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A Direct Route to Platinum NCN-Pincer Complexes Derived from 1,3-Bis(imino)benzenes and an Investigation into Their Activity as Catalysts for Carbon−Carbon Bond Formation

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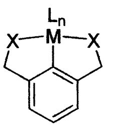
1,3-Bis(imino)lbenzenes [1,3-$C_6H_4(CH{=}NR)_2$], obtained from condensation of 1,3-isophthalaldehyde with primary amines (R = ^{t}Bu, Cy, Bu, Bn, Ph), were heated with K_2PtCl_4 at reflux for 48 h in glacial acetic acid to give ((2,6-bis(*N*-R-substituted)imino)phenyl)platinum(II) chloride complexes (15−52% yield). X-ray crystal structures of the R = ^{t}Bu and R = Ph complexes are reported. The byproducts were found to be 1,3-isophthalaldehyde and *N*-acetylamines. Quantitative chloride abstraction with $AgBF_4$ (R = ^{t}Bu) or AgOTf (R = ^{t}Bu, Cy) provided the corresponding cationic complexes containing water coordinated to platinum, as established by an X-ray crystal structure of ((2,6-bis(*N*-*tert*-butyl)imino)phenyl)aquoplatinum(II) trifluoromethanesulfonate. Use of 4−5 mol % of ((2,6-bis(*N*-cyclohexyl)imino)phenyl)aquoplatinum(II) trifluoromethanesulfonate accelerated the rate of the Michael reaction between ethyl α-cyanoacetate and methyl vinyl ketone and the Diels−Alder reaction between acrylonitrile and cyclopentadiene.

Introduction

Platinum group metal based pincer complexes of general structure **1** are currently the subject of much attention due to their application as catalysts and their incorporation into novel organometallic materials.[1] A major subcategory of **1** is terdentate NCN complexes of group 10 metals incorporating amino **2**,[2] oxazolinyl **3**,[3] and pyridinyl **4**[4] *trans*-chelating functionalities. In the synthesis of these complexes, the metals are introduced by either (i) transmetalation of M(II) (M = Ni, Pd, Pt) with a 2-metallo-1,3-disubstituted benzene[2a,3b−e] (ii) oxidative addition of M(0) (M = Ni, Pd, Pt) with a 2-halo-1,3-disubstituted benzene,[2b,i,j,3a] or (iii) directing group mediated cyclometalation of M(II) (M = Pd) with a 2-trimethylsilyl-1,3-disubstituted benzene.[2f] In general, the direct cyclometalation of 1,3-disubstituted benzenes does not occur at C-2 to give two fused five-membered rings; instead 4,6-bismetalated complexes are obtained preferentially.[5] A notable exception is **4**, obtained by platination of 1,3-bis(2-pyridyl)benzene; palladation of this same substrate proceeded by the alternative 4,6-disubstitution pathway.[4]



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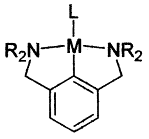
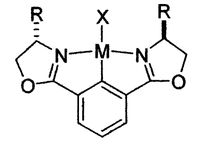
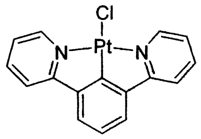


2 M = Ni, Pd, Pt



3 M = Pd, Pt
X = Cl, Br



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Prompted by this latter result, we sought to investigate the platination of simple 1,3-bis(imino)benzenes.

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(1) For recent reviews see: (a) Steenwinkel, P.; Gossage, R. A.; van Koten, G. *Chem. Eur. J.* **1998**, *4*, 759 (b) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750.

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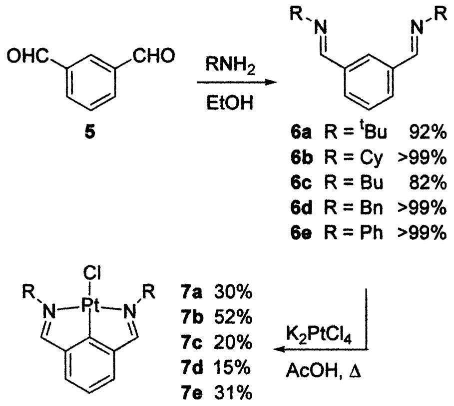
(3) Denmark, S. E.; Stavenger, R. A.; Faucher, A.-M.; Edwards, J. P. *J. Org. Chem.* **1997**, *62*, 3375. (b) Motoyama, Y.; Makihara, N.; Mikami, Y.; Aoki, K.; Nishiyama, H. *Chem. Lett.* **1997**, 951. (c) Stark, M. A.; Richards, C. J. *Tetrahedron Lett.* **1997**, *38*, 5881. (d) Motoyama, Y.; Mikami, Y.; Kawakami, H.; Aoki, K.; Nishiyama, H. *Organometallics* **1999**, *18*, 3584. (e) Stark, M. A.; Jones, G.; Richards, C. J. *Organometallics* **2000**, *19*, 1282.

(4) Cárdenas, D. J.; Echavarren, A. M.; de Arellano, M. C. R. *Organometallics* **1999**, *18*, 3337. In contrast, palladation to give two fused six-membered rings occurs readily: (b) Canty, A. J.; Minchin, N. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1987**, 1477. (c) Hartshorn, C. M.; Steel, P. J. *Organometallics* **1998**, *17*, 3487. (d) Canty, A. J.; Patel, J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2000**, *607*, 194.

(5) Trofimenko, S. *J. Am. Chem. Soc.* **1971**, *93*, 1808. (b) Trofimenko, S. *Inorg. Chem.* **1973**, *12*, 1215. (c) Chakladar, S.; Paul, P.; Nag, K. *Polyhedron* **1991**, *10*, 1513. (d) Chakladar, S.; Paul, P.; Venkatsubramanian, K.; Nag, K. *J. Chem. Soc., Dalton Trans.* **1991**, 2669. (e) Meijer, M. D.; Kleij, A. W.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **2001**, *640*, 166.

10.1021/om020566r CCC: $22.00

Scheme 1



Reaction of these substrates with palladium acetate had previously been reported to give 4,6-bispalladation,[5c−d] with a later paper describing predominantly monopalladation of position 4 plus formation of small amounts of an inseparable pincer complex.[6] At the onset of this program no general routes to platinum group pincer complexes incorporating Schiff base derived anionic terdentate NCN complexes were known. Recently the generation of such systems through the oxidative addition of Pt(0) into 2-bromo-1,3-bis(imino)benzenes was reported.[7] In this paper we describe the synthesis of a range of such complexes obtained by direct platination. Activation of the resulting complexes by halide abstraction and a study into the use of the resulting cationic species as Lewis acid catalysts are also described.

Results and Discussion

Starting from commercially available 1,3-isophthaldehyde **5** and a series of primary amines, the corresponding 1,3-bis(imino)benzenes **6a**−**e** were synthesized without difficulty (Scheme 1). After addition to a suspension of potassium tetrachloroplatinate in glacial acetic acid, the resulting reaction mixtures were heated at reflux for 48 h to give yellow-orange solutions containing a black platinum deposit. These conditions were required to ensure the consumption of potassium tetrachloroplatinate; shorter reaction times or lower temperatures resulted in reduced yields. Removal of the solvent, column chromatography, and recrystallization from CH_2Cl_2 provided new NCN Schiff base derived complexes as either yellow-orange (**7a**−**d**) or red (**7e**) air-stable crystalline solids. Their identity was initially established by the absence the aryl singlet in the ^{1}H NMR spectrum, and occupancy of this 1-position by platinum was revealed by coupling of the ^{195}Pt isotope to the protons at positions 3 and 5 ($^4J = 6.6{-}8.2$ Hz). Coordination of nitrogen to platinum was indicated by coupling to the iminyl protons ($^3J = 141{-}152$ Hz). Only a single platinacycle was isolated from each reaction mixture; the formation of alternative systems through metalation of position 4 or positions 4 and 6 was not observed. Repetition of the reaction with **6a** and examination of the resultant product mixture by ^{1}H NMR spectroscopy revealed **7a** (39%) and a 1:2 ratio of 1,3-isophthaldehyde and *N*-acetyl-*tert*-butylamine (both 56%). Thus the yield of the platinacycle is limited by competitive reaction of the imine functionalities with the solvent. Attempts to avoid this by use of toluene, acetonitrile, or methanol as reaction solvents did not lead to any product formation.

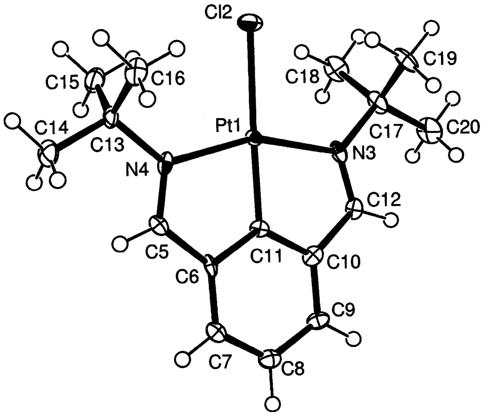


Figure 1. Representation of the crystal structure of **7a**. Selected bond distances (Å) and angles (deg): Pt(1)−C(11) = 1.915(6), Pt(1)−Cl(2) = 2.4192(19), Pt(1)−N(3) = 2.093(5), Pt(1)−N(4) = 2.097(5), N(3)−C(12) = 1.277(8), N(4)−C(5) = 1.285(8), C(11)−Pt(1)−N(3) = 78.4(2), C(11)−Pt(1)−N(4) = 78.9(2), N(3)−Pt(1)−N(4) = 157.2(2), C(11)−Pt(1)−Cl(2) = 175.89(17).

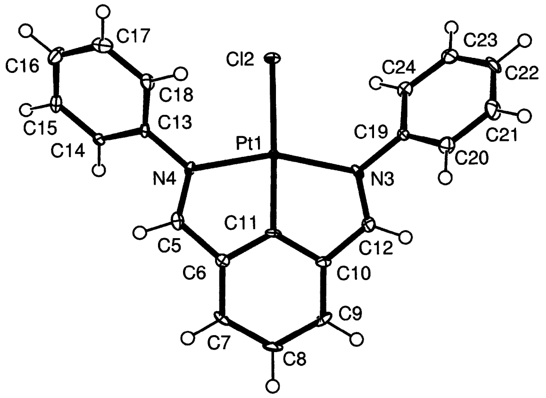


Figure 2. Representation of the crystal structure of **7e**. Selected bond distances (Å) and angles (deg): Pt(1)−C(11) = 1.908(6), Pt(1)−Cl(2) = 2.3914(18), Pt(1)−N(3) = 2.064(5), Pt(1)−N(4) = 2.061(5), N(3)−C(12) = 1.307, N(4)−C(5) = 1.298(8), C(11)−Pt(1)−N(3) = 79.1(2), C(11)−Pt(1)−N(4) = 79.2(2), N(3)−Pt(1)−N(4) = 157.9(2), C(11)−Pt(1)−Cl(2) = 174.93(19).

Slow evaporation of separate solutions of **7a** and **7e** in CH_2Cl_2 gave crystals suitable for X-ray analysis, which confirmed the structures as NCN-pincer complexes (Figures 1 and 2). The structure of **7a** reveals significantly longer Pt−N bonds (2.093(5) and 2.097(5) Å) than those found in related platinum NCN-pincer complexes **3** (R = ^{i}Pr, X = Cl, 2.032(10) and 2.035(10) Å[3d] and **4** (2.033(6) and 2.041(6) Å).[4a] The corresponding bond lengths are shorter in **7e** (2.061(5) and 2.064(5) Å). The distortion from the ideal square-planar geometry caused by the two fused five-membered rings is most apparent from the N(3)−Pt−N(4) bond angles of 157.2° (**7a**) and 157.9° (**7e**).

Although the yields arising from the platination step are moderate, the simplicity of the overall two-step

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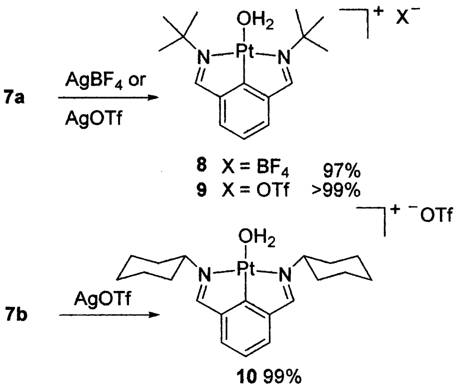
(6) Vila, J. M.; Gayoso, M.; Pereira, T.; Torres, M. L.; Fernández, J. J.; Fernández, A.; Ortigueira, J. M. *J. Organomet. Chem.* **1996**, *506*, 165.

(7) Hoogervorst, W. J.; Elsevier, C. J.; Lutz, M.; Spek, A. L. *Organometallics* **2001**, *20*, 4437.

Scheme 2



procedure makes this an attractive and direct route to new platinum NCN-pincer complexes. Existing routes based on oxidative addition or transmetalation require the relatively nontrivial synthesis of functionalized 1,2,3-trisubstituted benzenes. Furthermore, diversity of structure is readily introduced through variation of the starting amine. We have demonstrated here that primary amines containing adjacent tertiary, secondary, primary, benzylic, and aromatic groups may all be accommodated in this new procedure.

Nitrogen-based pincer complexes of group 10 metals have been applied as catalysts for the Kharasch addition,[2c−e] the aldol reaction,[2g,h] cyclopropanation,[3a] and the Michael reaction.[3c,e,8] With the exception of the Kharasch addition, which proceeds via a radical mechanism catalyzed by nickel complexes of general structure **2**, the other carbon−carbon bond forming reactions have all utilized cationic palladium complexes obtained by halide abstraction. Although platinum cationic complexes derived from **3** have been employed as stoichiometric stereocontrollers for asymmetric alkylation of aldimines,[3d] no examples of catalysis with platinum NCN complexes have been reported.

Halide abstraction was readily achieved by addition of either AgBF$_4$ to a solution of **7a** in acetone or AgOTf to solutions of **7a** or **7b** in dichloromethane (Scheme 2). No color changes occurred, but after removal of silver chloride by filtration, the resulting cationic complexes were isolated as orange or yellow air-stable crystalline solids. The identities of **8**−**10** were initially indicated by the presence of the groups BF$_4^-$ and TfO$^-$ in their respective IR specta, and that for **9** was confirmed by X-ray analysis of a crystal obtained by slow evaporation of an acetone solution (Figure 3). Compared to **7a** this displays a shorter platinum−carbon bond (1.889(5) vs 1.915(6) Å) consistent with an increase in the N(3)−Pt−N(4) bond angle from 157.2° in **7a** to 159.11(18)° in **9**. Significantly, water was revealed to be occupying the exchangeable coordination site with triflate as a hydrogen-bonded counterion. This differs from the assignment made to the complex obtained from addition of AgOTf to a platinum species of general structure **3** (X = Cl), the structure of which is drawn with the triflate coordinated to platinum.[3d] That the anion BF$_4^-$ is known to be a weaker metal coordinator than triflate[9] confirms the identity of **8** and is further supported by the number of peaks in the B−F stretching region of the IR spectrum due to hydrogen bonding with coordinated water.[10]

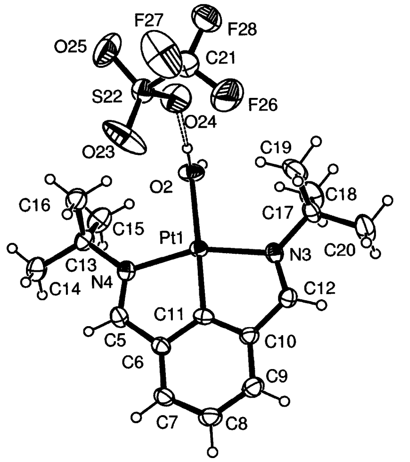
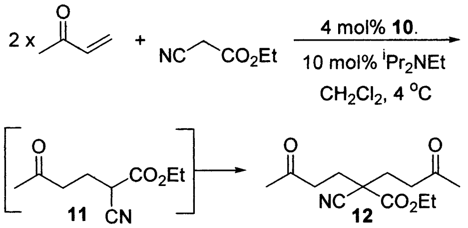


Figure 3. Representation of the crystal structure of **9**. Selected bond distances (Å) and angles (deg): Pt(1)−C(11) = 1.889(5), Pt(1)−O(2) = 2.188(4), Pt(1)−N(3) = 2.089(5), Pt(1)−N(4) = 2.083(4), N(3)−C(12) = 1.298(7), N(4)−C(5) = 1.290(7), C(11)−Pt(1)−N(3) = 79.9(2), C(11)−Pt(1)−N(4) = 79.9(2), N(3)−Pt(1)−N(4) = 159.11(18), C(11)−Pt(1)−O(2) = 178.7(2).

Scheme 3



For the first use of these complexes in catalysis we initially sought comparison with related palladium-based NCN cationic complexes derived from **3** which we have previously shown to be excellent catalysts for the Michael reaction with activated nitriles.[3c,e] Combination of ethyl cyanoacetate with 3 equiv of methyl vinyl ketone, together with 4 mol % **10** and 10 mol % Hünig's base (Scheme 3), resulted in an almost colorless reaction mixture in which clean conversion to the double Michael adduct **12** occurred within 24 h (Figure 4). Without **10** the same reaction conditions gave some uncatalyzed background reaction in this time period; yet in the earlier stages the formation of **12** is accelerated approximately 4-fold by the platinum catalyst. This reaction is significantly slower than those catalyzed by palladium NCN systems under similar conditions (e.g., 88% conversion after 3 h with 1 mol % catalyst[3c]).[11] The lower reactivity of platinum species compared to their palladium congeners is well known.[12] One of the advantages of this is the potential to observe intermediates in a catalytic cycle, and in this instance the mono Michael adduct **11** was detected, a species we had not

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[8] Dijkstra, H. P.; Meijer, M. D.; Patel, J.; Kreiter, R.; van Klink, G. P. M.; Lutz, M.; Spek, A. L.; Canty, A. J.; van Koten, G. *Organometallics* **2001**, *20*, 3159.

[9] Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927.

[10] Olgemöller, B.; Olgemöller, L.; Beck, W. *Chem. Ber.* **1981**, *114*, 2971.

[11] Half-lifes of 33−86 min have recently been determined for amine- and pyrazole-containing cationic palladium NCN complexes, ref 8.

[12] Clarke, M. L. *Polyhedron* **2001**, *20*, 151.

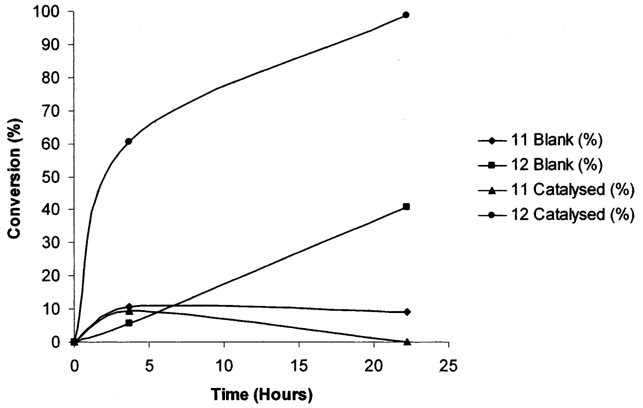


Figure 4. Michael reaction to give **11** and **12**.

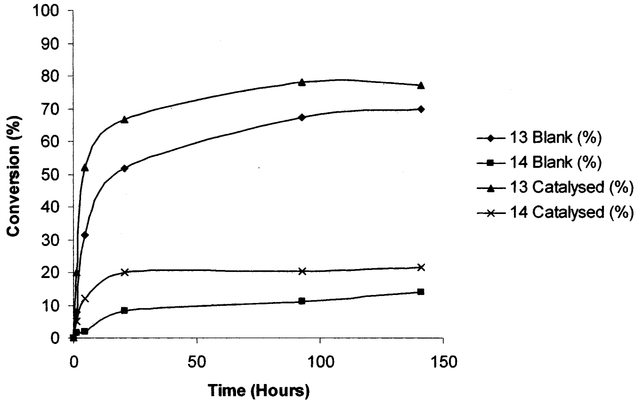
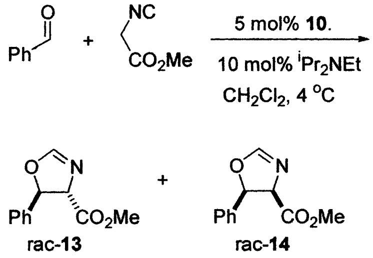


Figure 5. Aldol reaction to give **13** and **14**.

Scheme 4



observed in the previously reported palladium-catalyzed reaction. Attempted catalysis with the BF_4^- salt under the same conditions resulted in the deposition of a black precipitate from a green solution, and this reaction was not investigated further.

The aldol reaction between methyl isocyanoacetate and benzaldehyde has also been reported to be catalyzed by NCN palladium cationic pincer complexes.[2g,h,k,3c] Use of 5 mol % of **10** and 10 mol % Hünig's base was found to give some rate enhancement, although with little change in the diastereoselectivity between **13** and **14** (ca. 4:1 in both cases), and the rate of uncatalyzed reaction under the conditions employed is substantial even at 4 °C (Scheme 4, Figure 5). This result is consistent with a previous observation that cationic palladium complexes derived from **3** are also relatively poor catalysts for this transformation.[3c]

The potential for Lewis-acid activation of other nitrile-containing substrates was investigated with the Diels–Alder reaction between acrylonitrile and cyclopentadiene. A cationic platinum phosphinoaryloxazoline complex has previously been shown to act as a catalyst for the related Diels–Alder reaction between 2-chloroacrylonitrile and cyclopentadiene.[13] In the early stages of the reaction use of 5 mol % of **10** again resulted in an approximately 4-fold increase in the rate of formation of adducts **15** and **16**, the ratio of these two isomers changing from 1.5:1 in the absence of **10** to 2.1:1 in the faster reaction (Scheme 5, Figure 6). Under the conditions employed no dimerization of cyclopentadiene was observed.

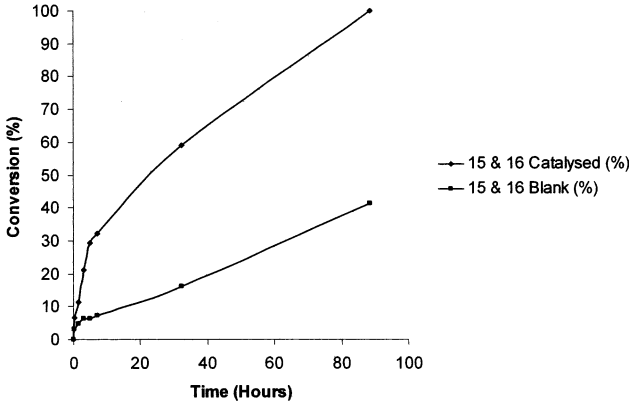
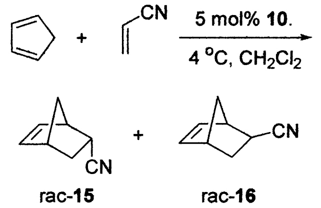


Figure 6. Diels–Alder reaction to give **15** and **16**.

Scheme 5



Conclusion

Reaction of 1,3-bis(imino)benzenes with K_2PtCl_4 in glacial acetic acid provides direct access to 2-platinum-substituted NCN-pincer complexes. The success of this procedure is a further example of a trend for direct platinations, leading to fused 5,5-metallocycles, proceeding where the corresponding palladations are unsuccessful. Activation of the resulting complexes by chloride abstraction proceeded smoothly, producing water-coordinated adducts with either tetrafluoroborate or triflate counterions. The triflate salt displays moderate activity as a catalyst for the Michael and Diels–Alder transformation of nitrile substrates. We are currently investigating more active platinacycles for application in these useful C–C bond forming reactions.

Experimental Section

All organometallic reactions were performed under an atmosphere of nitrogen employing standard Schlenk techniques. Glacial acetic acid of 99.8% purity was used as obtained. Dichloromethane was distilled from calcium hydride under nitrogen. Other solvents employed were not specifically dried. Petroleum ether refers to that fraction boiling in the range 40–60 °C. Column chromatography was performed on SiO_2 (40–63 μm). Coupling to ^{195}Pt ($^{x}J_{Pt}$) in NMR data is reported as the 34% component of the signal.

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(13) Blacker, A. J.; Clarke, M. L.; Loft, M. S.; Mahon, M. F.; Williams, J. M. J. *Organometallics* **1999**, *18*, 2867.

General Method for the Synthesis of 1,3-Bis((*N*-substituted)imino)phenylenes 6a–e Is Exemplified by the Synthesis of 1,3-Bis((*N*-*tert*-butyl)imino)phenylene 6a. Isophthaldehyde (2.5 g, 18.6 mmol) and *tert*-butylamine **6a** (4.5 mL, 3.1 g, 42.8 mmol) were refluxed in absolute ethanol (200 mL) for 30 min. The solvent was removed in vacuo, the residual material taken up in ethyl acetate and rapidly filtered through a small plug of silica, and the solvent removed in vacuo to give **6a** as a white solid containing 6% isophthaldehyde (4.34 g, 92% yield). An analytically pure sample was obtained by recrystallization from ethyl acetate/petroleum ether. Mp: 40 °C. IR (ν_{max}; CH_2Cl_2): 1641 (N=C) cm^{-1}. ^1H NMR (δ; 250 MHz, $CDCl_3$): 1.30 (18 H, s, CH_3), 7.42 (1 H, t, *J* 7.62, 5-H), 7.79 (2 H, dd, *J* 7.64 and 1.66, 4- & 6-H), 8.08 (1 H, s, 2-H), 8.32 (2 H, s, N=C*H*). $^{13}C\{^1H\}$ NMR (δ; 63 MHz, $CDCl_3$): 29.7 (CH_3), 57.4 ($C(CH_3)_3$), 127.7 (Ar, 5-C), 128.7 (Ar, 2-C), 129.4 (Ar, 4- and 6-C), 137.5 (Ar, 1- and 3-C). MS (*m*/*z*; FAB): 245 (M^+, 100%). High-resolution MS (*m*/*z*, FAB): found for MH^+ 245.2030. $C_{16}H_{25}N_2$ requires 245.2018. Similarly prepared were **6b** (>99%), **6c** (82%), **6d** (>99%), and **6e** (>99%). These materials were used without further purification.

Synthesis of ((2,6-Bis(*N*-*tert*-butyl)imino)phenyl)platinumchloride 7a. Potassium tetrachloroplatinate (0.466 g, 1.12 mmol) and **6a** (0.30 g, 1.2 mmol) were refluxed under nitrogen in glacial acetic acid for 48 h. After cooling the solvent was removed in vacuo and the residue was purified by column chromatography (CH_2Cl_2) and recrystallized (CH_2Cl_2) to give **7a** as a yellow-orange crystalline solid (0.159 g, 30% yield based on K_2PtCl_4). Mp: 300 °C (decomp). Anal. Found: C, 40.30; H, 4.81; N, 5.62. Calcd for $C_{16}H_{23}ClN_2Pt$: C, 40.59; H, 4.86; N, 5.92. IR (ν_{max}; CH_2Cl_2): 1599 (C=N) cm^{-1}. ^1H NMR (δ; 250 MHz, $CDCl_3$): 1.72 (s, 18 H, CH_3), 7.13 (1 H, t, *J* 7.6, 4-H), 7.38 (2 H, (66%) d, *J* 7.7, (34%) app t, $^4J_{PtH}$ 6.6, 3- and 5-H), 8.26 (2 H, (66%) s, (34%) d, $^3J_{PtH}$ 152.2, N=C*H*). ^1H NMR (δ; 250 MHz, acetone-d_6): 1.70 (18 H, s, CH_3), 7.16 (1 H, t, *J* 7.6, 4-H), 7.52 (2 H, (66%) d, *J* 7.6, (34%) dd, *J* 7.6 and $^4J_{PtH}$ 6.1, 3- and 5-H), 8.55 (2 H, (66%) s, (34%) d, $^3J_{PtH}$ 152.1, N=C*H*). $^{13}C\{^1H\}$ NMR (δ; 63 MHz, $CDCl_3$): 29.8 ((34%) d, $^3J_{PtC}$ 12.3, CH_3), 65.6 (34%) d, $^2J_{PtC}$ 88.2, ($C(CH_3)_3$), 122.5 (4-C), 127.1 ((34%) d, $^3J_{PtC}$ 22.6, 3- and 5-C), 142.4 ((34%) d, $^2J_{PtC}$ 113.2, 2- and 6-C), 171.5 ((34%) d, $^2J_{PtC}$ 118.3, N=CH), 1-C not observed. $^{13}C\{^1H\}$ NMR (δ; 63 MHz, acetone-d_6): 45.1 ($C(CH_3)_3$), 56.1 (34%) d, $^2J_{PtC}$ 25.0, ($C(CH_3)_3$), 122.8 (4-C), 128.2 ((34%) d, $^3J_{PtC}$ 22.4, 3- & 5-C), 143.5 ((34% d, $^2J_{PtC}$ 120.3, 2- and 6-C) 173.9 ((34%) d, $^2J_{PtC}$ 113.6, N=CH), 1-C not observed. MS (*m*/*z*; FAB): 473 (M^+, 9%), 438 (M − Cl, 100).

Repetition of this complexation with potassium tetrachloroplatinate (0.557 g, 1.34 mmol) and **6a** (0.35 g, 1.4 mmol) followed by filtration of the crude reaction mixture through Celite and evaporation of the solvent gave 0.56 g of a dark brown amorphous solid. Examination of this by ^1H NMR spectroscopy revealed a 0.7:1:2 ratio of **7a**, isophthaldehyde, and *N*-acetyl-*tert*-butylamine corresponding to a 39% yield of **7a** and 56% of the two organic products (i.e., an overall yield of 95% from **6a**). The structure of the amide was confirmed following its isolation by column chromatography (CH_2Cl_2/EtOAc). IR (ν_{max}; CH_2Cl_2): 1674 (C=O) cm^{-1}. ^1H NMR (δ; 250 MHz, $CDCl_3$): 1.30 (9 H, s, $(CH_3)_3$), 1.96 (3H, s, O=C−CH_3), 5.45 (1 H, br s, N*H*). $^{13}C\{^1H\}$ NMR (δ; 63 MHz, $CDCl_3$): 24.47 ($C(CH_3)_3$), 28.77 ($C(CH_3)_3$), 51.11 (O=C−CH_3), 169.52 (O=*C*); MS (*m*/*z*; FAB) 116 (M^+, 28%).

Synthesis of ((2,6-Bis(*N*-cyclohexyl)imino)phenyl)platinumchloride 7b. 6b (0.170 g, 0.57 mmol) and potassium tetrachloroplatinate (0.204 g, 0.49 mmol) were refluxed under nitrogen in glacial acetic acid (25 mL) containing 0.25% acetic anhydride for 48 h. The solvent was removed in vacuo and the residue purified by column chromatography (CH_2Cl_2) and recrystallized (CH_2Cl_2) to give **7b** as an orange crystalline solid (0.137 g, 53%). Mp: 226 °C Anal. Found: C, 44.95; H, 5.01; N, 4.90. Calcd for $C_{20}H_{27}ClN_2Pt(2H_2O)$: C, 44.90; H, 5.28; N, 5.24. IR (ν_{max}; CH_2Cl_2): 1595 (C=N) cm^{-1}. ^1H NMR (δ; 250 MHz, $CDCl_3$): 1.26 (3 H, m, CH_2), 1.48 (3 H, m, CH_2), 1.70 (3 H, m, CH_2), 1.79 (3 H, m, CH_2), 1.87 (4 H, m, CH_2), 2.20 (4 H, m, CH_2), 4.16 (2 H, m, N$CH(CH_2)$−), 7.10 (1 H, t, *J* 7.7, 4-H), 7.39 (2 H, (66%) d, *J* 7.7, (34%) t, $^4J_{PtH}$ 8.03, 3- and 5-H), 8.32 (2 H, (66%) s, (34%) d $^3J_{PtH}$ 147.4, N=C*H*). ^1H NMR (δ; 250 MHz, acetone-d_6): 1.20−1.53 (8H, m, CH_2), 1.70 (2 H, app d, *J* 11.0, CH_2), 1.85 (7 H, m, CH_2), 1.98 (3 H, m, CH_2), 4.0−4.3 (2 H, m, N$CH(CH_2)$−), 7.13 (1 H, t, *J* 7.6, 4-H), 7.53 (2 H, (66%) d, *J* 7.6, (34%) t, $^4J_{PtH}$ 7.8, 3- and 5- H), 8.65 (2 H, (66%) s, (34%) d $^3J_{PtH}$ 146.4, N=C*H*). $^{13}C\{^1H\}$ NMR (δ; 63 MHz, $CDCl_3$): 25.4 (CH_2), 25.4 (CH_2), 33.3 (CH_2), 67.6 ((34%) d, $^2J_{PtC}$ 17.2, N$CH(CH_2)$−), 122.3 (4-C), 126.3 ((34%) d, $^3J_{PtC}$ 26.9 3- and 5-C), 142.0 ((34%) d, $^2J_{PtC}$ 120, 2- and 6-C), 172.4 ((34%) d, $^2J_{PtC}$ 122.7, N=*C*), 1-C not observed. MS (*m*/*z*; FAB): 490 ($[M - Cl]^+$, 100%).

Synthesis of ((2,6-Bis(*N*-butyl)imino)phenyl)platinumchloride 7c. 6c (0.25 g, 1.0 mmol) and potassium tetrachloroplatinate (0.437 g, 1.05 mmol) were refluxed under nitrogen in distilled glacial acetic acid (20 mL) for 48 h. The solvent was removed in vacuo, and the residue was purified by column chromatography (25% acetone/petroleum ether) to give **7c** as a sticky orange solid, which was allowed to crystallize by slow evaporation of a CH_2Cl_2 solution (0.098 g, 20% yield, based on 1,3-bis((*N*-butyl)imino)benzene). Mp: 106 °C Anal. Found: C, 40.43; H, 4.77; N, 5.49. Calcd for $C_{16}H_{23}ClN_2Pt$: C, 40.55; H, 4.89; N, 5.91. IR (ν_{max}; CH_2Cl_2): 1593 (C=N) cm^{-1}. ^1H NMR (δ; 250 MHz, $CDCl_3$): 0.96 (6 H, t, *J* 7.3, CH_3), 1.38 (4 H, sextet, *J* 7.4, CH_2), 1.94 (4 H, pent, *J* 7.4, CH_2), 4.02 (4 H, (66%) t, *J* 7.1, (34%) dt, $^3J_{PtH}$ 36.3, CH_2), 7.10 (1 H, dd, *J* 7.6 and 8.0, 4-H), 7.41 (2 H, (66%) d, *J* 7.6, (34%) app t, $^4J_{PtH}$ 8.2, Ar, 3- and 5-H), 8.26 (2 H, (66%) s, (34%) d $^3J_{PtH}$ 143.5, N=C*H*). $^{13}C\{^1H\}$ NMR (δ; 63 MHz, $CDCl_3$): 13.7 (CH_3), 19.7 (CH_2), 32.6 (CH_2), 61.1 (NCH_2, (34%) d, $^2J_{PtC}$ 21.4), 122.3 (4-C), 126.2 ((34%) d, $^3J_{PtC}$ 28.0, 3- and 5-C), 141.5 ((34%) d, $^2J_{PtC}$ 113.2, 2- and 6-C), 175.4 ((34%) d, $^2J_{PtC}$ 126.0, N=*C*), 1-C not observed. MS (*m*/*z*; FAB): 436 ($[M - Cl]^+$, 100%).

Synthesis of ((2,6-Bis(*N*-benzyl)imino)phenyl)platinumchloride 7d. 6d (0.47 g, 1.5 mmol) and potassium tetrachloroplatinate (0.523 g, 1.26 mmol) were refluxed under nitrogen in distilled glacial acetic acid (20 mL) for 48 h. The solvent was removed in vacuo, and the residue was purified by column chromatography (gradient elution, neat CH_2Cl_2 to 5% EtOAc/CH_2Cl_2) to give **7d** as a bright yellow solid, which was further purified by recrystallization from CH_2Cl_2 (0.100 g, 15% yield, based on K_2PtCl_4). Mp: 212 °C dec. Anal. Found: C, 48.02; H, 3.53; N, 4.94. Calcd for $C_{22}H_{19}ClN_2Pt(2H_2O)$: C, 47.96; H, 3.66; N, 5.08. IR (ν_{max}; CH_2Cl_2): 1603 (C=N) cm^{-1}. ^1H NMR (δ; 250 MHz, $CDCl_3$): 5.31 (4 H, (66%) s, (34%) d $^3J_{PtH}$ 27.7, CH_2), 7.05 (1 H, t, *J* 4.0, 4-H), 7.40 (12 H, m, Ar), 8.16 (2 H, (66%) s, (34%) d, $^3J_{PtH}$ 145.0, N=C*H*). $^{13}C\{^1H\}$ NMR (δ; 63 MHz, $CDCl_3$): 63.4 ((34%) d, $^2J_{PtC}$ 22.0, CH_2), 122.4 (Ar), 126.7 ((34%) d, $^3J_{PtC}$ 26.8, Ar, 3- and 5-C), 128.3 (Ar), 129.1 (Ar), 129.7 (Ar), 136.0 (Ar), 141.5 (Ar), 143.7 (Ar), 176.4 ((34%) d, $^2J_{PtC}$ 125.8, N=*C*). MS (*m*/*z*; FAB): 505 ($[M - Cl]^+$, 85%), 415 (9.5%), 338 (100%).

Synthesis of ((2,6-Bis(*N*-phenyl)imino)phenyl)platinumchloride 7e. 6e (0.35 g, 1.2 mmol) and potassium tetrachloroplatinate (0.451 g, 1.09 mmol) were refluxed under nitrogen in glacial acetic acid (20 mL) for 48 h. The solvent was removed in vacuo, and the residue was initially purified by column chromatography (70% EtOAc/petroleum ether) followed by recrystallization from CH_2Cl_2 to give **7e** as a red crystalline solid (0.174 g, 31% yield based on K_2PtCl_4). Mp: 270 °C Anal. Found: C, 45.60; H, 3.01; N, 5.19. Calcd for $C_{20}H_{15}ClN_2Pt(2H_2O)$: C, 45.94; H, 3.08; N, 5.36. IR (ν_{max}; CH_2Cl_2): 1587 (C=N) cm^{-1}. ^1H NMR (δ; 250 MHz, $CDCl_3$): 7.24 (2 H, t, *J* 7.7, Ar), 7.35 (1 H, d, *J* 7.0, Ar), 7.41 (4 H, t, *J* 7.4, Ar), 7.52 (4 H, m, Ar), 7.65 (2 H, (66%) d, *J* 7.7, (34%) app t, $^4J_{PtH}$7.3, 3- and 5-H), 8.54 (2 H, (66%) s, (34%) d, $^3J_{PtH}$ 140.7, N=C*H*). $^{13}C\{^1H\}$ NMR (δ; 63 MHz, $CDCl_3$): 122.9 (4-C), 124.2

((34%) d, $^{3}J_{\text{PtC}}$ 12.9, 3- and 5-C), 128.03 (Ar), 128.2 (Ar), 128.5 (Ar), 128.6 (Ar), 142.1 (34%) d, $^{2}J_{\text{PtC}}$ 100.8, 2- and 6-C), 177.2 ((34%) d, $^{2}J_{\text{PtC}}$ 110.9, N═*C*), 1-C not observed. MS (*m*/*z*; FAB): 513 (M^+, 5%), 478 ([M − Cl], 100%).

Synthesis of ((2,6-Bis(*N-tert*-butyl)imino)phenyl)aquoplatinum(II) Tetrafluoroborate 8. 7a (0.158 g, 0.33 mmol) and silver tetrafluoroborate (0.066 g, 0.34 mmol) were stirred in acetone (25 mL) protected from light for 14 h, by which time the starting complex had been completely consumed (TLC, silica, CH_2Cl_2). The mixture was filtered through Celite to remove silver chloride and evaporated to dryness to give **8** as a yellow crystalline solid (0.180 g, 97%). Mp: 234 °C Anal. Found: C, 34.25; H, 4.48; N, 4.59. Calcd for $C_{16}H_{25}BF_4N_2OPt(H_2O)$: C, 34.24; H, 4.85; N, 4.99. IR ($\nu_{\max}$; KBr disk): 1067 (BF_4−), 1599 (C═N) cm^{-1}. ^{1}H NMR (δ; 250 MHz, acetone-d_6): 1.49 (18 H, s, C*H*$_3$), 7.24 (1 H, t, *J* 7.6, Ar, 4-H), 7.61 (2 H, (66%) d, *J* 7.5, (34%) app t, $^{4}J_{\text{PtH}}$ 7.8, Ar, 3- and 5-H), 8.70 (2 H, (66%) s, (34%) d $^{3}J_{\text{PtH}}$ 163.9, N═C*H*). ^{13}C{^{1}H} NMR (δ; 63 MHz, acetone-d_6): 29.1 (*C*H$_3$), 64.6 ((34%) d, $^{2}J_{\text{PtC}}$ 18.2, (*C*(CH$_3$)$_3$), 125.1 (4-C), 129.6 ((34%) d, $^{3}J_{\text{PtC}}$ 30.1, 3- and 5-C), 143.0 (2- and 6- C), 162.6 (1-C), 175.0 ((34%) d, $^{2}J_{\text{PtC}}$ 126.7, N═*C*). MS (*m*/*z*; FAB): 438 ([M − OH$_2$ − BF$_4$]$^+$, 100%).

Synthesis of ((2,6-Bis(*N-tert*-butyl)imino)phenyl)aquoplatinum(II) Trifluoromethanesulfonate 9. 7a (0.155 g, 0.33 mmol) and silver triflate (0.1 g, 0.4 mmol) were stirred in CH_2Cl_2 (25 mL) protected from the light and left for 14 h, by which time all the starting complex had been consumed (TLC, silica, CH_2Cl_2). The mixture was filtered through Celite to remove silver chloride, washing with acetone, and evaporated to dryness to give **9**, as a yellow crystalline solid (0.198 g, >99%). Mp: 244 °C. Anal. Found: C, 33.76; H, 4.12; N, 4.63. Calcd for $C_{17}H_{25}F_3N_2O_4PtS(2H_2O)$: C, 33.72; H, 4.16; N, 4.49. IR ($\nu_{\max}$; KBr disk): 1034 (SO), 1163.0 (CF$_3$), 1282.6 (SO), 1600.8 (C═N) cm^{-1}. ^{1}H NMR (δ; 250 MHz, acetone-d_6): 1.70 (18 H, s, C*H*$_3$), 7.16 (1 H, t, *J* 7.6, 4-H), 7.53 (2 H, (66%) d, *J* 7.6, (34%) dd, *J* 7.6 and $^{4}J_{\text{PtH}}$ 6.1, 3- and 5-H), 8.55 (2 H, (66%) s, (34%) d $^{3}J_{\text{PtH}}$ 152.1, N═C*H*). ^{13}C{^{1}H} NMR (δ; 63 MHz, acetone-d_6): 20.1 (*C*H$_3$), 64.6 ((34%) d, $^{2}J_{\text{PtC}}$ 17.7, *C*(CH$_3$)$_3$), 124.9 (4-C), 127.4 (q, $^{1}J_{\text{CF}}$ 328.4, *C*F$_3$), 129.5 ((34%) d, $^{3}J_{\text{PtC}}$ 29.2, 3- and 5-C), 142.9 ((34%) d, $^{2}J_{\text{PtC}}$ 129.4, 2- and 6-C), 162.6 ((34%) d, $^{1}J_{\text{PtC}}$ 1078.2, 1-C), 174.7 ((34%) d, $^{2}J_{\text{PtC}}$ 126.8, N═*C*). MS (*m*/*z*; FAB): 438 ([M − OH$_2$ − OTf]$^+$, 100%).

Synthesis of ((2,6-Bis(*N*-cyclohexyl)imino)phenyl)aquoplatinum(II) Trifluoromethanesulfonate 10. 7b (2.70 g, 5.1 mmol) and silver triflate (1.5 g, 6 mmol) were stirred in CH_2Cl_2 (45 mL) protected from the light and left for 24 h, by which time all the starting complex had been consumed (TLC, silica, CH_2Cl_2). The mixture was filtered through Celite eluting with acetone to remove silver chloride and evaporated to dryness to give **10**, as a red-orange crystalline solid (3.35 g, 99%). Mp: 262 °C. Anal. Found: C, 38.22; H, 4.37; N, 4.10. Calcd for $C_{21}H_{29}F_3N_2O_4PtS$: C, 38.36; H, 4.44; N, 4.26. IR ($\nu_{\max}$; KBr disk): 1030 (SO), 1161 (CF$_3$), 1597 (C═N) cm^{-1}. ^{1}H NMR (δ; 250 MHz, acetone-d_6): 1.25 (2 H, m, C*H*$_2$), 1.39 (2 H, m, C*H*$_2$), 1.51 (6 H, m, C*H*$_2$), 1.70 (2 H, m, C*H*$_2$), 1.88 (4 H, d, *J* 12.8, C*H*$_2$), 2.15 (4 H, d, *J* 11.9, C*H*$_2$), 3.21 (2 H, brs, Pt−O*H*$_2$), 3.74 (2 H, m, NC*H*(CH$_2$)−), 7.23 (1 H, t, *J* 7.9, 4-H), 7.57 (2 H, (66%) d, *J* 7.7, (34%) app t, $^{4}J_{\text{PtH}}$ 9.0, 3- and 5-H). ^{13}C{^{1}H} NMR (δ; 63 MHz, acetone-d_6): 25.7 (*C*H$_2$), 25.9 (*C*H$_2$), 33.2 (*C*H$_2$), 68.3 (N*C*H(CH$_2$)−), 124.7 (4-C), 128.6 ((34%) d, $^{3}J_{\text{PtC}}$ 33.6, 3- and 5-C), 142.8 ((34%) d, $^{2}J_{\text{PtC}}$ 125.79, 2- and 6-C), 176.1 ((34%) d, $^{2}J_{\text{PtC}}$ 131.3, N═*C*), 1-C not observed. MS (*m*/*z*; FAB): 490 ([M − OTf − OH$_2$]$^+$, 100%).

Michael Reaction to Give 11 and 12[3e]. A stock solution was prepared containing ethyl cyanoacetate (0.10 mL, 1.0 mmol), methyl vinyl ketone (0.24 mL, 2.9 mmol), Hünig's base (0.017 mL, 0.1 mmol), and CD_2Cl_2 (3 mL). An aliquot (1 mL) of this solution was transferred to a NMR tube (the blank reaction), and a further aliquot (1.5 mL) was transferred to a second NMR tube containing **10** (0.014 g, 0.02 mmol). Both samples were stored at 4 °C and their NMR spectra recorded periodically. The presence of **11** was revealed by a characteristic peak at 3.64 ppm (1 H, dd, *J* 8.7 and 6.1, NCC*H*−).

Aldol Reaction to Give 13 and 14.[14] A stock solution was prepared containing methyl isocyanoacetate (0.5 mL, 6 mmol), benzaldehyde (0.8 mL, 8 mmol), Hünig's base (0.1 mL, 0.6 mmol), and CD_2Cl_2 (3 mL). An aliquot (1 mL) of this solution was transferred to a NMR tube (the blank reaction). A further aliquot (1 mL) was transferred to a second NMR tube containing **10** (0.044 g, 0.07 mmol). Both samples were stored at 4 °C and their NMR spectra recorded periodically.

Diels−Alder Reaction to Give 15 and 16.[15] A stock solution was prepared containing acrylonitrile (0.1 mL, 1.5 mmol), freshly cracked cyclopentadiene (0.3 mL, 3.7 mmol), and CD_2Cl_2 (3.5 mL). An aliquot (1 mL) of this solution was transferred to a NMR tube (the blank reaction). A further aliquot (1 mL) was transferred to a second NMR tube containing **10** (0.015 g, 0.02 mmol). Both samples were stored at 4 °C and their NMR spectra recorded periodically.

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Supporting Information Available: Details of the X-ray structure determinations of **7a**, **7e**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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