

Synthesis and Characterization of Five-Coordinate $[\text{PtCl}(\text{L})(\text{N-N})(\text{olefin})]^+$ Complexes. Molecular Structure of $[\text{PtCl}(\text{pyridine})(2,9\text{-dimethyl-1,10-phenanthroline})(\text{ethylene})]-(\text{CF}_3\text{SO}_3)$

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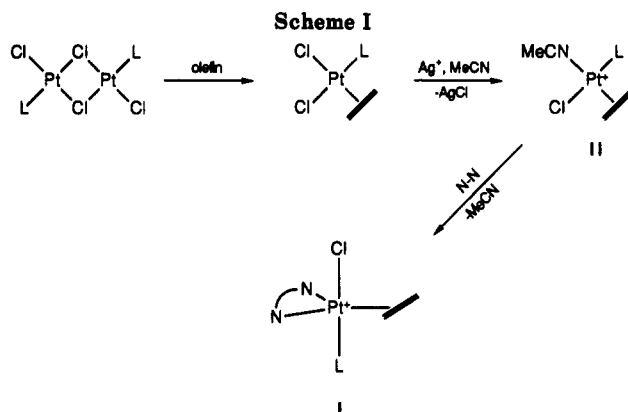
Cationic five-coordinate platinum(II) complexes of general formula $[\text{PtCl}(\text{L})(\text{N-N})(\text{olefin})]^+$ have been synthesized. Relevant chemical and spectral properties of the new complexes are discussed in comparison with related five-coordinate species. The X-ray crystal structure of the title complex has been determined. This crystallizes in the orthorhombic system, space group *Pbca* with $a = 12.808$ (5) Å, $b = 18.744$ (4) Å, $c = 19.445$ (3) Å, and $Z = 8$. Refinement converged at $R = 0.025$ ($R_w = 0.027$). The geometry of the five-coordinated platinum complex is bipyramidal, with the chloride and pyridine ligands in the apical positions and the olefin double bond in the equatorial plane.

Introduction

Recent studies from these laboratories led to the isolation and characterization of five-coordinate hydrocarbyl complexes, both neutral, $[\text{PtX}(\text{R})(\text{N-N})(\text{olefin})]$,¹ and cationic, $[\text{PtR}(\text{L})(\text{N-N})(\text{olefin})]^+$.² The five-coordinate neutral dihalo complexes have been known for a longer time,³ but no report concerning the related cationic species has yet appeared. It is worthy of note that previous comparisons² between the cited neutral and cationic hydrocarbyl complexes have disclosed some interesting aspects. For example, notable differences in stability of compounds containing the same N-N, R, and olefin ligands, but bearing in one apical position a neutral or an anionic ligand, respectively, were observed. Moreover, it was found² that the stability of the cationic complexes could be tuned by appropriate variation of the ligand L. This study, dealing with the synthesis and characterization of cationic halo complexes of general formula $[\text{PtCl}(\text{L})(\text{N-N})(\text{olefin})]^+$ (I), was aimed at extending the knowledge of the structure and properties of olefin complexes of five-coordinate Pt(II).

Results and Discussion

Synthesis and NMR Spectra. The hydrocarbyl complexes of general formula $[\text{PtR}(\text{L})(\text{N-N})(\text{olefin})]^+$, analogous to type I complexes were previously prepared from the corresponding $[\text{PtX}(\text{R})(\text{N-N})(\text{olefin})]$ species by substitution of the halide X with a neutral L ligand in the presence of a silver salt.² Some attempts to isolate type I complexes by applying the same procedure to dihalo complexes of the type $[\text{PtX}_2(\text{N-N})(\text{olefin})]$ were unsuccessful, since the selective substitution of one ligand was not attained. Instead, we found that suitable precursors of type I species are the four-coordinate compounds of the type *cis*- $[\text{PtCl}_2(\text{L})(\text{olefin})]$.⁴ These were reacted with an



equimolar quantity of a silver salt in dichloromethane solution in the presence of methyl cyanide. No attempt was made to isolate the products of this reaction, which is supposed to afford the stereoselective substitution of the chloride trans to the olefin. Further addition to the solution of the bidentate ligand transforms the four-coordinate cationic intermediate II into the type I product, according to the comprehensive Scheme I.

The choice of the N-N ligands was directed by the previous results¹ concerning the correlation between their steric features and their ability to stabilize the trigonal-bipyramidal geometry.

Four N-N ligands (Figure 1) were used, i.e. 2,9-dimethyl-1,10-phenanthroline (1), 1,10-phenanthroline (2), 6-methyl-2,2'-bipyridyl (3), and 2,2'-bipyridyl (4) (henceforth named dmphen, phen, mbpy, and bpy, respectively), displaying a wide range of stabilizing ability. All the ligands afforded isolable five-coordinate I products, but with different solution behavior, as discussed below.

The neutral L ligands (Figure 1) were methyl cyanide (a), pyridine (b), 4-methylpyridine (c), 4-chloropyridine (d), and dimethylamine (e). It is worthy of note that the

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Table I. Elemental Analysis for the Five-Coordinate Complexes [PtCl(L)(N-N)(ethylene)](BF₄)

complex	formula	fw	anal. found (calcd)		
			C	H	N
1a	C ₁₈ H ₁₉ BClF ₄ N ₃ Pt	594.7167	36.43 (36.35)	3.14 (3.22)	7.20 (7.07)
1b	C ₂₁ H ₂₁ BClF ₄ N ₃ Pt	632.7657	39.82 (39.86)	3.21 (3.35)	6.71 (6.64)
2b	C ₁₉ H ₁₇ BClF ₄ N ₃ Pt	604.7117	37.59 (37.74)	2.81 (2.83)	6.87 (6.95)
1c	C ₂₂ H ₂₃ BClF ₄ N ₃ Pt	646.7927	41.01 (40.85)	3.67 (3.58)	6.45 (6.50)
2c	C ₂₀ H ₁₉ BClF ₄ N ₃ Pt	618.7387	38.68 (38.82)	2.99 (3.10)	6.62 (6.79)
1d	C ₂₁ H ₂₀ BCl ₂ F ₄ N ₃ Pt	667.2107	37.86 (37.80)	3.10 (3.02)	6.32 (6.30)
2d	C ₁₉ H ₁₆ BCl ₂ F ₄ N ₃ Pt	639.1567	35.89 (35.70)	2.61 (2.52)	6.61 (6.57)
1e	C ₁₈ H ₂₃ BClF ₄ N ₃ Pt	598.7487	36.45 (36.11)	3.92 (3.87)	7.01 (7.02)
2e	C ₁₆ H ₁₉ BClF ₄ N ₃ Pt	570.6947	33.55 (33.67)	3.29 (3.36)	7.32 (7.36)
3b	C ₁₈ H ₁₉ BClF ₄ N ₃ Pt	594.7167	36.60 (36.35)	3.05 (3.22)	7.04 (7.07)
4c	C ₁₈ H ₁₉ BClF ₄ N ₃ Pt	594.7167	36.18 (36.35)	3.23 (3.22)	7.09 (7.07)

Table II. Selected ¹H NMR^a Data [δ (ppm), J_{Pt-H} (Hz)] for the Five-Coordinate Products [PtCl(L)(N-N)(ethylene)](BF₄)

complex	cation	N-CMe	resonances		
			ethylene	other	
1a ^b	[PtCl(MeCN)(dmphen)(ethylene)] ⁺	3.37	3.80 (70), (e, 4 H)	2.26 (12) (s, MeCN)	
1b ^c	[PtCl(py)(dmphen)(ethylene)] ⁺	3.70	3.96 (75) (app d, 2 H) 3.33 (70) (app d, 2 H)	8.40 (35) (d, H-2, H-6 of py)	
2b ^c	[PtCl(py)(phen)(ethylene)] ⁺		3.98 (81) (app d, 2 H) 3.34 (68) (app d, 2 H)	8.81 (d, H-2, H-9 of 1,10-phen) 8.80 (33) (d, H-2, H-6 of py)	
1c ^d	[PtCl(4-Mepy)(dmphen)(ethylene)] ⁺	3.70	3.96 (71) (app d, 2 H) 3.18 (65) (app d, 2 H)	8.13' (d, H-2, H-6 of 4-Mepy) 2.16 (s, 4-Mepy)	
2c ^e	[PtCl(4-Mepy)(phen)(ethylene)] ⁺		3.95 (74) (app d, 2 H) 3.30 (68) (app d, 2 H)	9.92 (d, H-2, H-9 of 1,10-phen) 8.68 (30) (d, H-2, H-6 of 4-Mepy) 2.25 (s, 4-Mepy)	
1d ^b	[PtCl(4-Clpy)(dmphen)(ethylene)] ⁺	3.49	3.83 (75) (app d, 2 H) 3.11 (68) (app d, 2 H)	8.08 (33) (d, H-2, H-6 of 4-Clpy)	
2d ^b	[PtCl(4-Clpy)(phen)(ethylene)] ⁺		3.91 (80) (app d, 2 H) 3.14 (70) (app d, 2 H)	9.74 (d, H-2, H-9 of 1,10-phen) 8.65 (33) (d, H-2, H-6 of 4-Clpy)	
1e ^c	[PtCl(Me ₂ NH)(dmphen)(ethylene)] ⁺	3.49	3.70 (75) (app d, 2 H) 3.33 (70) (app d, 2 H)	2.12 (35) (d, Me ₂ NH)	
2e ^c	[PtCl(Me ₂ NH)(phen)(ethylene)] ⁺		3.70 (75) (app d, 2 H) 3.30 (65) (app d, 2 H)	9.68 (d, H-2, H-9 of 1,10-phen) 2.40 (35) (d, Me ₂ NH)	
3b ^c	[PtCl(py)(mbpy)(ethylene)] ⁺	3.46	3.82 (75) (app d, 2 H) 3.20 (70) (app d, 2 H)	9.58 (d, H-6 of 6'-Me-2,2'-bpy) 8.50 (35) (d, H-2, H-6 of py)	
4c ^e	[PtCl(4-Mepy)(bpy)(ethylene)] ⁺		3.82 (75) (app d, 2 H) 3.18 (68) (app d, 2 H)	9.58 (d, H-6, H-6' of 2,2'-bpy) 8.57 (30) (d, H-2, H-6 of 4-Mepy) 2.32 (4-Mepy)	

^a 270 or 200 MHz. Abbreviations: s, singlet; d, doublet; app, apparent. ^b In CDCl₃/CD₂NO₂ (2:1) solution, CHCl₃ as internal standard. ^c In CD₃NO₂ solution, CH₃NO₂ as internal standard. ^d In CDCl₃ solution, CHCl₃ as internal standard. ^e AA'BB' multiplet. ^f ³J_{Pt-H} not evaluable.

synthesis of type I complexes from another species of the same type by exchange of L appears to be of poor feasibility (see below), while this procedure proved to be useful for hydrocarbyl cationic complexes.² Thus, the preparation of complexes with various L was restricted by the attainment of the corresponding type II intermediates.

All complexes are soluble in nitromethane, less so in chloroform. Elemental analyses (Table I) and conductivity measurements are consistent with type I formula. The assignment of the BPT geometry was made by NMR measurements (Table II), taking into account previous observations concerning related species,^{1,2} and confirmed in the case of [PtCl(py)(dmphen)(ethylene)](CF₃SO₃) by the X-ray analyses (see below).

The main feature of the NMR spectra is the high-field shift of the olefin proton signals with respect to those of the free ligand. The magnitude of the shift (1–2 ppm) is comparable with that of the analogous dichloro species⁵ and smaller than the corresponding shifts in neutral haloalkyl¹ and cationic hydrocarbyl² five-coordinate complexes. As already observed² for the latter two species, we note that the positive charge does not cause any appreciable down-field shift of the signals with respect to those

Table III. Selected Bond Distances (Å) and Angles (deg) in the Cation [PtCl(py)(dmphen)(ethylene)]⁺

Pt-Cl	2.304 (1)	Pt-C16	2.070 (6)
Pt-N1	2.236 (4)	Pt-N3	2.027 (4)
Pt-N2	2.230 (4)	C15-C16	1.40 (1)
Pt-C15	2.075 (6)	C-H(ethylene) _{av}	0.99 (5)
C16-Pt-N3	87.9 (2)	N1-Pt-C15	122.4 (2)
C15-Pt-N3	90.1 (2)	N1-Pt-N2	74.8 (1)
C15-Pt-C16	39.5 (2)	Cl-Pt-N3	178.9 (1)
N2-Pt-N3	88.4 (1)	Cl-Pt-C16	91.3 (1)
N2-Pt-C16	123.3 (2)	Cl-Pt-C15	89.7 (2)
N2-Pt-C15	162.8 (2)	Cl-Pt-N2	91.4 (1)
N1-Pt-N3	92.1 (1)	Cl-Pt-N1	88.9 (1)
N1-Pt-C16	161.9 (2)		

of the corresponding neutral species.

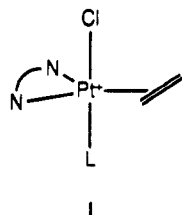
The pattern of the ethylene protons, i.e. two apparent doublets or an AA'BB' quartet, and that of the (*E*)-2-butene protons gave evidence of slow motion on the NMR time scale around the ||-Pt bond at room temperature. The same result holds for cationic hydrocarbyl derivatives.²

The olefin protons, as well as the doublet from the pyridine α protons, the MeCN singlet, and the Me₂NH doublet, show the typical coupling to ¹⁹⁵Pt, in agreement with metal coordination.

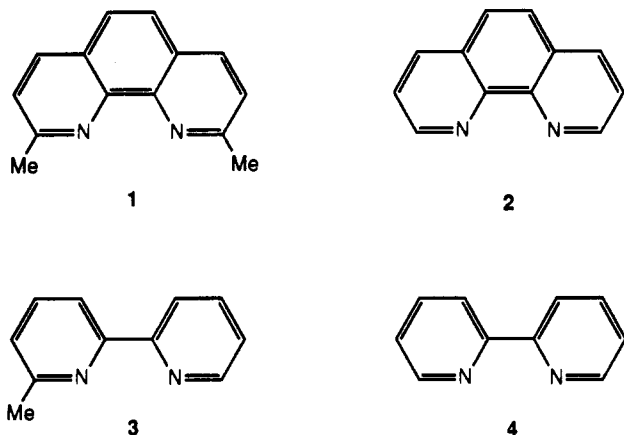
Molecular Structure of the Cation [PtCl(py)(dmphen)(ethylene)]⁺ as Its (CF₃SO₃)⁻ Salt. The stereochemistry of the title cation, as determined by X-ray dif-

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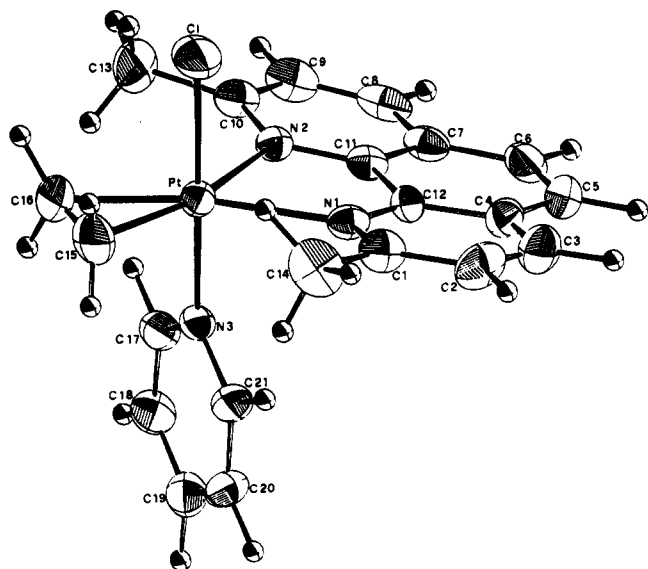
N-N ligands



L ligands

MeCN (a), py (b), 4-Me-py (c), 4-Cl-py (d), Me₂NH (e)

Figure 1.

Figure 2. Perspective view of the [PtCl(py)(dmphen)(ethylene)]⁺ cation showing the atom-numbering scheme.

fraction experiments, is illustrated in Figure 2. Relevant bond parameters are listed in Table III. The cation has trigonal-bipyramidal coordination geometry, very similar to that found in the related species. The dmphen and the ethylene ligands occupy the equatorial coordination sites, and the chlorine atom and the pyridine molecule define the axial positions [Cl-Pt-N(py) angle 178.9 (1)°]. The average plane of the dmphen rings is 9.4 (1)° out of the equatorial coordination plane. The Pt atom is 0.36 Å out of the dmphen plane on the side of the pyridine ligand. The idealized molecular symmetry is C_s, with the pyridine

Table IV. Comparison of Some Relevant Bond Distances (Å) in the Cation [PtCl(py)(dmphen)(ethylene)]⁺ with Those in Strictly Related Neutral Species

formula	Pt—C- (olefin)	C=C	Pt—N- (dmphen)	Pt—Cl	ref
[PtCl(py)(dmphen)- (ethylene)] ⁺	2.072 (6)	1.40 (1)	2.233 (4)	2.304 (1)	this work
[PtCl ₂ (dmphen)- (ethylene)]	2.083 (7)	1.41 (1)	2.236 (5)	2.311 (3)	5
[PtCl(SnPh ₂ Cl)(dm- phen)(ethylene)]	2.08 (1)	1.41 (2)	2.20 (1)	2.478 (3)	6

ring almost orthogonal to the plane bisecting the other ligands. The Pt—N(dmphen) distances are strictly equivalent and average 2.233 (4) Å. Pt—N(py), on the other hand, is much shorter [2.027 (4) Å] in spite of the equivalent basicity of the donor atoms. Although the two Pt—N interactions are not electronically equivalent and were not expected to be equal, the difference is too marked. It can be explained principally in terms of orbital misalignment in the Pt—N(dmphen) interactions caused by the rigidity of this ligand entailing an acute bite angle [N1—Pt—N2, 74.8 (1)°]. The distances of Pt—C(ethylene) [2.073 (6) Å] and Pt—Cl [2.304 (1) Å] are normal and, together with the just cited Pt—N(dmphen) values, can be usefully compared with the corresponding values of the most similar neutral species. This comparison aims to detect the effect, if any, of the net charge on the bond distances. Such a comparison is reported in Table IV and shows a substantial equivalence of the platinum ligand interactions, irrespective of the overall molecular charge. Therefore we can conclude that the effect of the net charge is very small and falls within the minor structural variations induced by the ligand substitutions.

Reactions. Some aspects of the reactivity of the complexes related to the olefin release reaction and to the exchange of the apical ligands were examined.

Concerning the olefin release, we note that the phen and the bpy complexes (2b, 2c, 2d, 2e, 4c) are rare examples⁷ of isolable five-coordinate olefin complexes in which the N-N ligand lacks the steric requirements usually needed to stabilize the adduct.¹ In the solid state such complexes do not appreciably release the olefin during storage for some months at 5 °C. This result is related to the kinetic stability of the complexes. In fact, slow olefin release in solution can be monitored by ¹H NMR spectroscopy. Thus, 2b and 2c give back the corresponding [PtCl(L)(phen)]⁺ species in ca. 3 days at room temperature in CD₃NO₂, while the loss of ethylene from 4b takes more than 10 days in CD₂Cl₂ or CD₃NO₂ solutions.

We note that in the case of neutral haloalkyl derivatives [PtX(R)(N-N)(olefin)]¹ five-coordinate adducts with bpy or phen could only be detected in solution through NMR spectroscopy, and the related dihalo complex [PtCl₂(bpy)(ethylene)]⁸ rapidly transforms in dichloroethane solution into the corresponding square-planar species.

Moreover, complex 3b, where 3 has a medium steric demand, dissolved in CD₃NO₂ and placed in a sealed NMR tube, does not exhibit appreciable olefin release after several days standing at room temperature. In contrast, haloalkyl five-coordinate complexes with N-N similar to 3,¹ rapidly equilibrate in solution with the corresponding four-coordinate species.

These and previous results indicate that the kinetic stability of type I complexes is higher than that of the corresponding neutral dihalo species⁸ and is further much

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greater than that of cationic² and neutral¹ hydrocarbyl derivatives.

Finally, as expected, no release of olefin is inferred by the ¹H NMR spectra of dmphen complexes after standing several days in solution. The attempt to obtain five-coordinate complexes of dmphen, starting from the corresponding square-planar species, failed. The complex [PtCl(dmphen)(4-Mepy)](BF₄) after standing 3 weeks in CD₃NO₂ solution under ethylene atmosphere, did not afford appreciable amounts of the five-coordinate complex. The same precursor did not react, within the same time, with a stoichiometric amount of acrylonitrile.

The failure of some attempts to exchange the L ligand, under the same conditions which allow the exchange for the hydrocarbyl derivatives similar to I, was noted above. In particular, no reaction was observed between aniline and the methyl cyanide complex 1a under the same experimental conditions as reported in ref 2. Furthermore, no change of the intensity of the MeCN resonance of the same complex was detectable after 3 days in solution in the presence of an excess of CD₃CN.

Also the treatment of complex 2c in CH₃NO₂ solution with a coordinating anion, aiming to form a neutral complex, was ineffective, while the facile coordination of chloride ions to cationic hydrocarbyl complexes was previously observed.² Finally, the addition of a stoichiometric amount of MeONa to a nitromethane solution of complex 1d was ineffective, and the starting compound was recrystallized after 48 h in good yield.

Experimental Section

¹H NMR spectra were recorded at 270 or 200 MHz on a Bruker AC-270 or a Varian XL-200 spectrometer, respectively. The complexes *cis*-[PtCl₂(MeCN)(ethylene)],⁹ *cis*-[PtCl₂(py)(ethylene)],⁴ *cis*-[PtCl₂(4-Mepy)(ethylene)],⁴ *cis*-[PtCl₂(Me₂NH)(ethylene)],⁴ [PtCl₂(dmphen)],⁵ and 6-methyl-2,2'-bipyridyl¹⁰ were prepared by adopting described procedures. The complex *cis*-[PtCl₂(4-Cppy)(ethylene)] was obtained by using the same procedure adopted for *cis*-[PtCl₂(py)(ethylene)]. Solvents and reagents were of AnalR grade and they were used without further purification.

Synthesis of 1a, 1b, 1c, 1d, 1e, 2e, and 3b. A solution (0.010 g/mL) of AgBF₄ (1 equiv) in methyl cyanide was added dropwise under nitrogen to the appropriate complex *cis*-[PtCl₂(L)(ethylene)] (0.100 g) dissolved in the minimum amount of a 1:1 mixture CH₂Cl₂/MeCN (6–20 mL). After 15 min of stirring at 0 °C, the suspension was filtered through a thin layer of Celite and the N-N ligand added to the clear filtrate. The volume of the solution was reduced under vacuum (3–4 mL) and the pale yellow complex crystallized by slow addition of diethyl ether. Yield: 70–80%.

Synthesis of [PtCl(py)(dmphen)](*E*)-MeCH=CHMe]-(BF₄). The above procedure was adopted by using *cis*-[PtCl₂(py)](*E*)-MeCH=CHMe] as the starting material. This complex was obtained by a method already reported for other *cis*-[PtCl₂(L)(olefin)]⁴ complexes: (*E*)-MeCH=CHMe was bubbled over a period of 10 min through a suspension of [Pt₂Cl₄py₂] (0.300 g, 0.435 mmol) in chloroform (20 mL). After stirring for 1 day in the dark, the yellow solution was concentrated, and the white complex was crystallized by adding *n*-pentane. Yield: 70%. ¹H NMR (CD₃NO₂, CH₃NO₂ as internal standard): 8.32 (J_{Pt-H} = 27 Hz) (d, H-2,H-6 of py), 4.55 (m, =CH), 3.74 (s, NCMe), 3.71 (s, NCMe), 1.53 (50) (d, MeCH=), 0.82 (44) (d, MeCH=).

Synthesis of 2b, 2c, 2d, and 4c. The complex *cis*-[PtCl₂(L)(ethylene)] was treated as reported above. After filtration of AgCl and addition of the N-N ligand to the clear solution, the solvent was removed under vacuum. The residue was extracted with dichloromethane and the pale yellow product crystallized by slow addition of diethyl ether. Yield: 70–80%.

Table V. Crystal Data and Experimental Details for [PtCl(py)(dmphen)(ethylene)](CF₃SO₃)

formula	C ₂₂ H ₂₁ ClF ₃ N ₃ O ₃ PtS
M _r , g mol ⁻¹	695.024
cryst syst	orthorhombic
space group	Pbca (No. 61)
a, Å	12.808 (5)
b, Å	18.744 (4)
c, Å	19.445 (3)
V, Å ³	4668 (2)
Z	8
d _{calcd} , g cm ⁻³	1.98
μ(Mo Kα), cm ⁻¹	63.3
F(000)	2688
cryst size, mm	0.23 × 0.33 × 0.13
transm factor range	0.59–1.00
scan mode	ω
θ range, deg	2–27
collected octants	+h,+k,+l
measd rflns	5634
scan width, deg	0.8 (+0.35 tan θ)
prescan speed, deg min ⁻¹	8
prescan acceptance σ(I)/I	0.5
max scan time, s	100
required counting σ(I)/I	0.01
no. of data used [I > 2σ(I)]	3756
no. of params refined	223
R, R _w	0.025, 0.027
k, g ^a	0.80, 1 × 10 ⁻³
quality-of-fit indicator ^b	0.78

^aThe weighting scheme employed was $w = k/[\sigma^2(F) + gF^2]$, where both k and g were independently determined. ^b $[\sum w(F_o - F_c)^2 / (N_{obs} - N_{par})]^{0.5}$.

Table VI. Fractional Atomic Coordinates for [PtCl(py)(dmphen)(ethylene)](CF₃SO₃)

	x	y	z
Pt	0.08456 (2)	0.78089 (1)	0.92466 (1)
Cl	-0.0829 (1)	0.8089 (1)	0.9585 (1)
N1	0.1450 (3)	0.8556 (2)	1.0050 (2)
N2	0.1086 (3)	0.7136 (2)	1.0179 (2)
C1	0.1501 (5)	0.9265 (3)	0.9990 (3)
C2	0.1931 (6)	0.9670 (3)	1.0538 (4)
C3	0.2265 (5)	0.9357 (3)	1.1120 (4)
C4	0.2200 (4)	0.8606 (3)	1.1189 (3)
C5	0.2527 (5)	0.8232 (4)	1.1794 (3)
C6	0.2398 (5)	0.7518 (4)	1.1845 (3)
C7	0.1915 (4)	0.7123 (3)	1.1300 (3)
C8	0.1708 (5)	0.6383 (3)	1.1341 (3)
C9	0.1155 (5)	0.6062 (3)	1.0829 (3)
C10	0.0816 (5)	0.6445 (3)	1.0251 (3)
C11	0.1583 (4)	0.7471 (3)	1.0703 (3)
C12	0.1774 (4)	0.8232 (3)	1.0638 (2)
C13	0.0143 (6)	0.6102 (3)	0.9718 (3)
C14	0.1119 (6)	0.9610 (4)	0.9352 (3)
C15	0.0495 (5)	0.8142 (4)	0.8255 (3)
H13	-0.010 (3)	0.847 (4)	0.822 (3)
H14	0.112 (3)	0.828 (4)	0.798 (3)
C16	0.0310 (5)	0.7408 (4)	0.8319 (3)
H15	-0.040 (2)	0.7196 (3)	0.832 (4)
H16	0.083 (3)	0.714 (3)	0.804 (3)
N3	0.2309 (3)	0.7545 (2)	0.8942 (2)
C17	0.2605 (5)	0.6862 (3)	0.8850 (3)
C18	0.3551 (5)	0.6667 (3)	0.8611 (3)
C19	0.4271 (4)	0.7194 (3)	0.8437 (3)
C20	0.3996 (4)	0.7900 (3)	0.8533 (3)
C21	0.3018 (4)	0.8070 (3)	0.8790 (3)
S	0.1434 (1)	0.49136 (9)	0.80078 (9)
O1	0.1795 (4)	0.4349 (2)	0.7562 (2)
O2	0.1166 (4)	0.4691 (2)	0.8691 (2)
O3	0.2030 (4)	0.5552 (2)	0.7965 (3)
C22	0.0199 (6)	0.5163 (3)	0.7647 (3)
F1	-0.0282 (4)	0.5661 (2)	0.8004 (3)
F2	-0.0472 (4)	0.4624 (2)	0.7625 (2)
F3	0.0280 (4)	0.5403 (3)	0.7006 (2)

Synthesis of [PtCl(4-Mepy)(bpy)](BF₄) and [PtCl(4-Mepy)(phen)](BF₄). The complex 4c (0.050 g, 0.084 mmol) was

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dissolved in nitromethane (5 mL). After 10 days, the solvent was removed under vacuum and the complex [PtCl(4-Mepy)-(bpy)](BF₄) crystallized from CH₂Cl₂/Et₂O (yield: 70%). Selected ¹H NMR data (in CD₃NO₂, CH₃NO₂ as internal standard: 9.48 (d, 1 H), 8.71 (d, H-2,H-6 of Mepy), 7.59 (d, H-3,H-5 of Mepy), 2.60 (s, Mepy). Anal. Calcd for C₁₆H₁₅BClF₄N₃Pt: C, 33.91; H, 2.67; N, 7.42. Found: C, 33.61; H, 2.71; N, 7.21.

By a similar procedure, [PtCl(4-Mepy)(phen)](BF₄) was obtained starting from 2c. Selected ¹H NMR data (in CD₃NO₂, CH₃NO₂ as internal standard): 9.62 (d, 1 H), 8.74 (d, H-2,H-6 of Mepy), 7.64 (d, H-3,H-5 of Mepy), 2.64 (s, Mepy).

Synthesis of [PtCl(4-Mepy)(dmphen)](BF₄). To a stirred solution of the complex [PtCl₂(dmphen)] (0.030 g, 0.063 mmol) in chloroform (10 mL) was added 0.012 g (0.15 mmol) of 4-Mepy. After 2 h was added at 0 °C the stoichiometric amount of AgBF₄ (0.012 g) dissolved in acetone (1.2 mL). After 20 min the suspension was filtered through a thin layer of Celite and the solvent removed under vacuum. The resulting solid was extracted with dichloromethane, and the product precipitated as a white solid by adding diethyl ether (yield: 65%). ¹H NMR (CD₃NO₂, CH₃NO₂ as internal standard): 8.73 (d, 1 H), 8.67 (d, 1 H), 8.30 (d, H-2,H-6 of Mepy), 8.12 (s, 2 H), 7.85 (d, 1 H), 7.73 (d, 1 H), 7.51 (d, H-3,H-5 of Mepy), 3.30 (s, NCMe), 2.58 (s, NCMe), 2.12 (s, 4-Mepy). Anal. Calcd for C₂₀H₁₉BClF₄N₃Pt: C, 38.82; H, 3.10; N, 6.79. Found: C, 38.83; H, 3.18; N, 6.73.

X-ray Structure Determination of [PtCl(C₂H₄)(C₁₄H₁₂N₂)(NC₆H₅)](CF₃SO₃). Crystals suitable for X-ray analysis were obtained with the following procedure. A solution of AgCF₃SO₃ (0.068 g, 0.27 mmol) in methyl cyanide (5 mL) was added dropwise under nitrogen to the complex *cis*-[PtCl₂(py)(ethylene)] (0.100 g, 0.27 mmol) dissolved in 20 mL of a 1:1 mixture of CH₂Cl₂/MeCN. After 15 min of stirring at 0 °C the suspension was filtered through a thin layer of Celite and the N-N ligand added to the clear filtrate. The volume of the solution was concentrated to 5 mL, and 1 mL of diethyl ether was added dropwise, producing white crystals, which were isolated after 24 h.

Single-crystal X-ray diffraction data were measured at room temperature on an Enraf-Nonius CAD4 diffractometer. The measured intensities were corrected for crystal decay and reduced to *F*₀ values. Crystal data and experimental details are summarized in Table V. The structure was solved by direct and Fourier methods¹¹ and refined by full matrix least-squares calculations. An absorption correction was applied after convergence of the isotropic refinement according to the empirical method by Walker and Stewart.¹²

Anisotropic thermal parameters were used for all non-hydrogen atoms. Aromatic hydrogen atoms were positioned at calculated positions and refined with fixed geometry with respect to their carrier atoms (C-H 1.08 Å). The positions of the hydrogen atoms of the ethylene molecule were found experimentally and refined under the constraints of equal C-H bonds and H...H contacts [C-H_{av}, 0.99 (5) Å]. A final difference-Fourier map gave peaks of residual electron density not exceeding 0.8 e Å⁻³. Fractional positional parameters for the refined atoms are listed in Table VI.

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Supplementary Material Available: Lists of hydrogen positions and anisotropic thermal parameters (3 pages). Ordering information is given on any current masthead page.

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Carbon–Carbon Bond Formation in Cationic Aryl–Olefin–Platinum(II) Complexes

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Cationic five-coordinate [Pt(3-R¹-4-R²-C₆H₃)(MeCN)(6-Me-py-2-CH=NPh)(C₂H₄)]⁺ complexes (R¹, R² = H, Me, OMe) undergo an unexpected rearrangement at 0 °C in chloroform solution, affording, after treatment with aqueous LiCl, the neutral four-coordinate species [Pt(2-Et-4-R¹-5-R²-C₆H₂)Cl(6-Me-py-2-CH=NPh)]. Pt–C_{aryl} bond breaking and making is involved in the whole process, resulting in a 1,2-shift of the platinum atom to an adjacent position of the benzene ring. The same compound is obtained, together with products deriving from a typical insertion, when an equimolar amount of ethylene is added to a chloroform solution of [Pt(3-R¹-4-R²-C₆H₃)(MeCN)(6-Me-py-2-CH=NPh)]⁺ at 0 °C. When higher (>3) ethylene/Pt ratios are used, only the five-coordinate [Pt(3-R¹-4-R²-C₆H₃CH₂CH₂)Cl(6-Me-py-2-CH=NPh)(C₂H₄)] complex is isolated. As the experimental data rule out the possibility of a (2-arylethyl)platinum to (2-ethylaryl)platinum rearrangement, different reaction paths are suggested for the two processes. When the two reactions are combined in a "one-pot" sequence, a regiocontrolled double alkylation of the aryl system can be obtained. The behavior of substrates containing bidentate nitrogen ligands having different five-coordination stabilizing effects is examined, and data concerning the reactions of propene and styrene are reported.

Introduction

One of the most fascinating topics in organometallic chemistry, for both theoretical and experimental reasons, concerns the insertion of a π-coordinated alkene into a cis metal-bound hydrocarbyl group.¹ Scarce examples of such

reactions are found in platinum(II) chemistry, however,² and several stable *cis* hydrocarbyl olefin complexes are

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