pt–PPh–CH₂–CH₂ segments exhibit gauche conformations, with torsion angles of  $\pm 36.9^{\circ}$  to  $\pm 82.7^{\circ}$ . Two of the four rings exhibit three additional gauche PPh–CH₂–CH₂–CH₂ or four-carbon segments, and the other rings exhibit four and five. The unsaturated analog syn-(*E,E*)-13c also crystallizes with gauche Pt–PPh–CH₂–CH₂ segments. One ring features only two additional gauche segments, and the other three (fourcarbon in each case). The Z C=C moiety enforces one anti linkage.

A final structural issue involves the size relationship between the macrocycle and the other ligands on platinum. Consider first **3e** (Scheme 1), which has a single *trans*-spanning  $P(CH_2)_{14}P$ bridge. A 180° rotation of the Cl-Pt-C₆F₅ moiety, with the smaller chlorine ligand passing under the bridge, is rapid on the NMR time scale and renders diastereotopic groups equivalent.^{3d} In **3c**, which has a shorter  $P(CH_2)_{10}P$  bridge, the rotational barrier becomes much higher and separate NMR signals for diastereotopic groups are observed. As can be visualized from V in Fig. 4, analogous 180° rotations would also exchange the diastereotopic phosphorus atoms of *anti*-1**5e**. However, since there are now two  $P(CH_2)_{14}P$  bridges, the larger The distance from the platinum to the *para* fluorine atom in *anti*-15e is 6.18 Å. This is nearly as great as the distance from platinum to the most remote macrocyclic carbons (7.19/6.85 Å). When the van der Waals radius of fluorine (1.47 Å) is added to the former value, and the van der Waals radius of carbon (1.70 Å) is subtracted from the latter values,²⁴ it is obvious that the "vehicle height" is much greater than the "bridge height" (7.65 Å *vs.* 5.49/5.15 Å). Accordingly, two ³¹P NMR signals are observed. However, with still longer methylene bridges, rotation of the Cl-Pt-C₆F₅ moiety should become possible, leading to dynamic NMR phenomena.

#### **3** Summary and prospective

Architecturally novel doubly trans-spanning diphosphine complexes are easily accessed by interligand alkene metatheses of the bis(phosphine) complexes 11c,d,e,f (Schemes 6, 9 and 10). Although the yields are lower than those of the singly trans-spanning diphosphine complexes obtained from 1c,e,f,g (Scheme 1), advanced-generation metatheses catalysts may offer improvements.¹⁹ In any event, conventional syntheses would require many additional steps. Curiously, intraligand metathesis products are observed only when the carbon bridges would be too short to span trans positions (Scheme 8). One attempt to extend these reactions to still more complex educts that can lead to higher polycycles was disappointing (Scheme 4). However, as will be described in future papers, others have been spectacularly successful.²⁵ Taken together, these investigations - as well as clever findings by others^{2,5} - are significantly advancing the utility of alkene metatheses in syntheses of topologically unusual inorganic and organometallic systems.

# **Experimental**

# General data

All reactions were conducted under N₂ (or H₂) atmospheres. Chemicals were treated as follows: THF, ether, benzene, and toluene, distilled from Na/benzophenone; CH₂Cl₂, distilled from CaH₂ (for reactions) or simple distillation (chromatography); hexanes and ethanol, simple distillation; HNEt₂, distilled from NaOH; CDCl₃, ClCH₂CH₂Cl (99%, Fluka), Ru(=CHPh)(PCy₃)₂(Cl)₂ (**2**, Strem), H₃B·SMe₂ (Fluka, 99%), Rh(PPh₃)₃(Cl) (Strem), 10% Pd/C (Lancaster or Acros), PPhH₂ (99%, Strem), *n*-BuLi (Acros, 2.5 M in hexanes), Br(CH₂)_{*n*}CH= CH₂ (*n* = 2, 98%, Fluka; 3, 95%, Aldrich; 4, 90%, Fluka; 5, 97%, Aldrich), used as received.

NMR spectra were obtained on Bruker or Jeol 400 MHz spectrometers. IR and mass spectra were recorded on ASI React-IR 1000 and Micromass Zabspec instruments, respectively. DSC and TGA data were obtained with a Mettler-Toledo DSC-821 instrument.²⁶ Microanalyses were conducted with a Carlo Erba EA1110 instrument (in-house).

### $PPh((CH_2)_2CH=CH_2)_2 (4a)^7$

A Schlenk flask was charged with PPhH₂ (0.514 g, 4.67 mmol) and THF (20 mL) and cooled to 0 °C. Then *n*-BuLi (2.5 M in hexanes, 3.75 mL, 9.4 mmol) was added dropwise with stirring over 10 min. The colorless solution turned yellow–orange. After 5 min, Br(CH₂)₂CH=CH₂ (0.95 mL, 9.4 mmol) was added. The solution became colorless. The cold bath was removed. After 3.5 h, solvent was removed by oil-pump vacuum. The residue was filtered through a silica plug (5 cm) with hexanes–toluene (1 : 1 v/v). The filtrate was taken to dryness by oil-pump vacuum to give **4a** (0.916 g, 4.20 mmol, 90%) as a colorless oil. Calc. for C₁₄H₁₉P: C, 77.06; H, 8.72. Found: C, 77.54; H, 9.51%.

# PPh((CH₂)₃CH=CH₂)₂ (4b)⁸

PPhH₂ (0.685 g, 6.23 mmol), THF (20 mL), *n*-BuLi (2.5 M in hexanes, 5.0 mL, 12.5 mmol) and Br(CH₂)₃CH=CH₂ (1.48 mL, 12.5 mmol) were combined in a procedure analogous to that for **4a**. An identical workup gave **4b** (1.41 g, 5.73 mmol, 92%) as a colorless oil.

NMR:²⁷ ¹H 7.55–7.51 (m, 2 H of Ph), 7.38–7.35 (m, 3 H of Ph), 5.81–5.73 (m, 2 H, 2CH=), 5.04–4.96 (m, 4 H, 2 =CH₂), 2.17–2.12 (m, 4 H, 2CH₂), 1.76–1.70 (m, 4 H, 2CH₂), 1.54–1.48 (m, 4 H, 2CH₂); ¹³C{¹H} ²⁸ 138.8 (d, ¹J_{CP} = 15.0, *i*-Ph), 138.4 (s, CH=), 132.6 (d, ²J_{CP} = 18.3, *o*-Ph), 128.9 (s, *p*-Ph), 128.5 (d, ³J_{CP} = 7.0, *m*-Ph), 115.0 (s, =CH₂), 35.4 (d, J_{CP} = 11.8, CH₂), 27.8 (d, J_{CP} = 10.8, CH₂), 25.4 (d, J_{CP} = 14.3, CH₂); ³¹P{¹H} –23.5 (s).

# PPh((CH₂)₄CH=CH₂)₂ (4c)

PPhH₂ (0.572 g, 5.20 mmol), THF (20 mL), *n*-BuLi (2.5 M in hexanes, 4.2 mL, 10.5 mmol) and Br(CH₂)₄CH=CH₂ (1.4 mL, 10.4 mmol) were combined in a procedure analogous to that for **4a**. An identical workup gave **4c** (1.27 g, 4.63 mmol, 89%) as a colorless oil. Calc. for C₁₈H₂₇P: C, 78.83; H, 9.85. Found C, 79.11; H, 10.04%.

NMR: ^{27 1}H 7.44 (m, 2 H of Ph), 7.26 (m, 3 H of Ph), 5.67 (m, 2 H, 2CH=), 4.86 (m, 4 H, 2 =CH₂), 1.98–1.91 (m, 4 H, 2CH₂), 1.64–1.59 (m, 4 H, 2CH₂), 1.42–1.29 (m, 8 H, 4CH₂); ¹³C{¹H}²⁸ 139.1 (s, CH=), 138.6 (d, ¹J_{CP} = 16.0, *i*-Ph), 132.7 (d, ²J_{CP} = 19.0, *o*-Ph), 129.1 (s, *p*-Ph), 128.7 (d, ³J_{CP} = 7.0, *m*-Ph), 114.8 (s, =CH₂), 33.8 (s, CH₂), 30.8 (d, J_{CP} = 11.0, CH₂), 28.4 (d, J_{CP} = 11.0, CH₂), 25.8 (d, J_{CP} = 13.0, CH₂); ³¹P{¹H} – 23.0 (s).

MS: ²⁹ 275 (4 $c^+$ , 100%), 192 ([4 $c - (CH_2)_4CH=CH_2$ ]⁺, 92%).

#### PPh((CH₂)₅CH=CH₂)₂ (4d)

PPhH₂ (0.606 g, 5.51 mmol), THF (20 mL), *n*-BuLi (2.5 M in hexanes, 4.5 mL, 11.3 mmol) and Br(CH₂)₅CH=CH₂ (1.73 mL, 11.4 mmol) were combined in a procedure analogous to that for **4a**. An identical workup gave **4d** (1.55 g, 5.12 mmol, 93%) as a colorless oil. Calc. for C₂₀H₃₁P: C, 79.47; H, 10.26. Found C, 78.89; H, 10.61%.

NMR:²⁷ ¹H 7.54–7.53 (m, 2 H of Ph), 7.38–7.36 (m, 3 H of Ph), 5.82–5.80 (m, 2 H, 2CH=), 5.02–4.94 (m, 4 H, 2 =CH₂), 2.05–2.00 (m, 4 H, 2CH₂), 1.73–1.70 (m, 4 H, 2CH₂), 1.45–1.36 (m, 12 H, 6CH₂); ¹³C{¹H} ²⁸ 139.4 (d, ¹J_{CP} = 18.3, *i*-Ph), 139.3 (s, CH=), 132.7 (d, ²J_{CP} = 18.4, *o*-Ph), 129.0 (s, *p*-Ph), 128.6 (d, ³J_{CP} = 6.7, *m*-Ph), 114.7 (s, =CH₂), 34.0 (s, CH₂), 31.1 (d, J_{CP} = 11.5, CH₂), 29.0 (s, CH₂), 28.6 (d, J_{CP} = 11.0, CH₂), 26.2 (d, J_{CP} = 13.6, CH₂); ³¹P{¹H} –23.3 (s).

MS: ²⁹ 303 (4d⁺, 100%), 206 ([4d - (CH₂)₅CH=CH₂]⁺, 62%).

# PPh((CH₂)₈CH=CH₂)₂ (4f)

PPhH₂ (0.152 g, 1.38 mmol), THF (10 mL), *n*-BuLi (2.5 M in hexanes, 1.1 mL, 2.8 mmol) and Br(CH₂)₈CH=CH₂ (0.55 mL, 2.75 mmol)^{3d} were combined in a procedure analogous to that for **4a**. An identical workup gave **4f** (0.521 g, 1.35 mmol, 98%) as a colorless oil.³⁰

NMR:^{27 1}H 7.52 (m, 2 H of Ph), 7.36 (m, 3 H of Ph), 5.80 (m, 2 H, 2CH=), 5.03–4.92 (m, 4 H, 2 =CH₂), 2.08–2.00 (m, 4 H, 2CH₂), 1.37–1.27 (m, 28 H, 14CH₂); ¹³C{¹H} ²⁸ 139.6 (s, CH=), 139.5 (d, ¹ $J_{CP}$  = 19.9, *i*-Ph), 132.7 (d, ² $J_{CP}$  = 18.3, *o*-Ph), 128.9 (s, *p*-Ph), 128.6 (d, ³ $J_{CP}$  = 9.1, *m*-Ph), 114.5 (s, =CH₂), 34.2 (s, CH₂), 31.6 (d,  $J_{CP}$  = 11.5, CH₂), 29.7 (s, CH₂), 29.6 (s, CH₂), 29.5 (s,

CH₂), 29.3 (s, CH₂), 28.7 (d,  $J_{CP} = 10.9$ , CH₂), 26.3 (d,  $J_{CP} = 13.4$ , CH₂); ³¹P{¹H} -23.2 (s). MS:²⁹ 387 (**4f**⁺, 100%).

# trans-(Cl)(C₆F₅)Pt(PPh((CH₃)₂CH=CH₂)₂)₂ (11a)

A Schlenk flask was charged with  $[Pt(\mu-Cl)(C_6F_5)(S(CH_2-CH_2)_2)]_2$  (12; 0.460 g, 0.474 mmol),⁹ 4a (0.424 g, 1.945 mmol) and CH₂Cl₂ (30 mL). The pale green mixture was stirred (14 h) and became colorless. Solvent was removed by oil-pump vacuum. The residue was filtered through neutral alumina (3.0 × 2.5 cm column) using 1 : 1 v/v CH₂Cl₂-hexanes. Solvent was removed from the product fraction by oil-pump vacuum to yield 11a as a colorless oil (0.627 g, 0.752 mmol, 79%). Calc. for C₁₄H₃₈ClF₅P₃Pt: C, 48.95; H, 4.56. Found: C, 49.33; H, 4.80%.

³⁶ NMR: ^{27 1}H 7.44 (m, 4 H of 2Ph), 7.35 (m, 6 H of 2Ph), 5.84– 5.75 (m, 4 H, 4CH=), 5.03–4.97 (m, 8 H, 4=CH₂), 2.37–2.27 (m, 8 H, 4CH₂), 2.19–2.09 (m, 8 H, 4CH₂); ¹³C{¹H} ^{31a,32,33} 137.8 (virtual t, ³⁴  $J_{CP} = 7.5$ , CH=), 131.6 (virtual t, ³⁴  $J_{CP} = 5.3$ , *o*-Ph), 130.6 (s, *p*-Ph), 130.0 (virtual t, ³⁴  $J_{CP} = 26.0$ , *i*-Ph), 128.7 (virtual t, ³⁴  $J_{CP} = 4.8$ , *m*-Ph), 115.6 (s, =CH₂), 28.4 (s, PCH₂CH₂), 22.6 (virtual t, ³⁴  $J_{CP} = 16.4$ , PCH₂); ³¹P{¹H} 10.7 (s,  $J_{PPt} = 2564$ ).³⁵

IR (cm⁻¹, oil film) 3080 (w), 2980 (w), 2934 (w), 2864 (w), 1640 (m), 1502 (s), 1459 (s), 1436 (s), 1108 (m), 1058 (m), 953 (s), 911 (s), 803 (s), 722 (s), 687 (s). MS:²⁹ 798 ([**11a** - Cl]⁺, 100%), 579 ([**11a** - Cl - **4a**]⁺, 40%), 411 ([**11a** - Cl - C₆F₅ - **4a**]⁺, 80%), 219 (**4a**⁺, 80%), 164 ([**4a** - (CH₂)₄CH=CH₂]⁺, 70%).

# trans-(Cl)(C₆F₅)Pt(PPh((CH₂)₃CH=CH₂)₂)₂ (11b)

Complex **12** (0.430 g, 0.443 mmol), **4b** (0.440 g, 1.79 mmol) and CH₂Cl₂ (25 mL) were combined in a procedure analogous to that for **11a** (17 h stirring). An identical workup gave **11b** as a colorless oil (0.675 g, 0.759 mmol, 86%). Calc. for  $C_{38}H_{46}$ -ClF₅P₂Pt: C, 51.27; H, 5.17. Found: C, 50.48; H, 5.12%.

NMR:^{27 1}H 7.47–7.43 (m, 4 H of 2Ph), 7.35–7.30 (m, 6 H of 2Ph), 5.76–5.66 (m, 4 H, 4CH=), 5.02–4.98 (m, 8 H, 4 =CH₂), 2.19–2.07 (m, 12 H, 6CH₂), 2.00–1.96 (m, 4 H, 2CH₂), 1.81–1.70 (m, 4 H, 2CH₂), 1.50–1.42 (m, 4 H, 2CH₂); ¹³C{¹H} ^{31,32,33} 137.6 (s, CH=), 131.5 (virtual  $t,^{34} J_{CP} = 5.3$ , *o*-Ph), 130.2 (s, *p*-Ph), 128.4 (virtual  $t,^{34} J_{CP} = 4.8$ , *m*-Ph), 115.8 (s, =CH₂), 35.1 (virtual  $t,^{34} J_{CP} = 7.1$ , PCH₂CH₂CH₂), 23.3 (s, PCH₂CH₂), 22.5 (virtual  $t,^{34} J_{CP} = 16.8$ , PCH₂); ³¹P{¹H} 10.2 (s,  $J_{PPt} = 2551$ ).³⁵

IR (cm⁻¹, oil film) 3080 (w), 2980 (w), 2934 (w), 2864 (w), 1640 (m), 1502 (s), 1459 (s), 1436 (s), 1108 (m), 1058 (m), 953 (s), 911 (s), 803 (s), 722 (s), 687 (s). MS:²⁹ 854 ([11b - Cl]⁺, 80%), 606 ([11b - Cl - 4b]⁺, 40%), 440 ([11b - Cl - C₆F₅ - 4b]⁺, 100%), 245 (4b⁺, 80%), 178 ([4b - (CH₂)₃CH=CH₂]⁺, 100%).

#### trans-(Cl)(C₆F₅)Pt(PPh((CH₂)₄CH=CH₂)₂)₂ (11c)

Complex 12 (0.522 g, 0.537 mmol), 4c (0.495 g, 1.81 mmol) and CH₂Cl₂ (30 mL) were combined in a procedure analogous to that for 11a (18 h stirring). An identical workup gave 11c as a colorless oil (0.738 g, 0.780 mmol, 73%). Calc. for C₄₂H₅₄-ClF₅P₂Pt: C, 53.31; H, 5.71. Found: C, 53.45; H, 5.85%.

NMR:²⁷ ¹H 7.39 (m, 4 H of 2Ph), 7.29 (m, 6 H of 2Ph), 5.71–5.60 (m, 4 H, 4CH=), 4.94–4.84 (m, 8 H, 4 =CH₂), 2.20–2.10 (m, 4 H, 2CH₂), 2.03–1.96 (m, 12 H, 6CH₂), 1.62–1.51 (m, 4 H, 2CH₂), 1.44–1.32 (m, 12 H, 6CH₂); ¹³C{¹H} ^{31a,32,33} 138.6 (s, CH=), 131.6 (virtual t, ³⁴  $J_{CP} = 5.1$ , *o*-Ph), 130.6 (virtual t, ³⁴  $J_{CP} = 25.9$ , *i*-Ph), 130.3 (s, *p*-Ph), 128.5 (virtual t, ³⁴  $J_{CP} = 4.7$ , *m*-Ph), 115.2 (s, =CH₂), 33.6 (s, CH₂), 30.7 (virtual t, ³⁴  $J_{CP} = 6.9$ , PCH₂CH₂CH₂), 23.6 (s, CH₂), 22.9 (virtual t, ³⁴  $J_{CP} = 16.6$ , PCH₂); ³¹P{¹H} 10.1 (s,  $J_{PPt} = 2543$ ).³⁵

IR (cm⁻¹, oil film) 3080 (w), 2930 (m), 2860 (w), 1640 (w), 1502 (s), 1459 (s), 1440 (s), 1108 (m), 1061 (s), 957 (s), 911 (s), 799 (s), 741 (s), 695 (s). MS: ²⁹ 910 ([**11c** - Cl]⁺, 40%), 741 ([**11c** - Cl - C₆F₅]⁺, 20%), 467 ([**11c** - Cl - C₆F₅ - **4c**]⁺, 50%), 385

 $\begin{array}{l} ([11c - Cl - C_6F_5 - 4c - (CH_2)_4CH=CH_2]^+, \, 45\%), \, 275 \, (4c^+, \\ 70\%), \, 192 \, ([4c - (CH_2)_4CH=CH_2]^+, \, 100\%). \end{array}$ 

# trans-(Cl)(C₆F₅)Pt(PPh((CH₂)₅CH=CH₂)₂)₂ (11d)

Complex 12 (0.260 g, 0.268 mmol), 4d (0.340 g, 1.13 mmol) and  $CH_2Cl_2$  (20 mL) were combined in a procedure analogous to that for 11a. An identical workup gave 11d as a colorless oil (0.497 g, 0.496 mmol, 93%). Calc. for  $C_{46}H_{62}ClF_5P_2Pt$ : C, 55.12; H, 6.19. Found: C, 54.75; H, 6.50.

NMR: ²⁷ ¹H 7.43–7.41 (m, 4 H of 2Ph), 7.34–7.28 (m, 6 H of 2Ph), 5.82–5.75 (m, 4 H, 4CH=), 5.01–4.93 (m, 8 H, 4 =CH₂), 2.20–2.12 (m, 4 H, 2CH₂), 2.01–1.95 (m, 12 H, 6CH₂), 1.70–1.55 (m, 4 H, 2CH₂), 1.45–1.30 (m, 20 H, 10CH₂); ¹³C{¹H} ^{31a,32,33} 139.1 (s, CH=), 131.6 (virtual t, ³⁴  $J_{CP} = 5.1$ , *o*-Ph), 130.7 (virtual t, ³⁴  $J_{CP} = 26.1$ , *i*-Ph), 130.3 (s, *p*-Ph), 128.5 (virtual t, ³⁴  $J_{CP} = 4.6$ , *m*-Ph), 114.9 (s, =CH₂), 33.9 (s, CH₂), 31.0 (virtual t, ³⁴  $J_{CP} = 7.0$ , PCH₂CH₂CH₂), 28.7 (s, CH₂), 24.1 (s, CH₂), 23.1 (virtual t, ³⁴  $J_{CP} = 16.7$ , PCH₂); ³¹P{¹H} 10.2 (s,  $J_{PPt} = 2543$ ).³⁵

IR (cm⁻¹, oil film) 3080 (w), 2930 (m), 2856 (m), 1640 (m), 1502 (s), 1459 (s), 1440 (s), 1061 (s), 957 (s), 907 (s), 799 (s), 741 (s), 694 (s). MS:²⁹ 966 ([11d - Cl]⁺, 20%), 797 ([11d - Cl - C₆F₅]⁺, 20%), 495 ([11d - Cl - C₆F₅ - 4d]⁺, 60%), 397 ([11d - Cl - C₆F₅ - 4d - (CH₂)₅CH=CH₂]⁺, 50%), 303 (4d⁺, 100%), 192 ([4d - (CH₂)₅CH=CH₂]⁺, 70%).

# trans-(Cl)(C₆F₅)Pt(PPh((CH₂)₆CH=CH₂)₂)₂ (11e)

Complex **12** (0.416 g, 0.430 mmol), **4e** (0.568 g, 1.719 mmol)^{3c} and CH₂Cl₂ (30 mL) were combined in a procedure analogous to that for **11a** (16 h stirring). A similar workup ( $2.5 \times 2.5$  cm column,  $3 : 1 \text{ v/v } \text{CH}_2\text{Cl}_2$ -hexanes) gave **11e** as a colorless oil (0.824 g, 0.779 mmol, 91%). Calc. for C₅₀H₇₀ClF₅P₂Pt: C, 56.73; H, 6.66. Found: C, 56.12; H, 6.58%.

NMR:²⁷ ¹H 7.40–7.37 (m, 4 H of 2Ph), 7.30–7.26 (m, 6 H of 2Ph), 5.81–5.68 (m, 4 H, 4CH=), 4.98–4.89 (m, 8 H, 4=CH₂), 2.10–2.09 (m, 4 H, 4PC*H*H'), 2.01–1.89 (m, 12 H, 4PCH*H*', 4C*H*₂CH=), 1.60–1.56 (m, 4 H, 4PCH₂C*H*H'), 1.34–1.24 (m, 28 H, 4PCH₂CH*H*', 12CH₂); ¹³C{¹H} ^{31a,32,33} 138.9 (s, CH=), 131.2 (virtual t, ³⁴  $J_{CP} = 5.1$ , *o*-Ph), 130.4 (virtual t, ³⁴  $J_{CP} = 25.8$ , *i*-Ph), 129.9 (s, *p*-Ph), 128.0 (virtual t, ³⁴  $J_{CP} = 4.4$ , *m*-Ph), 114.3 (=CH₂), 33.7 (s, CH₂CH=), 31.0 (virtual t, ³⁴  $J_{CP} = 6.5$ , PCH₂CH₂CH₂CH₂), 28.7 (s, CH₂), 28.6 (s, CH₂), 23.7 (s, CH₂), 22.7 (virtual t, ³⁴  $J_{CP} = 16.5$ , PCH₂); ³¹P{¹H} 9.3 (s, ¹ $J_{PPt} = 2540$ ).³⁵

IR (cm⁻¹, powder film) 3080 (w), 2930 (m), 2856 (w), 1502 (s), 1463 (s), 1436 (s), 1104 (m), 1061 (m), 1000 (m), 953 (s), 911 (s), 803 (m), 741 (s), 690 (s). MS:²⁹ 1059 (**11e**⁺, 2%), 1022 ([**11e** - Cl]⁺, 40%), 853 ([**11e** - Cl - C₆F₅]⁺, 22%), 489 ([**11e** - Cl - C₆F₅ - **4e**]⁺, 70%), 331 (**4e**⁺, 100%).

### trans-(Cl)(C₆F₅)Pt(PPh((CH₂)₈CH=CH₂)₂)₂ (11f)

Complex 12 (0.504 g, 0.519 mmol), 4f (0.839 g, 2.17 mmol) and  $CH_2Cl_2$  (30 mL) were combined in a procedure analogous to that for 11a (15 h stirring). An identical workup gave 11f as a colorless oil (0.898 g, 0.768 mmol, 74%). Calc. for  $C_{58}H_{86}$ - $ClF_5P_2Pt$ : C, 59.80; H, 7.72. Found: C, 59.52; H, 7.35%.

NMR: ²⁷ ¹H 7.43 (m, 4 H of 2Ph), 7.29 (m, 6 H of 2Ph), 5.82 (m, 4 H, 4CH=), 4.98 (m, 8 H, 4 =CH₂), 2.14–1.94 (m, 16 H, 8CH₂), 1.58 (m, 4 H, 2CH₂), 1.37–1.25 (m, 44 H, 22CH₂); ¹³C{¹H} ^{31a,32,33} 139.4 (s, CH=), 131.4 (virtual t, ³⁴  $J_{CP} = 5.1$ , *o*-Ph), 130.7 (virtual t, ³⁴  $J_{CP} = 25.6$ , *i*-Ph), 130.0 (s, *p*-Ph), 128.2 (virtual t, ³⁴  $J_{CP} = 6.9$ , PCH₂CH₂CH₂), 29.7 (s, CH₂), 29.3 (s, CH₂), 29.3 (s, CH₂), 29.3 (s, CH₂), 29.3 (s, CH₂), 29.0 (s, CH₂), 24.0 (s, CH₂), 22.9 (virtual t, ³⁴  $J_{CP} = 16.5$ , PCH₂); ³¹P{¹H} 10.1 (s,  $J_{PPt} = 2540$ ).³⁵

IR (cm⁻¹, oil film) 3080 (w), 2926 (s), 2856 (s), 1640 (w), 1502 (s), 1459 (s), 1061 (m), 957 (s), 907 (s), 799 (m), 741 (s), 695 (s). MS: ²⁹ 1134 ([**11f** - Cl]⁺, 100%), 965 ([**11f** - Cl - C₆ $F_5$ ]⁺, 70%).

# Metathesis of 11a; (Z,Z)-trans-(Cl)(C₆F₅)Pt-(PPh(CH₂)₂CH=CH(CH₂)₂)₂ ((Z,Z)-14a)

A two-necked flask was charged with **11a** (0.465 g, 0.558 mmol), Grubbs' catalyst **2** (*ca*. half of 0.036 g, 0.0390 mmol, 14 mol%) and CH₂Cl₂ (60 mL; the resulting solution is 0.0093 M in **11a**), and fitted with a condenser. The solution was refluxed. After 2 h, the remaining **2** was added. After 2 h, solvent was removed by oil-pump vacuum. The residue was filtered through neutral alumina ( $2.5 \times 2.5$  cm column) using CH₂Cl₂. Solvent was removed from the filtrate by oil-pump vacuum to give (*Z*,*Z*)-**14a** as a pale pink solid (0.371 g, 0.477 mmol, 86%), mp 218–220 °C (decomp.) (capillary). Calc. for C₃₀H₃₀ClF₅P₂Pt: C, 46.31; H, 3.86. Found: C, 46.81; H, 4.28%.

NMR: ²⁷ ¹H 7.45–7.39 (m, 4 H of 2Ph), 7.35–7.28 (m, 6 H of 2Ph), 5.79–5.75 (m, 4 H, 2CH=CH), 2.55–2.43 (m, 8 H, 4CH₂), 2.32–2.20 (m, 8 H, 4CH₂); ¹³C{¹H} ^{31*a*,32} 131.8 (s, CH=CH), 131.3 (virtual t, ³⁴  $J_{CP}$  = 4.8, *o*-Ph), 130.4 (virtual t, ³⁴  $J_{CP}$  = 25.9, *i*-Ph), 130.3 (s, *p*-Ph), 128.8 (virtual t, ³⁴  $J_{CP}$  = 4.8, *m*-Ph), 22.4 (s, CH₂), 21.5 (virtual t, ³⁴  $J_{CP}$  = 16.1, CH₂); ³¹P{¹H} 15.8 (s,  $J_{PPt}$  = 2511).³⁵

IR (cm⁻¹, powder film) 3030 (w), 2930 (w), 2856 (w), 1502 (s), 1459 (s), 1058 (m), 953 (s), 718 (s), 695 (s). MS:²⁹ 742 ([**14a** – Cl]⁺, 100%), 552 ([**14a** – Cl – PhP((CH₂)CH=CH(CH₂))]⁺, 30%).

# trans-(Cl)(C₆F₅)Pt(PPh((CH₂)₆)₂ (16a)

A two-necked flask was charged with **14a** (0.371 g, 0.477 mmol), 10% Pd/C (0.064 g, 0.0601 mmol Pd), ClCH₂CH₂Cl (20 mL) and ethanol (20 mL), flushed with H₂, and fitted with a balloon of H₂. The mixture was stirred for 69 h. Solvent was removed by oil-pump vacuum. The residue was filtered through neutral alumina (2.5 × 2.5 cm column) using 3 : 1 v/v hexanes–CH₂Cl₂. Solvent was removed from the filtrate by oil-pump vacuum to give **16a** as a white powder (0.240 g, 0.307 mmol, 64%), mp 145 °C (capillary), 147 °C (DSC;  $T_i/T_e/T_p/T_c/T_f$  120.7/145.3/147.0/149.0/179.8 °C). TGA: onset of mass loss, 285 °C ( $T_e$ ). Calc. for C₃₀H₃₄ClF₅P₂Pt: C, 46.07; H, 4.35. Found: C, 45.98; H, 4.43%.

NMR:²⁷ ¹H 7.44 (m, 4 H of 2Ph), 7.28 (m, 6 H of 2Ph), 2.52–2.58 (m, 4 H, 2CH₂), 2.28–2.24 (m, 4 H, 2CH₂), 1.91–1.88 (m, 4 H, 2CH₂), 1.70–1.65 (m, 8 H, 4CH₂), 1.55–1.53 (m, 4 H, 2CH₂); ¹³C{¹H} ^{31a,32} 132.1 (virtual t,³⁴  $J_{CP} = 25.4$ , *i*-Ph), 131.2 (virtual t,³⁴  $J_{CP} = 4.8$ , *o*-Ph), 130.0 (s, *p*-Ph), 128.5 (virtual t,³⁴  $J_{CP} = 4.7$ , *m*-Ph), 29.3 (s, CH₂), 24.9 (virtual t,³⁴  $J_{CP} = 15.9$ , CH₂), 23.4 (s, CH₂); ³¹P{¹H} 11.2 (s,  $J_{PPt} = 2488$ ).³⁵

IR (cm⁻¹, powder film) 2926 (m), 2860 (w), 1502 (s), 1459 (s), 1058 (s), 953 (s), 803 (s), 730 (s), 691 (s). MS:²⁹ 782 (**16a**⁺, 40%), 746 ([**16a** - Cl]⁺, 50%), 577 ([**16a** - Cl - C₆F₅]⁺, 100%).

#### Metathesis of 11b

Complex **11b** (0.176 g, 0.198 mmol), **2** (0.039 g, 0.0474 mmol, 24 mol%), and  $CH_2Cl_2$  (60 mL; resulting solution 0.0033 M in **11b**) were combined in a procedure analogous to that with **11a** (1.5 h, second catalyst charge, then 1.5 h). A similar workup (2.5 × 3 cm column) gave a white powder comprised of polymeric and/or oligomeric products (0.140 g, 0.168 mmol, 85%).

NMR:²⁷ ¹H 7.32 (m, 10 H, 2Ph), 5.30 (m, 4 H, 2CH=CH), 2.02–1.25 (m, 24 H, 12CH₂); ³¹P{¹H} 10.0 (br s,  $J_{PPt} = 2561$ ).³⁵

$$\begin{split} MS: {}^{29}\ 1632\ ([2\cdot Pt-Cl]^+,\, 30\%), {}^{36}\ 1463\ ([2\cdot Pt-Cl-C_6F_5]^+,\\ 20\%), {}^{36}\ 630\ (Pt(PPh((CH_2)_3CH=)_2)_2^+,\, 100\%). \end{split}$$

# Metathesis of 11c; syn-(E,E)-trans-(Cl)(C₆F₅)-Pt(PPh(CH₂)₄CH=CH(CH₂)₄P(CH₂)₄CH=CH(CH₂)₄Ph) (syn-(E,E)-13c)

Complex **11c** (0.191 g, 0.202 mmol), **2** (0.020 g, 0.0242 mmol, 12 mol%), and CH₂Cl₂ (300 mL; resulting solution is 0.00067 M

in **11c**) were combined in a procedure analogous to that with **11a** (3 h, second catalyst charge, then 3 h; ³¹P{¹H} NMR of residue ( $\delta$ , CDCl₃): 18.7 (28%), 12.6 (11%), 12.0 (19%), 11.6 (23%), 11.1 (19%)) A similar workup (2.5 × 5 cm column using 2 : 1 v/v hexanes–CH₂Cl₂; solvent removal from first fractions) gave *syn*-(*E*,*E*)-**13c** as a white solid (0.0379 g, 0.0426 mmol, 21%), mp 265–268 °C (decomp.) (capillary). Calc. for C₃₈H₄₆ClF₅P₂Pt: C, 51.26; H, 5.17. Found: C, 51.12; H, 5.25%.

¹⁰ NMR: ²⁷ ¹H 7.21 (m, 2 H of 2Ph), 7.13–7.10 (m, 8 H of 2Ph), 5.50 (t,  $J_{\rm HH}$  = 3.6, 4 H, 2CH=CH), 2.53–2.45 (m, 8 H, 4CH₂), 2.29–2.25 (m, 4 H, 2CH₂), 2.09–2.07 (m, 4 H, 2CH₂), 1.97–1.93 (m, 4 H, 2CH₂), 1.82–1.79 (m, 4 H, 2CH₂), 1.67–1.55 (m, 8 H, 4CH₂); ¹³C{¹H} ^{31,32} 131.5 (s, CH=CH), 130.7 (virtual t, ³⁴  $J_{\rm CP}$  = 4.7, o-Ph), 130.0 (s, p-Ph), 128.0 (virtual t, ³⁴  $J_{\rm CP}$  = 4.6, m-Ph), 32.2 (s, CH₂), 31.1 (virtual t, ³⁴  $J_{\rm CP}$  = 8.3, CH₂), 27.4 (virtual t, ³⁴  $J_{\rm CP}$  = 17.2, CH₂), 25.8 (s, CH₂); ³¹P{¹H} 18.7 (s,  $J_{\rm PPt}$  = 2623).³⁵

IR (cm⁻¹, powder film) 2930 (m), 2849 (w), 1498 (s), 1455 (s), 1436 (s), 1058 (s), 953 (s), 768 (s), 718 (s). MS:²⁹ 890 (13c⁺, 10%), 854 ([13c - Cl]⁺, 100%), 686 ([13c - Cl - C₆F₅]⁺, 60%).

The column was subsequently rinsed with  $CH_2Cl_2$ . Similar concentration of the fractions gave a white solid (0.0754 g, 0.0848 mmol, 42%) comprised of polymeric and/or oligomeric products.

¹ ³¹P{¹H} 12.6 (s,  $J_{PPt} = 2583$ , ³⁵ 19%), 12.0 (s,  $J_{PPt} = 2552$ , ³⁵ 14%), 11.6 (s,  $J_{PPt} = 2573$ , ³⁵ 45%), 11.1 (s,  $J_{PPt} = 2498$ , ³⁵ 22%). MS: ²⁹ 1742 ([2·Pt - Cl]⁺, 10%), ³⁶ 1576 ([2·Pt - Cl - C₆F₅]⁺, 5%), ³⁶ 549 ([13c - Cl - C₆F₅ - (CH₂)₁₀]⁺, 100%).

# syn-trans-(Cl)( $C_6F_5$ )Pt(PPh(CH₂)₁₀P(CH₂)₁₀Ph) (syn-15c)

Complex **13c** (0.0379 g, 0.0426 mmol), 10% Pd/C (0.019 g, 0.018 mmol Pd), ClCH₂CH₂Cl (10 mL), ethanol (10 mL), and H₂ were combined in a procedure analogous to that for **16a**. After 132 h, a similar workup (column rinsed with 2 : 1 v/v hexanes–CH₂Cl₂) gave *syn***-15c** as a white powder (0.036 g, 0.0405 mmol, 95%), mp 256–258 °C (decomp.) (capillary), 255 °C (DSC;  $T_i/T_c/T_p/T_c/T_f$  210.1/242.2/254.6/260.6/271.4 °C). TGA: onset of mass loss, 328 °C ( $T_e$ ). Calc. for C₃₈H₅₀ClF₅-P₂Pt: C, 51.04; H, 5.60. Found: C, 51.00; H, 5.61%.

NMR:^{27 1}H 7.18 (m, 2 H of 2Ph), 7.11 (m, 8 H of 2Ph), 2.56– 2.53 (m, 4 H, 2CH₂), 2.42–2.35 (m, 4 H, 2CH₂), 1.97–1.84 (m, 8 H, 4CH₂), 1.70–1.63 (m, 10 H, 5CH₂), 1.57–1.50 (m, 10 H, 5CH₂), 1.48–1.40 (m, 4 H, 2CH₂); ¹³C{¹H} ^{31a,32} 130.9 (virtual t,³⁴  $J_{CP} = 24.1$ , *i*-Ph), 130.7 (virtual t,³⁴  $J_{CP} = 5.2$ , *o*-Ph), 130.0 (s, *p*-Ph), 127.9 (virtual t,³⁴  $J_{CP} = 4.6$ , *m*-Ph), 29.5 (virtual t,³⁴  $J_{CP} =$ 7.3, CH₂), 27.4 (s, CH₂), 26.6 (virtual t,³⁴  $J_{CP} = 17.1$ , CH₂), 25.7 (s, CH₂), 24.8 (s, CH₂); ³¹P{¹H} 16.2 (s,  $J_{PPt} = 2612$ ).³⁵

IR (cm⁻¹, oil film) 2926 (w), 2856 (w), 1502 (m), 1459 (m), 1231 (s), 1119 (s), 980 (s), 953 (s), 803 (m), 741 (m), 695 (m). MS:²⁹ 894 (**15c**⁺, 35%), 858 ([**15c** - Cl]⁺, 100%), 689 ([**15c** - Cl - C₆F₅]⁺, 50%).

# Metathesis of 11d; $syn-trans-(Cl)(C_6F_5)Pt(PPh(CH_2)_{12}P(CH_2)_{12}-Ph)$ (syn-15d)

Complex **11d** (0.103 g, 0.103 mmol), **2** (0.018 g, 0.0218 mmol, 21 mol%), and CH₂Cl₂ (55 mL; resulting solution 0.0019 M in **11d**) were combined in a procedure analogous to that with **11a** (2 h, second catalyst charge, 2 h). The residue (³¹P{¹H} NMR ( $\delta$ , CDCl₃): 10.6 (s, 12%), 10.1 (br s,  $J_{PPt} = 2532.1, 88\%)$ )³⁵ was charged with 10% Pd/C (0.030 g, 0.028 mmol Pd), ClCH₂CH₂Cl (10 mL) and ethanol (10 mL), flushed with H₂, and fitted with a balloon of H₂. The mixture was stirred for 144 h. Solvent was removed by oil-pump vacuum. The residue was filtered through neutral alumina (2.5 × 2.5 cm column) using 3 : 1 v/v hexanes-CH₂Cl₂. Solvent was removed from the filtrate to give *syn*-**15d** as a white powder (0.005 g, 0.0053 mmol, 5%). Calc. for C₄₂H₅₈ClF₅P₂Pt: C, 53.08; H, 6.11. Found: C, 53.34; H, 6.12%.

NMR:²⁷¹H 7.21–7.12 (m, 10 H, 2Ph), 2.53 (m, 4 H, 2CH₂), 2.17 (m, 4 H, 2CH₂), 1.95–1.80 (m, 8 H, 4CH₂), 1.56–1.41 (m, 32 H, 16CH₂); ¹³C{¹H} ^{31,32} 130.9 (virtual t, ³⁴  $J_{CP}$  = 4.5, *o*-Ph), 130.0 (s, *p*-Ph), 127.9 (virtual t, ³⁴  $J_{CP}$  = 3.7, *m*-Ph), 30.2 (virtual t, ³⁴  $J_{CP}$  = 7.4, CH₂), 27.8 (s, CH₂), 27.3 (s, CH₂), 26.8 (virtual t, ³⁴  $J_{CP}$  = 17.2, CH₂), 26.5 (s, CH₂), 24.9 (s, CH₂); ³¹P{¹H} 12.5 (s,  $J_{PPt}$  = 2590).³⁵

 $\begin{array}{l} \text{(s, } J_{\text{PPt}} = 2590).^{35} \\ \text{MS:}^{29} \ 949 \ (15d^+, \ 30\%), \ 913 \ ([15d - Cl]^+, \ 100\%), \ 743 \\ ([15d - Cl - C_6F_5]^+, \ 70\%). \end{array}$ 

# Metathesis of 11e; trans-(Cl)(C₆F₅)-

# Pt(PPh(CH₂)₆CH=CH(CH₂)₆P(CH₂)₆CH=CH(CH₂)₆Ph) (13e)

Complex **11e** (0.250 g, 0.236 mmol), **2** (0.0019 g, 0.0231 mmol, 10 mol%), and  $CH_2Cl_2$  (70 mL; resulting solution 0.0034 M in **11e**) were combined in a procedure analogous to that with **11a** (2.5 h, second catalyst charge, 2.5 h). An identical workup gave **13e** and other metathesis products as a pale pink powder (0.230 g, 0.230 mmol, 97%). Calc. for  $C_{46}H_{62}ClP_2F_5Pt$ : C, 55.12; H, 6.23. Found: C, 54.91; H, 6.00%.

NMR:²⁷ ¹H 7.41–7.05 (m, 10 H, 2Ph), 5.35–5.20 (m, 4 H, 2CH=), 2.40–2.33 (m, 2 H of 4PCH₂), 2.02–1.76 (m, 18 H; 6 H of 4PCH₂, 4 H of 4PCH₂CH₂, 4CH₂CH=), 1.48–1.23 (m, 28 H; 4 H of 4PCH₂CH₂, 12CH₂); ³¹P{¹H} (partial) 15.2 (s, 4%), 14.8 (s, 5%), 13.5 (s, ¹J_{PtP} = 2579, ³⁵ 44%), 12.3 (s, 9%), 10.9 (s, 8%), 9.3 (s, 12%), 8.7 (s, 18%).

IR (cm⁻¹, powder film) 3057 (w), 2926 (w), 2853 (m), 1502 (m), 1459 (m), 1436 (m), 1104 (m), 1058 (m), 957 (s), 803 (m), 737 (s), 690 (s). MS:²⁹ 1969 ([2·Pt - Cl]⁺, 30%),36 1798 ([2·Pt - Cl - C₆F₅]⁺, 20%),³⁶ 966 ([13e - Cl]⁺, 45%), 797 ([13e - Cl - C₆F₅]⁺, 100%).

# trans-(Cl)(C₆F₅)Pt(PPh(CH₂)₁₄P(CH₂)₁₄Ph) (15e)

Complex 13e and other metathesis products (0.154 g, 0.153 mmol), 10% Pd/C (0.016 g, 0.015 mmol Pd), ClCH₂CH₂Cl (6.5 mL), ethanol (6.5 mL), and H₂ were combined in a procedure analogous to that for 16a. After 48 h, a similar workup (3 × 2.5 cm column rinsed with CH₂Cl₂) gave crude 15e as a white powder (0.119 g, 0.118 mmol, 77%).

NMR:²⁷ ¹H 7.45–7.12 (m, 10 H, 2Ph), 2.40–2.36 (m, 4 H, 2PCH₂), 2.15–2.14 (m, 4 H, 2PCH₂), 1.88–1.87 (m, 4 H, 2PCH₂CH₂), 1.77–1.75 (m, 4H, 2PCH₂CH₂), 1.46–1.23 (m, 40 H, 20CH₂); ³¹P{¹H} (partial) 11.8 (s, ¹J_{PtP} = 2579, ³⁵ **15e**, 52%).

MS: ²⁹ 1977 ([2·Pt – Cl]⁺, 20%), ³⁶ 1809 ([2·Pt – Cl – C₆F₅]⁺, 10%), ³⁶ 1006 (15e⁺, 40%), 970 ([15e – Cl]⁺, 100%), 801 ([15e – Cl – C₆F₅]⁺, 90%).

The sample was chromatographed on neutral alumina ( $10 \times 2.5$  cm column) using 1 : 3 v/v CH₂Cl₂-hexanes. The two least polar fractions were collected to give *syn*-**15e** (0.048 g, 0.0477 mmol, 31%) as a white powder, mp 155–157 °C, and *anti*-**15e** (0.011g, 0.0100 mmol, 7%) as a white powder.

*syn***-15e**: Calc. for C₄₆H₆₆ClP₂F₅Pt: C, 54.89; H, 6.61. Found: C, 54.93; H, 6.75.

NMR:²⁷ ¹H ^{33b} 7.17–7.08 (m, 10 H, 2Ph), 2.35–2.28 (m, 4 H, 4PC*HH'*), 2.15–2.04 (m, 4 H, 4PC*HH'*), 1.82–1.80 (m, 4 H, 4PC*H*₂C*HH'*), 1.73 (m, 4 H, 4PC*H*₂C*HH'*), 1.47–1.11 (m, 40 H, 20C*H*₂); ¹³C{¹H} ^{31a,32,33} 130.3 (virtual t, ³⁴  $J_{CP}$  = 4.6, *o*-Ph), 130.2 (virtual t, ³⁴  $J_{CP}$  = 26.0, *i*-Ph), 129.5 (s, *p*-Ph), 127.6 (virtual t, ³⁴  $J_{CP}$  = 4.4, *m*-Ph), 30.4 (virtual t, ³⁴  $J_{CP}$  = 6.4, PCH₂C*H*₂C*H*₂), 27.9 (s, CH₂), 27.3 (s, CH₂), 27.0 (s, CH₂), 26.9 (s, CH₂), 24.2 (s and overlapping virtual t, ³⁴  $J_{CP}$  = 17.5, PCH₂CH₂ and PCH₂); ³¹P{¹H} 11.8 (s, ¹ $J_{PIP}$  = 2560).³⁵

IR (cm⁻¹, powder film) 2926 (m), 2856 (m), 1502 (s), 1463 (m), 1058 (m), 957 (s). MS: ²⁹ 1006 (**15e**⁺, 40%), 970 ([**15e** - Cl]⁺, 100%), 801 ([**15e** - Cl - C₆F₅]⁺, 60%).

*anti*-15e: Calc. for C₄₆H₆₆ClP₂F₅Pt: C, 54.89; H, 6.61. Found: C, 54.87; H, 6.91.

NMR:²⁷¹H 7.82–7.78 (m, 2H of 2Ph), 7.41–7.39 (4H of 2Ph), 7.30–7.10 (m, 4H of 2Ph), 2.30–2.26 (m, 2 H of 4PC*H*H'),³⁷ 2.14–2.05 (m, 2 H of 4PC*H*H'),³⁷ 1.87–1.82 (m, 4 H of 4PCH*H*'),³⁷ 1.62–1.10 (m, 48 H, 24CH₂); ¹³C{¹H} (partial,

some assignments tentative)^{31*a*,37} 133.7 (s, *m*-Ph), 133.6 (s, *m*-Ph'), 130.4 (br s, 2 *p*-Ph), 129.60 (s, *i*-Ph), 129.58 (s, *i*-Ph'), 127.8 (virtual t,³⁴  $J_{CP} = 8.5$ , *o*-Ph), 127.99 (virtual t,³⁴  $J_{CP} = 8.5$ , *o*-Pp'), 30.06 (virtual t,³⁴  $J_{CP} = 11.5$ , CH₂), 30.04 (virtual t,³⁴  $J_{CP} = 11.5$ , CH₂), 28.2 (s, CH₂), 28.0 (s, CH₂), 27.7 (br s, CH₂), 27.4 (br s, CH₂), 27.1 (br s, CH₂), 26.9 (br s, CH₂), 24.2 (br s, CH₂), 23.7 (br s, CH₂); ³¹P{¹H} 15.8 (² $J_{PP'} = 426.8$ , ¹ $J_{PPt} = 2610$ ),³⁵ 11.2 (² $J_{P'P} = 426.8$ , ¹ $J_{P'Pt} = 2556$ ).³⁵

IR (cm⁻¹, powder film) 2926 (s), 2856 (s), 2362 (w), 2335 (w), 1502 (s), 1459 (m), 1440 (s), 1061 (s), 957 (s). MS:²⁹ 1006 (**15e**⁺, 20%), 971 ([**15e** - Cl]⁺, 90%), 799 ([**15e** - Cl - C₆F₅]⁺, 100%).

# Metathesis of 11f: trans-(Cl)( $C_6F_5$ )-Pt( $PPh(CH_2)_8CH=CH(CH_2)_8P(CH_2)_8CH=CH(CH_2)_8Ph$ ) (13f)

Complex 11f (0.273 g, 0.233 mmol), 2 (ca. half of 0.050 g, 0.0608 mmol, 26 mol%), and  $CH_2Cl_2$  (70 mL; resulting solution 0.0033 M in 11f) were combined in a procedure analogous to that with 11a (2 h, second catalyst charge, 3.5 h). A similar workup (2.5 × 3 cm column) gave 13f and other metathesis products as a pale pink solid (0.238 g, 0.214 mmol, 92%). Calc. for  $C_{54}H_{78}ClF_5P_2Pt$ : C, 58.20; H, 6.88. Found: C, 57.84; H, 7.30%.

NMR:²⁷ ¹H 7.44–7.14 (m, 10 H, 2Ph), 5.36 (m, 4 H, 2CH= CH), 2.27–1.86 (m, 16 H, 8CH₂), 1.46–1.11 (m, 48 H, 24CH₂); ³¹P{¹H} 13.5 (s, 7%), 13.1 (s,  $J_{PPt} = 2566$ ,³⁵ 34%), 12.6 (11%), 10.7 (s,  $J_{PPt} = 2522$ ,³⁵ 23%), 10.5 (s,  $J_{PPt} = 2522$ , 25%).³⁵

MS: ²⁹ 1079 ([13f - Cl]⁺, 100%), 909 ([13f - Cl - C₆F₅]⁺, 80%).

# syn-trans-(Cl)( $C_6F_5$ )Pt(PPh(CH₂)₁₈P(CH₂)₁₈Ph) (syn-15f)

Complex **13f** and other metathesis products (0.171 g, 0.154 mmol), 10% Pd/C (0.027 g, 0.0262 mmol Pd), ClCH₂CH₂Cl (10 mL), ethanol (10 mL), and H₂ were combined in a procedure analogous to that for **16a**. After 71 h, a similar workup (³¹P{¹H} NMR of residue ( $\delta$ , CDCl₃): 11.9 (8%), 10.8 (39%), 10.3 (27%), 10.1 (21%), 8.7 (5%); 2.5 × 5 cm column) gave *syn*-**15f** as a colorless oil (0.026 g, 0.023 mmol, 15%).³⁰

NMR:^{27 1}H 7.50–7.10 (m, 10 H, 2Ph), 2.15 (m, 10 H, 5CH₂), 1.35 (m, 62 H, 31CH₂); ¹³C{¹H} ^{31a,32} 131.4 (virtual t, ³⁴  $J_{CP} = 4.9$ , *o*-Ph), 130.8 (virtual t, ³⁴  $J_{CP} = 26.0$ , *i*-Ph), 130.1 (s, *p*-Ph), 128.3 (virtual t, ³⁴  $J_{CP} = 4.8$ , *m*-Ph), 31.0 (virtual t, ³⁴  $J_{CP} = 6.8$ , CH₂), 28.9, 28.8, 28.7, 28.6, 28.5, 28.4, 24.1 (s, CH₂), 23.6 (virtual t, ³⁴  $J_{CP} = 17.2$ , CH₂); ³¹P{¹H} 10.8 (s,  $J_{PPt} = 2551$ ).³⁵

MS: ²⁹ 1081 ([**15f** - Cl]⁺, 100%), 913 ([**15f** - Cl - C₆F₅]⁺, 90%).

# $H_{3}B \cdot PPh((CH_{2})_{6}CH=CH_{2})_{2} (17e)$

A Schlenk flask was charged with **4e** (0.304g, 0.920 mmol)^{3c} and THF (2 mL), cooled to -20 °C (N₂, acetone), and H₃B·SMe₂ (0.0698g, 0.920 mmol) was added. The solution was stirred for 1 h at -20 °C and 30 min at room temperature. Solvent was removed by rotary evaporation and oil-pump vacuum. The residue was filtered through neutral alumina (6 × 2.5 cm column) using 1 : 1 v/v CH₂Cl₂–hexanes. Solvent was removed from the product fraction by oil-pump vacuum to give **17e** as a colorless oil (0.205 g, 0.595 mmol, 65%). Calc. for C₂₂H₃₈BP: C, 76.74; H, 11.12. Found: C, 76.46; H, 11.39%.

NMR:²⁷ ¹H 7.73–7.70 (m, 2 H of Ph), 7.60–7.47 (m, 3 H of Ph), 5.82–5.76 (m, 2 H, 2CH=), 5.01–4.92 (m, 4 H, 2 =CH₂), 2.02–1.99 (m, 4 H, 2CH₂CH=), 1.87–1.81 (m, 4 H, 2PCH₂), 1.57 (m, 2 H, CH₂), 1.37–1.26 (m, 14 H, 7CH₂), 1.0–0.2 (br, 3 H, BH₃); ¹³C{¹H}²⁸ 138.6 (s, CH=), 131.8 (d,  $J_{CP}$  = 7.6, *o*-Ph), 131.1 (d,  $J_{CP}$  = 2.2, *p*-Ph) 128.7 (d,  $J_{CP}$  = 9.5, *m*-Ph), 128.6 (d, ¹ $J_{CP}$  = 51.3, *i*-Ph), 114.5 (s, =CH₂), 33.6 (s, CH₂CH=), 30.9 (d,  $J_{CP}$  = 13.0, CH₂), 28.6 (s, CH₂), 28.5 (s, CH₂), 25.6 (d,  $J_{CP}$  = 36.0, CH₂), 22.7 (s, CH₂); ³¹P{¹H} 15.3 (apparent d, ¹J(¹¹B,³¹P) = 75.1).

IR (cm⁻¹, oil film) 2930, 2856, 2374, 2339, 1640, 1463, 1436, 1116, 1061, 996, 907, 799, 745, 695. MS:²⁹ 341 ([**17e** - 3H]⁺,³⁸ 40%), 331 ([**17e** - H₃B]⁺, 100%).

# $H_3B \cdot PPh(CH_2)_6CH=CH(CH_2)_6$ (18e)

A two-necked flask was charged with **17e** (0.141 g, 0.409 mmol), **2** (*ca.* half of 0.017 g, 0.0205 mmol, 5 mol%), and CH₂Cl₂ (180 mL, the resulting solution is 0.0023 M in **17e**), and fitted with a condenser. The solution was refluxed. After 2.5 h, the remaining **2** was added. After 2.5 h, solvent was removed by rotary evaporation and oil-pump vacuum. The residue was filtered through neutral alumina (5 × 2.5 cm column) using CH₂Cl₂. Solvent was removed from the filtrate by rotary evaporation and oil-pump vacuum to give **18e** as a pale pink oil (0.080 g, 0.253 mmol, 62%). Calc. for C₂₀H₃₄BP: C, 75.95; H, 10.83. Found: C, 75.20; H, 11.25%.

NMR: ²⁷ ¹H 7.72–7.70 (m, 2 H of Ph), 7.49–7.46 (m, 3 H of Ph), 5.47-5.43/5.42-5.39/5.38-5.33 (3m, 2 H, 2CH=), 2.13-1.82 (m, 8 H, 2CH₂CH=, 2PCH₂), 1.57-1.27 (m, 16 H, 8CH₂), 1.0-0.3 (br, 3H, BH₃); ³¹P{¹H} 15.2 (m).

IR (cm⁻¹, oil film) 2926, 2853, 2370, 2339, 1436, 1112, 1061, 969, 741, 695. MS: ²⁹ 629 ([2·P]⁺, 20%), ³⁶ 617 ([2·P - H₃B]⁺, 25%), ³⁶ 605 ([2·P - 2H₃B]⁺, 30%), ³⁶ 315 (18e⁺, 80%), 303 ([18e - H₃B]⁺, 100%).

# H₃B·PPh(CH₂)₁₄ (19e)

A Fischer–Porter bottle was charged with **18e** (0.072 g, 0.228 mmol), Rh(PPh₃)₃(Cl) (0.021 g, 0.0028 mmol, 10 mol%), and benzene (25 mL), and flushed with H₂. The mixture was stirred under H₂ (6 atm) for 20 h. Solvent was removed by oil-pump vacuum. The residue was chromatographed on neutral alumina ( $10 \times 2.5$  cm column) using 1 : 1 v/v CH₂Cl₂–hexanes. Solvent was removed from the product fraction by oil-pump vacuum to give **19e** as a colorless oil (0.056 g, 0.176 mmol, 77%). Calc. for C₂₀H₃₆BP: C, 75.74; H, 11.40. Found: C, 75.28; H, 11.54%.

NMR:^{27 1}H 7.73–7.70 (m, 2 H of Ph), 7.49–7.46 (m, 3 H of Ph), 2.00–1.84 (m, 4 H, 2PCH₂), 1.57–1.21 (m, 24 H, 12CH₂), 1.1–0.3 (br, 3H, BH₃);  ${}^{13}C{}^{1}H{}^{28}$  131.3 (d,  $J_{CP} = 8.2$ , *o*-Ph), 130.9 (d,  $J_{CP} = 2.3$ , *p*-Ph) 130.2 (d,  ${}^{1}J_{CP} = 53.1$ , *i*-Ph), 128.7 (d,  $J_{CP} = 9.5$ , *m*-Ph), 28.9 (d,  $J_{CP} = 11.5$ , CH₂), 26.8 (s, CH₂), 26.57 (s, CH₂), 26.54 (s, CH₂), 26.3 (s, CH₂), 23.8 (d,  $J_{CP} = 34.5$ , CH₂), 21.5 (d,  $J_{CP} = 2.4$ , CH₂);  ${}^{31}P{}^{1}H{}$  15.4 (apparent d,  ${}^{1}J{}^{(11}B{}^{,31}P) = 69.6$ ).

IR (cm⁻¹, oil film) 2926, 2853, 2374, 2343, 1459, 1435, 1112, 1065, 1000, 737, 691. MS:²⁹ 609 ( $[2 \cdot P - 2H_3B]^+$ , 30%),³⁶ 315 ( $[19e - 3H]^+$ , 100%),³⁸ 305 ( $[19e - H_3B]^+$ , 60%).

# trans-(Cl)(C₆F₅)Pt(PPh(CH₂)₁₄)₂ (16e)

A Schlenk flask was charged with **19e** (0.112 g, 0.352 mmol) and HNEt₂ (2 mL). The mixture was heated to 50 °C and stirred for 45 min. The HNEt₂ was removed by oil-pump vacuum, and the residue vacuum dried at 50 °C for an additional 20 min. This operation was repeated twice (final cycle: 2 h, 50 °C) to give crude  $\overrightarrow{PPh(CH_2)_{14}}$  (**20e**). The flask was charged with **12** (0.085 g, 0.088 mmol)⁹ and CH₂Cl₂ (6 mL), and the mixture was stirred (16 h). Solvent was removed by oil-pump vacuum. The residue was chromatographed on neutral alumina (9 × 2.5 cm column) using 1 : 1 v/v CH₂Cl₂-hexanes. Solvent was removed from the product fraction by oil-pump vacuum to yield **16e** as a colorless oil, which solidified over the course of several days (0.042 g, 0.0417 mmol, 24% based on **19e**). Calc. for C₄₆H₆₆ClF₅P₂Pt: C, 54.89; H, 6.61. Found: C, 54.71; H, 6.55%.

NMR: ²⁷ ¹H 7.50–7.45 (m, 4 H of 2Ph), 7.36–7.28 (m, 6 H of 2Ph), 2.16–2.12 (m, 4 H of 4PCHH'),³⁷ 1.95–1.92 (m, 4 H of 4PCHH'),³⁷ 1.65–1.63 (m, 4 H of 4PCH₂C*HH*'),³⁷ 1.56–1.30 (m, 44 H; 4 H of 4PCH₂C*HH*', 20CH₂);³⁷ ¹³C{¹H} ^{31a,32,33} 131.2

(virtual t,³⁴  $J_{CP} = 5.2$ , *o*-Ph), 130.9 (virtual t,³⁴  $J_{CP} = 25.8$ , *i*-Ph), 129.8 (s, *p*-Ph), 128.1 (virtual t,³⁴  $J_{CP} = 4.7$ , *m*-Ph), 28.9 (virtual t,³⁴  $J_{CP} = 6.6$ , PCH₂CH₂CH₂), 26.8 (s, CH₂), 26.63 (s, CH₂), 26.59 (s, CH₂), 26.3 (s, CH₂), 21.8 (s, CH₂), 21.2 (virtual t,³⁴  $J_{CP} = 16.6$ , PCH₂); ³¹P{¹H} 7.2 (s, ¹ $J_{PPt} = 2520$ ).³⁵

IR (cm⁻¹, powder film) 2926, 2856, 2374, 1502, 1455, 1112, 1061, 957, 803, 745, 695. MS: ²⁹ 1006 (**16e**⁺, 15%), 970 ([**16e** - Cl]⁺, 40%), 801 ([**16e** - Cl - C₆F₅]⁺, 60%)]⁺, 495 ([**16e** - Cl - C₆F₅ - **20e**]⁺, 90%), 305 (**20e**⁺, 100%).

#### Crystallography.¹⁵

Toluene solutions of *syn*-15e, *anti*-15e and 16e were layered with ethanol. The samples were stored at -20 °C. After three to thirty days, colorless prisms had formed. Complexes 16a, *syn*-(E, E)-13c, and *syn*-15c were suspended in methanol and warmed. THF was added until the samples were homogeneous. The mixtures were kept at room temperature. After one day, colorless prisms had formed.

Data were collected as outlined in Table 1. Cell parameters were obtained from 10 frames using a 10° scan and refined with  $\geq$ 6873 reflections (*syn*-15e, 10003; *anti*-15e, 7885; 16e, 9914; 16a, 6873; *syn*-(*E*,*E*)-13c, 8701; *syn*-15c, 23439). Lorentz, polarization, and absorption corrections were applied.³⁹ The space groups were determined from systematic absences and subsequent least-squares refinement. The structures were solved by direct methods. The parameters were refined with all data by full-matrix-least-squares on  $F^2$  using SHELXL-97.⁴⁰ Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were fixed in idealized positions using a riding model. Scattering factors were taken from literature.⁴¹ The quality of the crystal of *syn*-15c, which contained two independent molecules in the unit cell, was lower than the others.

CCDC reference numbers: *syn*-15e, 159809; *anti*-15e, 227266; 16e, 227267; 16a, 227269; *syn*-(*E*,*E*)-13c, 227270; *syn*-15c, 227268.

See http://www.rsc.org/suppdata/dt/b4/b400156g/ for crystallographic data in CIF or other electronic format.

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