Preparation of Metallacycles with Anionic Terdentate [C,N,N′] Ligands by Intramolecular Oxidative Addition of C−X (X = Br, Cl) Bonds to [Pt(dba)$_2$]. An Unexpected Effect of Chloro Substituents

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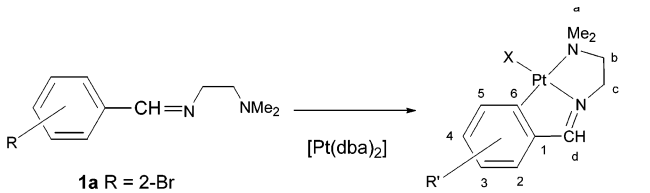
*Summary: The reactions of [Pt(dba)$_2$] with ligands C$_6$R$_n$H$_{5-n}$CHNCH$_2$CH$_2$NMe$_2$ (**1a**, R = 2-Br; **1b**, R = 2,3,4,5,6-Cl$_5$; **1c**, R = 2,3,6-Cl$_3$; and **1d**, R = 2,6-Cl$_2$) produce the corresponding [C,N,N′] cyclometalated platinum(II) compounds [PtX{C$_6$R$_n$H$_{4-n}$CHNCH$_2$CH$_2$NMe$_2$}] (**2a**−**d**) via intramolecular oxidative addition of C−Br or C−Cl bonds. All the new compounds were characterized by elemental analyses and mass and NMR spectroscopy, and [PtBr(Me$_2$NCH$_2$CH$_2$NCHC$_6$H$_4$)] (**2a**) and [PtCl(Me$_2$NCH$_2$CH$_2$NCH(3,5-C$_6$H$_2$Cl$_2$)] (**2f**) were also characterized crystallographically.*

An important mode of activation of carbon−halogen bonds is by chelate-assisted oxidative addition to a low-valent metal. Such processes are well documented for the reaction of potentially tridentate [C,N,N′] ligands with W(0),[1] Mo(0),[2] Ni(0),[3] Pd(0),[4] or Pt(II)[5] substrates, and oxidative addition of C−Br bonds at Pd(0)[6] or Pt(0)[7] precursors has also been reported for [N,C,N] ligands. Taking into account that the order of relative reactivity for group 10 complexes toward the C(aryl)−halide bond is Ni(0) > Pd(0) > Pt(0) and C−I > C−Br > C−Cl,[8] it is not surprising that intramolecular activation of C(aryl)−Cl bonds at platinum(0) has not been reported.

We report the reactions of the platinum(0) compound [Pt(dba)$_2$] (dba = dibenzylideneacetone) with nitrogen donor ligands RCHNCH$_2$CH$_2$NMe$_2$, in which R is an *ortho*-halosubstituted aryl ring. We performed these reactions in order to analyze the scope of intramolecular oxidative addition of C−Br or C−Cl bonds as a new method to prepare cyclometalated platinum(II) compounds with terdentate ligands. Previously reported methods to obtain such compounds with [N,C,N] or [C,N,N′] nitrogen donor ligands include transmetalation reactions of lithium derivatives[9] or cyclometalation[5,10] at platinum(II) substrates.

Scheme 1



1a R = 2-Br
1b R = 2,3,4,5,6-Cl$_5$
1c R = 2,3,6-Cl$_3$
1d R = 2,6-Cl$_2$
1e R = 2-Cl
1f R = 2,3,5-Cl$_3$

2a X = Br; R′ = H
2b X = Cl; R′ = 2,3,4,5-Cl$_4$
2c X = Cl; R′ = 2,3-Cl$_2$
2c′ X = Cl; R′ = 2,5-Cl$_2$
2d X = Cl; R′ = 2-Cl

Imines **1a**−**f** were easily obtained by reaction between Me$_2$N(CH$_2$)$_2$NH$_2$ and the corresponding aldehyde, in toluene at room temperature. Subsequent treatment of these potentially terdentate ligands with [Pt(dba)$_2$] in THF afforded the metallacycles [PtX{C$_6$R$_n$H$_{4-n}$-CH=NCH$_2$CH$_2$NMe$_2$}] (**2**), with three fused [5,5,6]-membered rings in the case of ligands **1a**−**d** (Scheme 1).

The new compounds were obtained as brown or deep red solids, which are soluble in the common organic solvents. All these complexes were characterized by elemental analysis, ^{1}H, ^{13}C (**2a** and **2d**), and ^{195}Pt NMR, and mass spectra (FAB and MALDI), and **2a** was also characterized crystallographically. In the ^{1}H NMR spectra, the Me$_2$N and CHN= resonances were coupled to platinum, showing the coordination of both nitrogen atoms to the metal. Compounds bearing a chloro substituent at the C^2 position of the aryl ring show a

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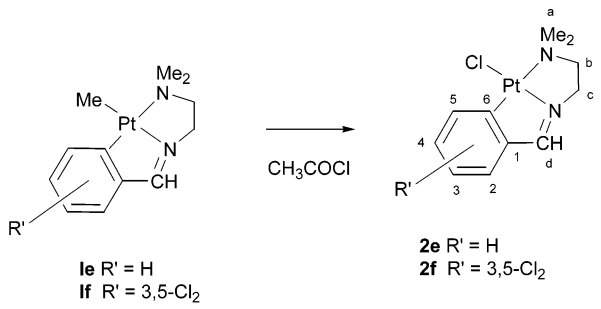
Scheme 2



downfield shift of the imine resonance which is consistent with a N=CH···Cl interaction between the imine proton and the chlorine atom. Similar shifts have been reported for analogous compounds with chloro or fluoro substituents. This interaction, which reinforces the planarity of the ArC=N fragment, has been confirmed in some cases by X-ray crystal structure determination.[11]

In the case of ligand **1c**, which presents two nonequivalent potential metalation sites (C^6 and C^2), a 2:1 mixture of compounds **2c** and **2c′** was obtained. The ^{1}H NMR spectra clearly showed that the oxidative addition occurs preferably in the less hindered C−Cl bond, to afford compound **2c** as a major isomer (metalation at C^6).

The FAB mass spectra of the new complexes show intense signals corresponding to M, M−X, and in some cases M−2X fragments, and weak signals corresponding to dinuclear species (2M−X). All these signals are also observed in the MALDI mass spectra, but the signals corresponding to the dinuclear species M−2X are more intense in this case. Nevertheless, the X-ray structures of compounds **2a** and **2f** (see below) show the monomeric nature of these derivatives, and consequently the signals attributable to 2M−X can be explained by dimerization produced in the ionization chamber, as described for related derivatives.[3,12]

When the imines **1e** and **1f** were treated with [Pt(dba)$_2$] in THF, the formation of the expected metallacycle by activation of the *ortho* C−Cl bond was not observed. In contrast, the formation, in very low yield, of a hydride platinum compound was detected in the case of **1e** ($\delta = -11.89$, J(HPt) = 925 Hz), along with other materials which could not be identified. The NMR data are consistent with the formation of a five-membered metallacycle by activation of a C−H bond, in which the hydride ligand is in *trans* position relative to the methinic nitrogen.[13]

To elucidate whether this failure to obtain the cyclometalated compounds [PtCl(Me$_2$NCH$_2$CH$_2$NCHC$_6$H$_4$)] (**2e**) and [PtCl(Me$_2$NCH$_2$CH$_2$NCH(3,5-C$_6$H$_2$Cl$_2$)] (**2f**) was attributable to a low thermodynamic stability of the corresponding cyclometalated platinum(II) compounds or to the synthetical procedure, the preparation of compounds **2e** and **2f** was attempted by an alternative route. Cycloplatinated compounds containing the [C,N,N′] terdentate ligands used in this work and a methyl ligand such as [PtMe(Me$_2$NCH$_2$CH$_2$NCHC$_6$H$_4$)] (**Ie**)[5b] or [PtMe(Me$_2$NCH$_2$CH$_2$NCH(3,5-C$_6$H$_2$Cl$_2$)] (**If**)[11g] have been described in the literature and substitution of methyl for chloro ligands at platinum can be achieved in mild conditions using acetyl chloride in methanol solution.[14] Using this method, compounds **2e** and **2f** were obtained in high yield from the methyl precursors, as depicted in Scheme 2. Compounds **2e** and **2f** were characterized by ^{1}H NMR, FAB and MALDI mass spectra, and elemental analyses, and **2f** was also characterized crystallographically.

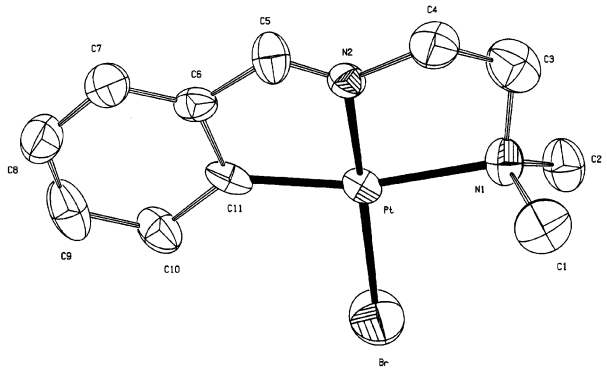


Figure 1. Molecular structure of compound **2a**.

The new metallacycles, compounds **2a**−**f**, were characterized by ^{195}Pt and ^{13}C (**2a**, **2d**, **2e**, and **2f**) NMR spectra. Couplings to ^{195}Pt are also observed in the ^{13}C NMR spectra for the iminic carbon as well as for aromatic carbons C^1, C^2, C^4, and C.[5] The metalated carbon C^6 appears as a downfield shifted singlet for which platinum satellites were not observed. The ^{195}Pt NMR spectra show only one signal, the position of which is consistent with the nature of the ligands bound to platinum(II).[15] The values indicate a downfield shift on increasing the chlorination of the aryl ring, which is consistent with deshielding of the platinum nucleus.

Crystal Structures. Suitable crystals of compounds **2a** and **2f** were grown in acetone solution. The crystal structures are composed of discrete molecules separated by van der Waals distances. The structures are shown in Figures 1 and 2, and selected molecular dimensions are listed in Table 1. In both cases a fused [5,5,6] tricyclic system containing a five-membered metallacycle, a chelate ring with two nitrogen atoms, and the phenyl group results from terdentate [C,N,N′] coordination of the ligand. A bromo (**2a**) or a chloro (**2f**) ligand completes the distorted square-planar coordination around the platinum center; the largest tetrahedral distortion is observed for **2f**. In each case, the metallacycle is nearly coplanar with the coordination plane, the dihedral angle between the mean planes being 2.12° (**2a**) and 4.06° (**2f**).

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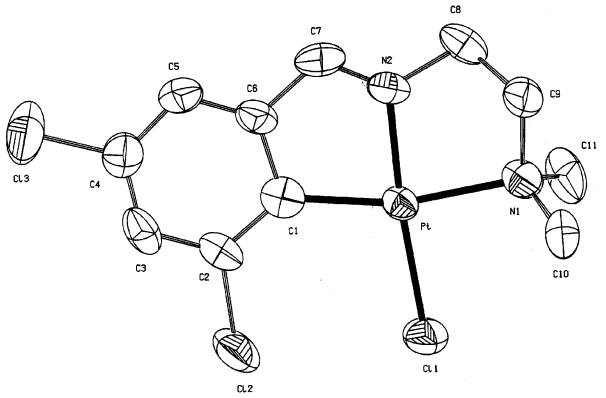

Figure 2. Molecular structure of compound **2f**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compound 2a and 2f with Estimated Standard Deviations

compound **2a**		compound **2f**	
Pt−N(1)	2.141(8)	Pt−N(1)	2.141(12)
Pt−C(11)	1.958(10)	Pt−C(1)	2.008(14)
Pt−N(2)	1.979(8)	Pt−N(2)	1.970(10)
Pt−Br	2.3979(16)	Pt−Cl(1)	2.301(4)
N(1)−C(3)	1.473(14)	N(1)−C(9)	1.52(2)
N(2)−C(5)	1.199(12)	N(2)−C(7)	1.27(2)
N(2)−C(4)	1.476(13)	N(2)−C(8)	1.47(2)
C(3)−C(4)	1.561(16)	C(8)−C(9)	1.47(2)
C(5)−C(6)	1.458(14)	C(6)−C(7)	1.45 (2)
N(2)−Pt−C(11)	79.4(3)	N(2)−Pt−C(1)	81.1(5)
N(1)−Pt−N(2)	84.7(3)	N(1)−Pt−N(2)	83.8(5)
C(11)−Pt−Br	99.4(3)	C(1)−Pt−Cl(1)	104.0(4)
N(1)−Pt−Br	96.6(2)	N(1)−Pt−Cl(1)	91.2(3)

Bond lengths and angles are well within the range of values obtained for analogous cyclometalated compounds.[5,16] In particular, the imine C=N bond lengths lie in the usual range, and Pt−amine distances are larger than Pt−imine distances, consistent with the weaker ligating ability of amines for platinum. Most bond angles at platinum are close to the ideal value of 90°, and the smallest angles correspond to the terdentate ligand. For **2f**, the angle C(1)−Pt−Cl(1) chlorine ligand is 104.0°; this large value, as well as the greater distortion of the coordination sphere of the platinum observed for this compound, is consistent with the steric hindrance created by the presence of a chlorine atom in the C(5) of the phenyl ring.

Conclusions

The obtained results indicate that while intramolecular oxidative addition of a C−Br bond at $[Pt(dba)_2]$ occurs easily (ligand **1a**), activation of a C−Cl bond can only be achieved for imine ligands in which both *ortho* positions of the aryl ring contain a chloro substituent (**1b**−**d**). Ligands containing only one chloro substituent in an *ortho* position (**1e**−**f**) failed to produce the cyclometalated compounds. This is an unexpected result, which cannot be explained by the standard effect of the substituents. It is remarkable that ligands **1b** and **1c** afford the corresponding metallacycles by oxidative addition, even if there is a chloro atom in the position adjacent to the C−Cl bond to be activated, whereas $2\text{-}ClC_6H_4CH{=}NCH_2CH_2NMe_2$ does not undergo the reaction. These results suggest that oxidative addition of these ligands to $[Pt(dba)_2]$ takes place in two steps, the coordination of both nitrogen atoms to platinum, followed by the oxidative addition reaction. The effect of the second *ortho* C−Cl bond is to facilitate the oxidative addition, via an N=CH···Cl interaction in the intermediate coordination complex, which reinforces the planarity of the ArC=N fragment and brings the C−Cl bond close to the metal (see above), in agreement with a three-center mechanism involving attack of the metal at the aryl−halogen bond.[17] In addition, this finding can explain the fact that the *ortho*-C−H bond of ligand $2\text{-}ClC_6H_4CH{=}NCH_2CH_2NMe_2$ (bond energy = 110 kcal/mol) undergoes the oxidative addition in preference to the weaker and more polar C−Cl bond (bond energy = 95 kcal/mol).

Experimental Section

Mass and NMR spectra were performed by the Serveis Científico-Tècnics de la Universitat de Barcelona. Microanalyses were performed by the Institut de Química Bio-orgànica de Barcelona (Consejo Superior de Investigaciones Científicas). FAB-mass spectra were carried out in a VG-Quattro spectrometer with a 3-nitrobenzyl alcohol matrix. MALDI mass spectra were obtained on a Voyager DE-RP (TOF) spectrometer equipped with a nitrogen laser (337 nm, 3 ns pulse). ^{1}H, ^{13}C, and ^{195}Pt NMR spectra were recorded by using Varian Gemini 200 (^{1}H, 200 MHz), Varian XL300FT (^{13}C, 75.4 MHz), Varian Mercury 400 (^{1}H−^{13}C gHSQC; ^{1}H, 400 MHz; ^{13}C, 100.6 MHz), and Bruker 250 (^{13}C, 62.5 MHz;^{195}Pt, 54 MHz) spectrometers and referenced to $SiMe_4$ (^{1}H, ^{13}C) and H_2PtCl_6 in D_2O (^{195}Pt). δ values are given in ppm and J values in Hz.

Preparation of Compounds. Compounds **1a**−**f**,[11g] $[Pt(dba)_2]$,[18] $[PtMe(Me_2NCH_2CH_2NCH(C_6H_4)]$ (**Ie**),[5b] and $[PtMe(Me_2NCH_2CH_2NCH(3,5\text{-}C_6H_2Cl_2)]$ (**If**)[11g] were prepared as reported.

$[PtBr(Me_2NCH_2CH_2NCHC_6H_4)]$ (**2a**) was obtained from 0.287 g (0.432×10^{-3} mol) of $Pt(dba)_2$ and 0.110 g (0.431×10^{-3} mol) of ligand $2\text{-}BrC_6H_4CHNCH_2CH_2NMe_2$ (**1a**) in 25 mL of THF. The mixture was stirred at room temperature under N_2 for 5 h, and insoluble materials were filtered off. The solvent was evaporated in vacuo, and the remaining residue was treated with diethyl ether to yield a brown solid. Yield: 140 mg (72%). Anal. Found: C, 29.6; H, 3.1; N, 6.0. Calcd for $C_{11}H_{15}BrN_2Pt$: C, 29.34; H, 3.36; N, 6.22. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.92 [s, J(Pt−H) = 14, 6H, H^a]; 3.09 [t, J(H−H) = 6, 2H, H^b]; 3.98 [t, J(H−H) = 6, J(H−Pt) = 36, 2H, H^c]; 6.98 [td, J(H−H) = 8, J(H−H) = 1, 1H, H^3]; 7.19 [m, 2H, H^2, H^4]; 7.90 [d, J(H−H) = 8, J(H−Pt) = 44, 1H, H^5]; 8.11 [s, J(H−Pt) = 145, 1H, H^d]. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 49.21 [s, C^a]; 54.29 [s, J(Pt−C) = 48, C^c]; 65.87 [s, J(Pt−C) = 26, C^b]; 123.22 [s, C^3]; 127.67 [s, J (Pt−C) = 36, C^2]; 131.71 [s, J(Pt−C) = 44, C^4]; 135.84 [s, J(Pt−C) = 62, C^5]; 142.25 [s, C^6]; 149.10 [s, C^1]; 171.77 [s, J(Pt−C) = 112, C^d]. ^{195}Pt NMR (54 MHz, $CDCl_3$): δ −3578 [s, br]. FAB-MS, m/z: 451 [M], 369 [M − Br].

$[PtCl(Me_2NCH_2CH_2NCHC_6Cl_4)]$ (**2b**) was obtained from 0.3 g (0.452×10^{-3} mol) of $Pt(dba)_2$ and 0.16 g (0.459×10^{-3} mol) of ligand $C_6Cl_5CHNCH_2CH_2NMe_2$ (**1b**) in 25 mL of THF. The mixture was stirred at 50 °C under N_2 for 5 h, and insoluble materials were filtered off. The solvent was evaporated in vacuo, and the remaining residue was treated with diethyl ether to yield a brown solid, which was purified by elution on a SiO_2 column using $CHCl_3$/MeOH (100:5) as eluent.

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Table 2. Crystallographic and Refinement Data for Compounds 2a and 2f

	2a	2f
formula	$C_{11}H_{15}BrN_2Pt$	$C_{11}H_{13}Cl_3N_2Pt$
fw	450.25	474.67
temp, K	293(2)	293(2)
wavelength, Å	0.71069	0.71069
cryst syst	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_12_12_1$
a, Å	9.413(2)	6.9050(10)
b, Å	11.045(7)	10.7360(10)
c, Å	12.970(7)	18.7980(10)
β, deg	108.15(3)	
V, Å^3; Z	1281.4(11); 4	1393.5(3); 4
d(calcd), Mg/m^3	2.334	2.262
abs coeff, mm^{-1}	14.040	10.623
F(000)	832	888
no. of reflns coll/unique	3715/3715 [R(int) = 0.0399]	8148/2012 [R(int) = 0.0562]
no. of data/restraint/params	3715/0/136	1962/0/155
GOF on F^2	0.882	1.065
R_1 ($I > 2\sigma(I)$)	0.0374	0.0419
wR_2 (all data)	0.0968	0.1127
peak and hole, e Å^{-3}	0.655 and −0.660	0.579 and −0.511

Yield: 80 mg (33%). Anal. Found: C, 24.7; H, 2.0; N, 4.9. Calcd for $C_{11}H_{11}Cl_5N_2Pt$: C, 24.31; H, 2.04; N, 5.15. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.88 [s, J(Pt−H) = 17, 6H, H^a]; 3.14 [t, J(H−H) = 6, 2H, H^b]; 4.12 [t, J(H−H) = 6, 2H, H^c]; 9.01 [s, J(H−Pt) = 134, 1H, H^d]. ^{195}Pt NMR (54 MHz, $CDCl_3$): δ −3034 [s, br]. Maldi-MS, m/z: 505 [M − Cl], 471 [M − 2Cl].

[PtCl(Me$_2$NCH$_2$CH$_2$NCH(2,3-C$_6$H$_3$Cl$_2$))] (2c) and [PtCl(Me$_2$NCH$_2$CH$_2$NCH(2,5-C$_6$H$_3$Cl$_2$))] (2c′). The mixture of isomers **2c** and **2c′** was obtained from 0.3 g (0.452×10^{-3} mol) of Pt(dba)$_2$ and 0.13 g (0.452×10^{-3} mol) of ligand 2,3,6-$C_6H_2Cl_3CHNCH_2CH_2NMe_2$ (**1c**) in 25 mL of THF using the procedure reported for **2b**. Yield: 85 mg (40%). The major isomer **2c** can be separated by careful elution on a SiO_2 column using $CHCl_3$/MeOH (100:4) as eluent. Anal. Found: C, 27.9; H, 2.9; N, 5.7. Calcd For $C_{11}H_{13}Cl_3N_2Pt$: C, 27.83; H, 2.76; N, 5.90%. FAB-MS, m/z: 475 [M], 440 [M − Cl]. Maldi: 911 [2M − Cl]. ^{1}H NMR (250 MHz, $CDCl_3$) **2c** (major isomer): δ 2.89 [s, J(H−Pt) = 15 Hz, 6H, H^a]; 3.11 [t, J(H−H) = 6 Hz, 2H, H^b]; 4.04 [t, J(H−Pt) = 33 Hz, J(H−H) = 6 Hz, 2H, H^c]; 7.19 [d, J(H−Pt) = 43 Hz, J_{HH} = 8 Hz, 1H, H^5]; 7.34 [d, J(H−H) = 8 Hz, 1H, H^4]; 8.69 [s, J(H−Pt) = 146 Hz, 1H, H^d]. ^{195}Pt NMR (54 MHz, $CDCl_3$): δ −3122.9. ^{1}H NMR (250 MHz, $CDCl_3$) **2c′** (minor isomer): δ 2.86 [s, J(H−Pt) = 15 Hz, 6H, H^a]; 3.09 [t, J(H−H) = 6 Hz, 2H, H^b]; 3.98 [t, J(H−Pt) = 33 Hz, J(H−H) = 6 Hz, 2H, H^c]; {6.87 [d, J(H−H) = 8 Hz, 1H]; 7.19 [d, J(H−H) = 8 Hz, 1H], H^4, H^3}, 8.71 [s, J(H−Pt) = 136 Hz, 1H, H^d].

[PtCl(Me$_2$NCH$_2$CH$_2$NCH(2-C$_6$H$_3$Cl))] (**2d**) was obtained from 0.375 g (0.550×10^{-3} mol) of Pt(dba)$_2$ and 0.136 g (0.550×10^{-3} mol) of ligand 2.6-$C_6H_3Cl_2CHNCH_2CH_2NMe_2$ (**1d**) in 25 mL of THF using the procedure reported for **2b**. Yield: 110 mg (45%). Anal. Found: C, 30.2; H, 2.9; N, 6.5. Calcd for $C_{11}H_{14}Cl_2N_2Pt$: C, 30.01; H, 3.21; N, 6.36. ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.90 [s, J(Pt−H) = 12, 6H, H^a]; 3.12 [t, J(H−H) = 5, 2H, H^b]; 4.08 [t, J(H−H) = 5, J(H−Pt) = 27, 2H, H^c]; 6.94 [dd, J(H−H) = 6, J(H−H) = 1, 1H, H^3]; 7.18 [t, J(H−H) = 6, 1H, H^4]; 7.62 [d, J(H−H) = 6, J(H−Pt) = 34, 1H, H^5]; 8.72 [s, J(H−Pt) = 115, 1H, H^d]. ^{13}C NMR (75 MHz, $CDCl_3$): δ 47.70 [s, C^a]; 53.80 [s, J(Pt−C) = 49, C^c]; 65.00 [s, C^b]; 122.75 [s, C^3]; {131.56 [s, J(Pt−C) = 54]; 132.47 [s, J(Pt−C) = 53], C^4 , C^5}; 131.84 [s, C^2]; 143.54 [s, C^1]; 145.37 [s, C^6]; 168.77 [s, J(Pt−C) = 105, C^d]. ^{195}Pt NMR (54 MHz, $CDCl_3$): δ −3402 [s, br]. FAB-MS, m/z: 441 [M], 403 [M − Cl]. Maldi-MS, m/z: 843 [2M − Cl].

[PtCl(Me$_2$NCH$_2$CH$_2$NCHC$_6$H$_4$)] (**2e**) was obtained from reaction of 50 mg (0.130×10^{-3} mol) of compound **Ie** with 0.2 mL (2.81×10^{-3} mol) of CH_3COCl in 10 mL of a CH_2Cl_2/MeOH mixture. The solution was stirred until the color changed from red to orange (ca. 10 min), and the solvent was removed in the rotary evaporator to yield an orange solid. Yield: 46 mg (88%). Anal. Found: C, 32.3; H, 3.9; N, 6.6. Calcd for $C_{11}H_{15}ClN_2Pt$: C, 32.56; H, 3.72; N, 6.90. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.88 [s, J(Pt−H) = 13, 6H, H^a]; 3.07 [t, J(H−H) = 6, 2H, H^b]; 3.86 [td, J(H−H) = 6, J(H−H) = 1, J(H−Pt) = 34, 2H, H^c]; 6.99 [td, J(H−H) = 7, J(H−H) = 1, 1H, H^3]; 7.17 [dd, J(H−H) = 8, J(H−H) = 1, 1H, H^2]; 7.21 [td, J(H−H) = 7, J(H−H) = 1, 1H, H^4]; 7.69 [d, J(H−H) = 8, J(H−Pt) = 42, 1H, H^a]; 7.91 [t, J(H−H) = 1, J(H−Pt) = 143, 1H, H^d]. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ 48.96 [s, C^a]; 54.55 [s, J(Pt−C) = 48, C^c]; 66.09 [s, J(Pt−C) = 26, C^b]; 123.50 [s, C^3]; 127.86 [s, J(Pt−C) = 38, C^2]; 131.66 [s, J(Pt−C) = 44, C^4]; 134.25 [s, J(Pt−C) = 56, C^5]; 143.31 [s, C^6]; 149.54 [s, J(Pt−C) = 90, C^1]; 172.12 [s, J(Pt−C) = 109, C^d]. ^{195}Pt NMR (54 MHz, $CDCl_3$): δ −3462 [s, br]. FAB-MS, m/z: 405 [M], 370 [M − Cl].

[PtCl(Me$_2$NCH$_2$CH$_2$NCH(3,5-C$_6$H$_2$Cl$_2$))] (**2f**) was similarly prepared from **If**. Yield: 50 mg (95%). Anal. Found: C, 27.6; H, 3.0; N, 5.6. Calcd for $C_{11}H_{13}Cl_3N_2Pt$: C, 27.83; H, 2.76; N, 5.90. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.89 [s, J(Pt−H) = 16, 6H, H^a]; 3.12 [t, J(H−H) = 6, 2H, H^b]; 4.07 [t, J(H−H) = 6, J(H−Pt) = 32, 2H, H^c; {7.12 [d, J(H−H) = 2, 1H]; 7.31 [d, J(H−H) = 2, 1H], H^2, H^4}; 8.37 [s, J(H−Pt) = 130, 1H, H^d]. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 48.80 [s, C^a]; 54.85 [s, C^c]; 66.43 [s, C^b]; {125.84 [s, J(C−Pt) = 37]; 133.34 [s, J(C−Pt) = 35], C^2, C^4}; {129.21 [s]; 133.88 [s], C^3, C^5}; 144.03 [s, C^6]; 153.00 [s, J(Pt−C) = 73, C^1]; 171.37 [s, J(Pt−C) = 99, C^d]. ^{195}Pt NMR (54 MHz, $CDCl_3$): δ −3150 [s, br]. FAB-MS, m/z: 473 [M], 438 [M − Cl], 403 [M − 2Cl].

X-ray Structure Analysis. Prismatic crystals were selected and mounted on an Enraf-nonius CAD4 four-circle diffractometer (**2a**) or on a MAR345 diffractometer with an image plate detector (**2f**). Intensities were collected with graphite-monochromatized Mo Kα radiation. Lorentz polarization but not absorption corrections were made. The structures were solved by Patterson synthesis (**2a**) or by direct methods (**2f**), using the SHELXS computer program,[19] and refined by the full-matrix least-squares method, with the SHELXL97 computer program[19] using 3715 (**2a**) or 1962 (**2f**) reflections (very negative intensities were not assumed). For **2f**, the chirality of the structure was defined from the Flack coefficient, which is equal to 0.00(16) for the given results.[20] Further details are given in Table 2.

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Supporting Information Available: Tables giving all bond lengths and angles, refined and calculated atomic coordinates, and anisotropic thermal parameters for **2a** and **2f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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