Synthesis, Characterization, and Reactions of Platinum and Rhodium Complexes of the Hybrid Phosphorus–Nitrogen Ligand $4\text{-}CH_3C_6H_4C[N(SiMe_3)](NPPh_2)$: X-ray Structures of $[ML_2(PPh_2NHC(4\text{-}CH_3C_6H_4)NH)]X$ (M = Pt, X = Cl; M = Rh, X = BF_4)

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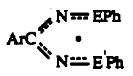
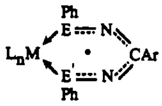
The reaction of $4\text{-}CH_3C_6H_4C[N(SiMe_3)_2](NPPh_2)$ with $[Pt(PEt_3)Cl_2]_2$ or $[Rh(cod)Cl]_2$ in a 2:1 molar ratio in THF produces the monodentate complexes *trans*-$Pt(PEt_3)[PPh_2NC(4\text{-}CH_3C_6H_4)N(SiMe_3)_2]Cl_2$ (**4a**) and $Rh(cod)[PPh_2NC(4\text{-}CH_3C_6H_4)N(SiMe_3)_2]Cl$ (**4b**), which were characterized by ^1H and ^{31}P NMR spectroscopy. The reaction of **4a** with PhSeCl in a 1:2 molar ratio yields $Pt(PEt_3)Cl[PPh_2NHC(4\text{-}CH_3C_6H_4)NH]Cl$ (**5**), which was identified by ^1H and ^{31}P NMR spectroscopy and by X-ray crystallography. This complex crytallizes in the space group $P\bar{1}$ with $a = 11.840(1)$ Å, $b = 14.523(8)$ Å, $c = 10.081(3)$ Å, $\alpha = 107.93(3)°$, $\beta = 90.00(2)°$, $\gamma = 87.60(2)°$, $Z = 2$, and $R = 0.044$ for 2950 observed reflections. The $PPh_2NHC(4\text{-}CH_3C_6H_4)NH$ ligand in **5** is chelated via phosphorus and nitrogen to platinum with the PPh_2 and PEt_3 groups in *cis* positions and hydrogen-bonding [d(H(N)–Cl) = 2.20 Å] between the NH group attached to phosphorus and the chloride counterion. By contrast, the ^1H–^{15}N HMQC spectra of **5** indicate that *in solution* the other NH group ($\delta(^1H) = 12.73$ ppm) is involved in strong hydrogen-bonding with the chloride counterion. The decomposition of **4a** in boiling THF also yields **5**. Possible pathways for the formation of **5** by these two different routes are discussed. The reaction of $4\text{-}CH_3C_6H_4C[N(SiMe_3)_2](NPPh_2)$ with $[Rh(cod)Cl]_2$ in acetone in the presence of $NaBF_4$ produces $[Rh(cod)(PPh_2NHC(4\text{-}CH_3C_6H_4)NH)]BF_4$ (**8**), which was characterized by ^1H and ^{31}P NMR spectra and by X-ray crystallography. The crystals of **8** are triclinic, space group $P\bar{1}$, with $a = 13.844(6)$ Å, $b = 14.236(7)$ Å, $c = 9.156(5)$ Å, $\alpha = 99.08(4)°$, $\beta = 105.08(4)°$, $\gamma = 68.84(3)°$ $Z - 2$, and $R = 0.074$ for 2929 observed reflections. The $PPh_2NHC(4\text{-}CH_3C_6H_4)NH$ ligand in **8** is chelated to rhodium in a fashion similar to that observed for **5**. The reaction of $4\text{-}CH_3C_6H_4C[N(SiMe_3)_2](NPPh_2)$ with $[Rh(CO)_2Cl]_2$ in a 2:1 molar ratio in THF produces $Rh(CO)[PPh_2NHC(4\text{-}CH_3C_5H_4)NH]Cl$ identified by ^1H, ^{13}C, and ^{31}P NMR and IR spectroscopic data.

Introduction

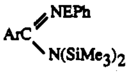
Recently we reported the unexpected formation of the resonance-stabilized radicals $ArCN_2(EPh)_2^{\bullet}$ (Ar = aryl; E = S, Se), **1a**.[1] These radicals are generated by the reaction of $Ar[N(SiMe_3)_2][NSiMe_3]$ with PhECl in a 1:3 molar ratio and are remarkably persistent at room temperature, but nitrogen-centered dimerization occurs within several hours to give the diazenes *trans*-ArENC(Ph)N=NC(Ph)NEAr.[1] However, preliminary attempts to trap **1a** as the corresponding metal complexes **2a**, e.g. by generation of **1a** in the presence of $PtCl_2(PhCN)_2$ or $[Rh(CO)_2Cl]_2$, were unsuccessful. Consequently, we adopted an alternative strategy involving the coordination of the ligands **3a**[1b] to a metal prior to radical formation. The preparation of such metal complexes did not proceed cleanly, so we turned our attention to the generation of the related hybrid radical $ArCN_2(PPh_2)(E'Ph)$ (**1b**) as the corresponding metal complexes **2b**. The synthesis of the ligand **3b** was first reported by Roesky and co-workers[2] in 1988; however, only one report had since appeared concerning its reactions with transitions metals.[3] This paper describes some coordination chemistry of the *N*-(diphenylphosphino-*N'*,*N'*-bis(trimethylsilyl)benzamidine ligand **3c** with the platinum group metals, and the results of our efforts to generate complexes of the type **2b**.



1a E = E' = S, Se
1b E = PPh, E' = S, Se



2a E = E' = S, Se
2b E = PPh, E' = S, Se



3a E = S, Se
3b E = PPh, Ar = Ph
3c E = PPh, Ar = $4\text{-}CH_3C_6H_4$

Experimental Section

Reagents and General Procedures. All reactions and manipulations were performed under an atmosphere of dry argon gas using standard Schlenk techniques. All solvents were dried and distilled before use: THF, hexanes, diethyl ether (sodium benzophenone), CH_2Cl_2 (P_2O_5), and acetone (CaH_2). The compounds $[PtCl_2(PEt_3)]_2$,[4] $[Rh(cod)Cl]_2$,[5] and PhSCl[6] were prepared according to the published procedure. $[Rh(CO)_2Cl]_2$, *n*-BuLi, $HN(SiMe_3)_2$, $4\text{-}CH_3C_6H_4CN$, chlorodiphenylphosphine, and PhSeCl (Aldrich) were used as received. The elemental analyses were performed by the microanalytical service within the Chemistry Department at The University of Calgary.

Instrumentation. Infrared spectra were recorded as solutions (KBr solution cell) or Nujol mulls (KBr plates) on a Nicolet DX-5 FTIR spectrometer. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AM-400 spectrometer operating at 161.978 MHz in THF. A D_2O insert was used as the lock for the phosphorus-31 spectra. Routine proton and carbon-13 NMR spectra were run on a Bruker AC-200 at 200.132 and 50.323 MHz, respectively. The solvent deuterium resonance served as the lock for both nuclei. Phosphorus-31 chemical shifts are reported in ppm relative to 85% H_3PO_4; proton and carbon-13 chemical shifts are reported in ppm relative to the residual protonated solvent. The 2D

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^{1}H–^{15}N HMQC[7] (heteronuclear multiple quantum coherence) spectra were obtained on a Bruker AMX-500 spectrometer as described previously.[8] A standard four-pulse-HMQC sequence was used.[7] The ^{15}N-decoupled HMQC spectra were acquired using GARP. The proton and nitrogen resonance frequencies were 500.139 and 50.693 MHz, respectively. Chemical shifts were referenced to internal tetramethylsilane (^{1}H) and external nitromethane (^{15}N).

Preparations. (a) 4-$CH_3C_6H_4C[N(SiMe_3)_2][NPPh_2]$ (3c). $HN(SiMe_3)_2$ (20.8 mL, 0.1 mol) in Et_2O (50 mL) was added dropwise at 0 °C to a solution of *n*-BuLi (40 mL of a 2.5 M solution in hexanes, 0.1 mol) in 100 mL of Et_2O. The solution was allowed to warm to room temperature and stirred for 30 min. 4-$CH_3C_6H_4CN$ (12.0 mL, 0.1 mol) was added dropwise to the above solution of $LiN(SiMe_3)_2$. The reaction mixture was stirred for 2 h at ambient temperature and then cooled to −78 °C. Chlorodiphenylphosphine (22.1 g, 18.0 mL, 0.1 mol) in THF (50 mL) was added dropwise, and the reaction mixture was stirred and allowed to warm to room temperature. The solvent was removed under vacuum, the residue was extracted with CH_2Cl_2 (50 mL), and the extract was filtered through Celite to remove LiCl. The filtrate was evaporated to dryness and the residue recrystallized from CH_2Cl_2/hexanes (1:5) giving **3c** as a yellow solid in 75% yield. Anal. Calcd for $C_{26}H_{35}N_2PSi_2$: C, 67.49; H, 7.62; N, 6.06. Found: C, 67.37; H, 7.31; N, 5.95. ^{1}H NMR ($CDCl_3$): 0.13 (s, Me_3Si, 18H), 2.39 (s, $CH_3C_6H_4$, 3H), 7.13–7.66 (m, C_6H_5 and $CH_3C_6H_4$, 14H).

(b) *trans*-$Pt(PEt_3)(PPh_2NC(4\text{-}CH_3C_6H_4)N(SiMe_3)_2)Cl_2$ (4a). A solution of **3c** (0.12 g, 0.26 mmol) in THF (20 mL) was added dropwise to a THF (or CH_2Cl_2) solution (20 mL) of $[Pt(PEt_3)Cl_2]_2$ (0.10 g, 0.13 mmol) at 0 °C. The resultant pale yellow solution was allowed to warm to ambient temperature and stirred for 1 h. The solvent was evaporated to dryness and the pale yellow residue recrystallized from THF/pentane at −18 °C; yield 62%. Anal. Calcd for $C_{32}H_{50}N_2Cl_2P_2PtSi_2$: C, 45.38; H, 5.95; N, 3.31. Found: C, 44.29; H, 5.88; N, 3.26. ^{1}H NMR ($CDCl_3$): 0.15 (s, Me_3Si, 18H), 1.16 (dt, PCH_2CH_3, 9H), 1.81 (m, PCH_2CH_3, 6H), 2.31 (s, $CH_3C_6H_4$, 3H), 7.00–7.75 (m, C_6H_5 and $CH_3C_6H_4$, 14H).

(c) $Rh(cod)(PPh_2NC(4\text{-}CH_3C_6H_4)N(SiMe_3)_2)Cl$ (4b). This was prepared in THF (or CH_2Cl_2) by using a procedure similar to that described for the synthesis of **4a**. The residue was recrystallized from CH_3CN, giving **4b** as an orange microcrystalline product in 45% yield. Anal. Calcd for $C_{32}H_{47}N_2ClPRhSi_2$: C, 57.58; H, 6.68; N, 3.95. Found: C, 56.32; H, 6.42; N, 3.92. ^{1}H NMR ($CDCl_3$): 0.15 (s, Me_3Si, 18H), 2.30 (m, $CH_3C_6H_4$ and aliphatic cod CH_2, 11H), 3.50 (s, br, olefinic cod CH, 2H), 5.40 (s, br, olefinic cod CH, 2H), 7.24–7.71 (m, C_5H_5 and $CH_3C_6H_4$, 14H).

(d) *cis*-$[Pt(PEt_3)Cl(PPh_2NHC(C_6H_4CH_3)NH)]Cl$ (5). A solution of **3c** (0.12 g, 0.26 mmol) in THF (20 mL) was added dropwise to a THF solution (20 mL) of $[Pt(PEt_3)Cl_2]_2$ (0.10 g, 0.13 mmol) at 0 °C. The resultant pale yellow solution was allowed to warm to ambient temperature and then gently refluxed for 2–3 h. The solvent was evaporated to dryness and the pale yellow residue recrystallized from THF at ambient temperature, giving colorless crystals of **5**·0.5THF in 42% yield. Anal. Calcd for $C_{28}H_{38}H_2ClO_{0.5}P_2Pt$: C, 45.53; H, 5.19; N, 3.79. Found: C, 44.77; H, 5.10; N, 3.64. IR (Nujol): ν_{NH} 3393, 3324 cm^{-1}. ^{1}H NMR ($CDCl_3$): 0.94 (dt, PCH_2CH_3, 9H), 1.62–1.92 (m, PCH_2CH_3, C_4H_8O, 8H), 2.35 (s, $CH_3C_6H_4$, 3H), 3.73 (m, C_4H_8O, 2H), 7.40 (s, PNH, 0.80H), 7.25–8.19 (m, C_6H_5 and $CH_3C_6H_4$, 14H), 12.73 (s, PtNH, 0.75H, ^2J(Pt–H) = 46 Hz).

(e) $[Rh(cod)(PPh_2NHC(4\text{-}CH_3C_6H_4)NH)]BF_4$ (6). A solution of **3c** (0.28 g, 0.608 mmol) in acetone (15 mL) was added dropwise to an acetone solution (15 mL) of $[Rh(cod)Cl_2]_2$ (0.15 g, 0.304 mmol) in the presence of $NaBF_4$ (0.067 g, 0.608 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 3–4 h. After such time, a cloudy precipitate (NaCl) was observed. The solvent was evaporated to dryness and the orange residue extracted with acetone (15 mL). An equivalent volume of Et_2O was gently layered into the solution and the mixture allowed to stand undisturbed at ambient temperature for several days, giving orange crystals of **6** in 35% yield. Anal. Calcd for $C_{28}H_{31}N_2BF_4PRh$: C, 54.57; H, 5.07; N, 4.55. Found: C, 50.99; H, 4.75; N, 4.55.[9] IR (CH_2Cl_2 solution): ν_{NH} 3394, 3323 cm^{-1}; ν_{BF} 1056 cm^{-1}. ^{1}H NMR (acetone-d_6): 2.40 (s, $CH_3C_6H_4$ and aliphatic cod CH_2, 11 H), 4.16 (s, br, olefinic cod CH, 2H), 5.91 (s, br, olefinic CH, 2H), 7.36–7.89 (m, C_6H_5 and $CH_3C_6H_4$, 14H), 8.65 (s, br, NH, 1.1H), 9.12 (s, br, NH, 0.7H).

Table I. Crystallographic Data for *cis*-$[Pt(PEt_3)(PPh_2NHC(4\text{-}CH_3C_6H_4)NH)Cl]Cl\cdot THF$ (**5**·**THF**) and $[Rh(cod)(PPh_2NHC(4\text{-}CH_3C_6H_4)NH)]BF_4\cdot(CH_3)_2CO$ (**6**·$(CH_3)_2CO$)

formula	$C_{30}H_{42}N_2OP)_2Cl_2Pt$	$C_{31}H_{37}BF_4N_2OP_2Rh$
fw	774.62	674.33
space group	$P\bar{1}$	$P\bar{1}$
a, Å	11.840(1)	13.844(6)
b, Å	14.523(8)	14.236(7)
c, Å	10.081(3)	9.156(5)
α, deg	107.93(3)	99.08(4)
β, deg	90.00(2)	105.08(4)
γ, deg	87.60(2)	68.84(3)
V, Å^3	1647.7(9)	1620(1)
T, °C	23	−103
λ, Å	0.710 69	0.710 69
ρ_{calcd}, g cm^{-1}	1.807	1.382
μ, mm^{-1}	4.525	0.624
R^a	0.044	0.074
$R_w{}^b$	0.045	0.082

^{a} $R = \sum\|F_o| - |F_c\|/\sum|F_o|$. ^{b} $R_w = [\sum w\delta^2/\sum wF_o{}^2]^{1/2}$.

(f) $Rh(CO)(PPh_2NHC(4\text{-}CH_3C_6H_4)NH)Cl$ (8). A solution of **3c** (0.24 g, 0.514 mmol) in THF (20 mL) was added dropwise to a THF solution (15 mL) of $[Rh(CO)_2Cl]_2$ (0.10 g, 0.257 mmol) at −78 °C. The solution was allowed to warm to room temperature, stirred for 30 min, and reduced in volume to approximately 10 mL. Upon continued stirring under a steady stream of argon gas, a pale yellow precipitate was isolated from the solution, giving **8**·THF in 45% yield. Anal. Calcd for $C_{25}H_{27}N_2O_2PRhCl$: C, 53.93; H, 4.89; N, 5.03. Found: C, 53.11; H, 4.82; N, 5.04. IR (CH_2Cl_2 solution): ν_{CO} 1991 cm^{-1}. IR (Nujol): ν_{CO} 1979 cm^{-1}; ν_{NH} 3279, 3172 cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.34 (s, $CH_3C_6H_4$, 3H), 6.80 (s, NH, 1H), 7.19–7.886 (m, NH, C_6H_5 and $CH_3C_6H_4$, 15H). ^{13}C NMR ($CDCl_3$): 189.4 (dd, CO, ^1J(Rh–C) = 68 Hz, ^2J(C–P) = 17 Hz).

X-ray Analyses. (a) 5. A suitable colorless crystal of *cis*-$[Pt(PEt_3)Cl(PPh_2NHC(C_6H_4CH_3)NH)]Cl\cdot THF$ (**5**·**THF**) was obtained by recrystallization from THF at ambient temperature. Accurate cell dimensions and a crystal orientation matrix were determined on a Rigaku AFC6S diffractometer by a least-squares fit of the setting angles of 15 reflections with 2θ in the range 20–25°. Intensity data were collected by the $\omega/2\theta$ method using a scan speed of 4.0°/min, scan width of $(1.05 + 0.35 \tan\theta)°$, and monochromatized Mo Kα radiation in the range $2 < 2\theta < 50°$ with $h = -13$ to 13, $k = -10$ to 10, and $l = 0$ to 11. Three reflections were monitored every 100 min of exposure time and showed insignificant variations. The intensities of 6139 reflections were measured, of which 2950 had $I > 3\sigma(I)$. Data were corrected for Lorentz, polarization, and absorption effects,[10] the correction range being 0.642–0.989. Crystal data are given in Table I, and the positional parameters are given in Table II.

The structure was solved by the heavy-atom method. Refinement of the structure was by full-matrix least-squares calculations, initially with isotropic and finally with anisotropic temperature factors for the non-hydrogen atoms. At an intermediate stage in the refinement, a difference map revealed maxima consistent with the positions of hydrogen atoms which were included in the subsequent cycles of refinement at idealized positions (C–H and N–H = 0.95 Å) with fixed isotropic temperature factors. Refinement converged with $R = 0.044$ and $R_w = 0.045$. In the refinement cycles, weights were derived from the counting statistics. Scattering factors were those of Cromer and Waber[11] and Stewart, Davidson, and Simpson,[12] and allowance was made for anomalous dispersion.[13] A difference map calculated at the conclusion of the refinement had no chemically significant features. The computer

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Table II. Final Fractional Coordinates (×10^4) and Equivalent Isotropic Temperature Factors, B_{eq} (Å^2 × 10^3), with Esd's in Parentheses for *cis*-[Pt(PEt$_3$)(PPh$_2$NHC(4-CH$_3$C$_6$H$_4$)NH)Cl]-Cl·THF (**5**·THF)

atom	*x*	*y*	*z*	B_{eq}
Pt(1)	8098(1)	1975(1)	4879(1)	44(1)
Cl(1)	9197(3)	1394(4)	6384(5)	105(3)
Cl(2)	3476(3)	2248(3)	2555(4)	56(2)
P(1)	6784(3)	2364(2)	3563(3)	40(2)
P(2)	9714(3)	2342(3)	3981(4)	50(2)
N(1)	5593(8)	2050(8)	4214(9)	44(7)
N(2)	6705(9)	1650(9)	5801(11)	65(8)
C(1)	6527(10)	3628(9)	3683(12)	41(7)
C(2)	5856(11)	3917(10)	2795(14)	59(9)
C(3)	5629(13)	4910(12)	3012(19)	82(12)
C(4)	6140(15)	5569(11)	4096(19)	75(12)
C(5)	6802(13)	5296(10)	5017(17)	65(11)
C(6)	7010(11)	4310(10)	4814(14)	51(9)
C(7)	6764(10)	1654(10)	1734(12)	43(8)
C(8)	6425(13)	745(10)	1360(16)	63(10)
C(9)	6509(14)	157(11)	−34(17)	68(11)
C(10)	6999(12)	487(13)	−1007(15)	62(10)
C(11)	7359(11)	1416(14)	−630(15)	72(11)
C(12)	7231(11)	1995(10)	752(12)	52(8)
C(13)	5682(9)	1782(10)	5403(13)	51(8)
C(14)	4675(10)	1638(9)	6143(12)	45(8)
C(15)	4677(11)	1936(11)	7592(14)	65(10)
C(16)	3770(12)	1851(12)	8382(16)	76(11)
C(17)	2803(11)	1464(13)	7696(17)	86(12)
C(18)	2799(12)	1174(12)	6288(18)	82(11)
C(19)	3702(10)	1265(11)	5477(16)	67(10)
C(20)	1772(14)	1424(16)	8574(20)	124(16)
C(21)	10673(12)	2995(12)	5292(16)	74(11)
C(22)	10241(18)	3937(15)	6199(21)	123(18)
C(23)	10558(11)	1270(12)	3045(16)	73(10)
C(24)	10067(15)	709(13)	1693(19)	100(15)
C(25)	9545(12)	3089(12)	2856(15)	78(11)
C(26)	10628(12)	3409(13)	2297(17)	90(12)
THF Solvate: Coordinates (×10^3) and B_{eq} (×10^2)				
O(1)	309(4)	530(4)	133(5)	37(5)
C(27)	263(5)	595(2)	93(4)	19(4)
C(28)	184(3)	547(4)	−17(5)	25(4)
C(29)	210(4)	447(3)	−37(3)	25(4)
C(30)	310(3)	444(3)	49(5)	19(4)

programs used for data processing were part of TEXSAN[14] installed on a Silicon Graphics Personal Iris 4D/35 computer. The structure was solved and refined using the program SHELX76[15], and Figure 1 was plotted using ORTEP II.[16]

(b) **6.** A suitable colorless crystal of [Rh(cod)(PPh$_2$NHC(4-CH$_3$C$_6$H$_4$)NH)]BF$_4$·(CH$_3$)$_2$CO (**6**·(CH$_3$)$_2$CO) was obtained by recrystallization from acetone/diethyl ether at ambient temperature. Accurate cell dimensions and a crystal orientation matrix were determined on a Rigaku AFC6S diffractometer by a least-squares fit of the setting angles of 18 reflections with 2θ in the range 20–29°. Intensity data were collected by the $\omega/2\theta$ method using a scan speed of 4.0°/min, scan width of (1.52 + 0.35 tan θ)°, and monochromatized Mo Kα radiation in the range $2 < 2\theta < 50°$ with $h = -14$, $k = -11$ to 11, and $l = 0$ to 10. Three reflections were monitored every 100 min of exposure time and showed insignificant variations. The intensities of 5987 reflections were measured, of which 2929 had $I > 3\sigma(I)$. Data were corrected for Lorentz effects, as described previously for **5**, the correction range being 0.861–0.999. Crystal data are given in Table I, while the positional parameters are given in Table III.

The structure was solved in a manner analogous to that for **5**. The BF$_4^-$ anion was disordered with boron located over two sites and the four fluorine atoms distributed over five sites; the site occupancy factors for the fluorine atoms were allowed to refine. The acetone solvate and cylooctadiene carbon atoms show large thermal vibrations, reflecting disorder. Refinement converged with $R = 0.074$ and $R_w = 0.082$. Figure 3 was plotted using ORTEP II.[15]

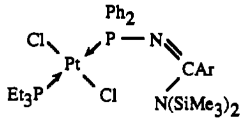
Table III. Final Fractional Coordinates (×10^4) and Equivalent Isotropic Temperature Factors, B_{eq} (Å^2, × 10^3), with Esd's in Parentheses for [Rh(cod)(PPh$_2$NHC(4-CH$_3$C$_6$H$_4$)NH)]-BF$_4$·(CH$_3$)$_2$CO (**6**·(CH$_3$)$_2$CO)

atom	*x*	*y*	*z*	B_{eq}	sof
Rh	3138(1)	3404(1)	4982(1)	55(1)	
P(1)	2143(2)	2482(2)	5059(4)	34(1)	
N(1)	3084(6)	1423(6)	5832(10)	34(5)	
N(2)	4277(7)	2261(7)	6247(13)	48(6)	
C(1)	1369(5)	2017(4)	3416(8)	31(6)	
C(2)	380(5)	2681(4)	2758(8)	41(7)	
C(3)	−236(5)	2366(4)	1445(8)	56(8)	
C(4)	137(5)	1387(4)	790(8)	69(9)	
C(5)	1125(5)	723(4)	1447(8)	56(8)	
C(6)	1741(6)	1038(6)	2760(9)	37(8)	
C(7)	1257(6)	2963(6)	6356(9)	34(6)	
C(8)	583(6)	2455(6)	6448(9)	51(8)	
C(9)	−23(6)	2777(6)	7549(9)	65(10)	
C(10)	45(6)	3607(6)	8557(9)	70(12)	
C(11)	718(6)	4114(6)	8464(9)	84(14)	
C(12)	1324(6)	3792(6)	7364(9)	60(9)	
C(13)	4086(8)	1472(8)	6447(13)	33(6)	
C(14)	4864(5)	623(4)	7331(8)	34(6)	
C(15)	5554(5)	820(4)	8657(8)	40(7)	
C(16)	6295(5)	25(4)	9492(8)	43(7)	
C(17)	6346(5)	−968(4)	9001(8)	43(7)	
C(18)	5657(5)	−1165(4)	7676(8)	43(7)	
C(19)	4916(5)	−369(4)	6840(8)	39(6)	
C(20)	7125(11)	−1820(11)	9916(16)	62(9)	
C(21)	2156(10)	4309(11)	3151(23)	70(10)	
C(22)	1849(9)	4778(10)	4388(23)	64(10)	
C(23)	2158(12)	5646(11)	5223(27)	103(13)	
C(24)	3259(14)	5555(12)	5564(40)	205(24)	
C(25)	4061(12)	4460(12)	5536(30)	104(15)	
C(26)	4345(14)	3896(16)	4390(28)	107(15)	
C(27)	3947(13)	4183(19)	2780(31)	186(23)	
C(28)	2799(11)	4562(13)	2274(22)	104(12)	
Acetone Solvate and BF$_4$ Ion: Coordinates and B_{eq} (×10^3)					
O	217(1)	6(1)	647(1)	67(6)	
C(29)	105(4)	−69(4)	669(6)	416(34)[a]	
C(30)	203(1)	−71(1)	642(2)	79(11)	
C(31)	271(4)	−163(4)	653(6)	396(31)[a]	
B(1)	718(1)	211(1)	750(2)	69(9)[a]	0.50
B(2)	706(1)	260(1)	842(2)	81(11)[a]	0.50
F(1)	751(1)	182(1)	905(2)	147(14)	0.91(4)
F(2)	618(1)	289(1)	759(2)	126(12)	0.88(3)
F(3)	694(2)	128(2)	649(2)	303(41)	0.75(5)
F(4)	756(2)	318(2)	865(4)	443(51)	0.85(6)
F(5)	822(2)	187(3)	724(3)	525(99)	0.72(9)

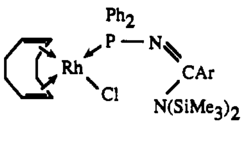
[a] Atoms allowed isotropic thermal vibrations.

Results and Discussion

Synthesis of ML$_2$(PPh$_2$NC(4-CH$_3$C$_6$H$_4$)N(SiMe$_3$)Cl (4a, M = Pt; 4b, M = Rh). The reaction of 2 molar equiv of **3c** with [Pt(PEt$_3$)Cl$_2$]$_2$ or [Rh(cod)Cl]$_2$ in THF or CH$_2$Cl$_2$ at 0 °C produces the monodentate metal–phosphine complexes **4a,b** as



4a Ar = 4-CH$_3$C$_6$H$_4$



4b Ar = 4-CH$_3$C$_6$H$_4$

air-stable solids. Both reactions were monitored by ^{31}P{^{1}H} NMR spectroscopy and were observed to proceed very cleanly. The products have been characterized by microanalysis and by ^{31}P{^{1}H} and ^{1}H NMR spectroscopy. ^{31}P NMR data are given in Table IV.

The ^{31}P NMR spectrum of **4a** in THF solution shows two doublets at 44.7 and 12.6 ppm, each with ^{195}Pt satellites. These resonances can be assigned to the PPh$_2$ and PEt$_3$ groups, respectively. The ^2J(P–P) value of 497 Hz indicates that the

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(14) *TEXSAN*: *Single Crystal Structure Analysis Software*, Version 1.2; Molecular Structure Corp.: The Woodlands, TX 77381, 1992.

(15) Sheldrick, G. M. *SHELX76*: *A program for crystal structure analyses*; University Chemical Laboratory: Cambridge, U.K., 1976.

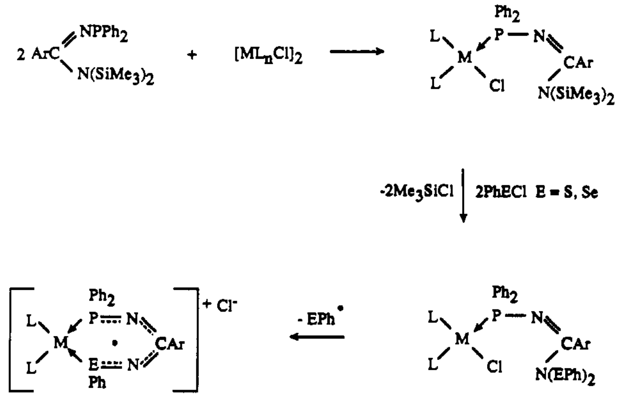
(16) Johnson, C. K. ORTEP II. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Table IV. $^{31}P\{^1H\}$ NMR Spectroscopic Data[a]

compd	$\delta(^{31}P)$, ppm		*J*, Hz	
3[b]	PPh_2	35.1 (s)		
4a[c]	PPh_2	44.7 (d)	$^1J(^{195}Pt-^{31}P) = 2623$	$^2J(^{31}P-^{31}P) = 497$
	PEt_3	12.6 (d)	$^1J(^{195}Pt-^{31}P) = 2493$	$^2J(^{31}P-^{31}P) = 497$
4b[c]	PPh_2	60.3 (d)	$^1J(^{103}Rh-^{31}P) = 157$	
5[c]	PPh_2	67.0 (s)	$^1J(^{195}Pt-^{31}P) = 3789$	
	PEt_3	4.9 (s)	$^1J(^{195}Pt-^{31}P) = 2956$	
6[d]	PPh_2	89.1 (d)	$^1J(^{103}Rh-^{31}P) = 169$	
8[c]	PPh_2	89.1 (d)	$^1J(^{103}Rh-^{31}P) = 169$	

[a] Chemical shifts are quoted in ppm relative to 85% H_3PO_4. [b] CH_2Cl_2 solution. [c] THF solution. [d] Acetone solution.

Scheme I. "Stepwise" Strategy for the Proposed Synthesis of $[ML_2(PPh_2NC(Ar)NEPh^{\bullet})]Cl$



phosphine groups are coordinated *trans* to one another,[17] while the platinum–phosphorus coupling constants are typical of known *trans*-$Pt(PR_3)_2Cl_2$ complexes.[18] A single doublet is observed at 60.3 ppm [$^1J(^{103}Rh-^{31}P) = 157$ Hz] in the ^{31}P NMR spectrum of **4b**. Both compounds **4a,b** show a sharp singlet at ~0.2 ppm in their ^1H NMR spectra, which suggests that the two trimethylsilyl groups are attached to the same nitrogen atom or that a rapid 1,3-nitrogen shift occurs at room temperature.[19] During the course of this work, it was discovered that a compound analogous to **4b**, $Rh(cod)(PPh_2NC(Ph)N(SiMe_3)_2)Cl$ had also been prepared by Reed.[3] Our spectroscopic results are in good agreement.

Reactions of 4a with PhECl (E = S, Se). The reaction of **4a** with 2 molar equiv of PhSeCl was investigated in an attempt to prepare a complex of the type **2b** via the route depicted in Scheme I. In dry THF at −78 °C this reaction yields colorless crystals of a platinum–phosphine complex **5**, together with Ph_2Se_2 and Me_3SiCl. A ^{31}P NMR spectrum of **5** in THF at 23 °C reveals two singlets at 67.0 [$^1J(^{195}Pt-^{31}PPh_2) = 3789$ Hz] and 4.9 ppm [$^1J(^{195}Pt-^{31}PEt_3) = 2956$ Hz]. The positive increase in the chemical shift for the PPh_2 group (from 44.7 to 67.0 ppm) is characteristic of chelate ring formation,[17] while the lack of observable $^2J(P-P)$ coupling indicates a *cis* configuration of the phosphine ligands. The significant increase in the $^1J(^{195}Pt-^{31}P)$ values suggests that both phosphine groups are now *trans* to much harder, less polarizable ligands. Furthermore, monitoring of the crude reaction mixture by ^{77}Se NMR spectroscopy demonstrates that Se_2Ph_2 is the sole selenium-containing product in solution and that a SePh group has not been incorporated into the complex.

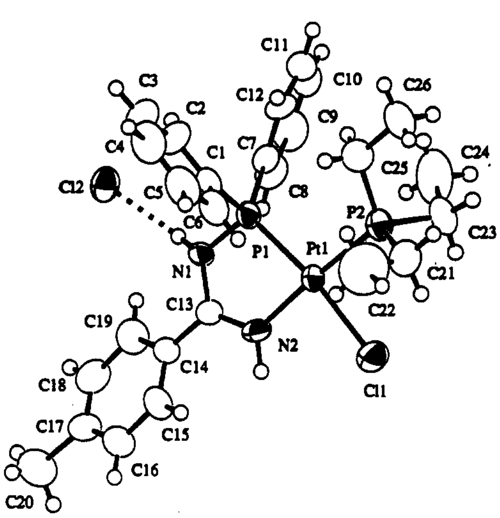


Figure 1. ORTEP plot for *cis*-$[Pt(PEt_3)(PPh_2NHC(4\text{-}CH_3C_6H_4)NH)Cl]Cl$ (**5**) with the THF molecule omitted.

Table V. Selected Bond Distances (Å) and Bond Angles (deg) for *cis*-$[Pt(PEt_3)(PPh_2NHC(4\text{-}CH_3C_6H_4)NH)Cl]Cl\cdot THF$ (**5**·THF)

Cl(1)–Pt(1)	2.324(4)	P(1)–Pt(1)	2.211(3)
P(2)–Pt(1)	2.269(3)	N(2)–Pt(1)	2.035(10)
N(1)–P(1)	1.69(1)	C(1)–P(1)	1.82(1)
C(13)–N(1)	1.37(1)	C(13)–N(2)	1.30(1)
Cl(2)···H(N1)	2.20		
P(1)–Pt(1)–Cl(1)	168.6(1)	P(2)–Pt(1)–Cl(1)	88.4(1)
P(2)–Pt(1)–P(1)	102.5(1)	N(2)–Pt(1)–Cl(1)	88.1(3)
N(2)–Pt(1)–P(1)	81.0(3)	N(2)–Pt(1)–P(2)	176.2(3)
N(1)–P(1)–Pt(1)	101.7(3)	C(1)–P(1)–Pt(1)	119.1(4)
C(13)–N(1)–P(1)	117.8(8)	C(13)–N(2)–Pt(1)	122.8(8)
N(2)–C(13)–N(1)	115.9(10)		

Interestingly, an ^1H NMR spectrum of **5** reveals that, in addition to the peaks expected for the alkyl and aryl groups, two slightly broadened resonances are observed at 12.73 (integral 0.75 H) and 7.40 ppm (integral 0.80 H). The high-frequency signal at 12.73 ppm is characteristic of an acidic, hydrogen-bonded proton,[20] and this resonance also displays ^{195}Pt sidebands with $J(^{195}Pt-^1H) = 46$ Hz. Both protons exchange with D_2O, and the more acidic proton exchanges more rapidly, as expected. These resonances are due to the presence of two different NH functionalities within the chelate ligand, which implies that a 1,3-migration between the two nitrogen sites has occurred. This interpretation is further supported by infrared and 2D $^1H-^{15}N$ HMQC NMR studies (see later). Thus, the spectroscopic studies suggest the identity of **5** as *cis*-$[Pt(PEt_3)Cl(PPh_2NHC(4\text{-}CH_3C_6H_4)NH)]Cl$, which is confirmed by an X-ray stuctural analysis.

The reaction of 2 molar equiv of PhSCl with **4a** also produces **5**, as illustrated by ^{31}P NMR studies. A possible pathway for these reactions is discussed briefly below.

Crystal and Molecular Structure of 5. Figure 1 is an ORTEP diagram showing the important features of **5**, together with the atomic numbering scheme. Selected bond lengths and bond angles are given in Table V. The structure comprises two monomeric *cis*-$[Pt(PEt_3)Cl(PPh_2NHC(4\text{-}CH_3C_6H_4)NH)]Cl$ units and two molecules of cocrystallized THF per unit cell. The geometry of the Pt(II) center is approximately square planar, as expected, with the $PPh_2NHC(4\text{-}CH_3C_6H_4)NH$ ligand chelating to Pt via P(1) and N(2) to form a five-membered ring. The bond angles around Pt sum to exactly 360°. In agreement with the ^{31}P NMR data, the PPh_2 and PEt_3 groups are in mutually *cis* positions. The Pt–P, Pt–N, and Pt–Cl bond distances fall within the ranges expected and are typical of such complexes.[21,22]

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(21) Berry, D. E.; Browning, J.; Bushnell, G. W.; Dixon, K. R.; Pidcock, A. *Can. J. Chem.* **1989**, *67*, 48.

Within the ligand, the P(1)–N(1) bond length of 1.69 Å is in the normal range for a phosphorus–nitrogen single bond. The C(13)–N(1) and C(13)–N(2) distances of 1.37(1) and 1.30(1) Å, respectively, are intermediate between those expected for single (1.46 Å) and double (1.26 Å) bonds and indicate some delocalization about the N–C–N framework. This feature has been observed in the structures of some related tridentate N,N,S platinum and palladium complexes.[23] The delocalization is also reflected in the P(1)–N(1)–C(13) bond angle of 117.8°, a significant deviation from that expected for a tetrahedral sp^3 nitrogen atom. At an intermediate stage in the refinement, a difference map revealed maxima consistent with the presence of hydrogen atoms on N(1) and N(2), and these were included at their idealized positions. Hydrogen bonding between the proton on N(1) and the chloride counterion (H(N1)···Cl = 2.20 Å) provides further confirmation of the location of H(N1). This is the first example of a structurally characterized metal complex of this class of ligand.

In contrast to the evidence obtained from the X-ray study, the ^{1}H NMR spectroscopic data suggest that in solution it is H(N2) [12.73 ppm, $^2J(^{195}\text{Pt}–^1\text{H})$ = 46 Hz] and not H(N1) which is involved in a strong hydrogen-bonding interaction with the chloride counterion. This apparent discrepancy between the solution- and solid-state structures of **5** was further investigated by 2D ^{1}H–^{15}N HMQC NMR spectroscopy.

2D ^{1}H–^{15}N HMQC (Heteronuclear Multiple Quantum Coherence) NMR Studies of 5. The application of 2D ^{1}H–^{15}N (^{15}N, $I = 1/2$, natural abundance = 0.365%) NMR spectroscopic techniques to inorganic compounds has shown increasing popularity in recent years, especially with respect to the unambiguous assignment of NH resonances.[24,25] For ligands containing PNH moieties, a 2D study can provide information such as $\delta(^{15}\text{N})$, $^1J(^{15}\text{N}–^1\text{H})$, and $^1J(^{31}\text{P}–^{15}\text{N})$. Figure 2a shows the 2D ^{1}H–^{15}N HMQC spectrum obtained for a $CDCl_3$ solution of **5** at room temperature in the region 6–14 ppm. Two sets of 2D ^{1}H–^{15}N cross peaks are observed at δ 7.40/–223 and δ 12.73/–261 ppm, which are separated by $^1J(^{15}\text{N}–^1\text{H})$ values of 85 and 95 Hz, respectively. The similarity of the $^1J(^{15}\text{N}–^1\text{H})$ values suggests that the electronic environments about N(1) and N(2) are also similar, which is consistent with the information obtained from the X-ray data. $^1J(^{31}\text{P}–^{15}\text{N})$ coupling is not observed in this experiment due to insufficient resolution (SW = 704 ppm).

Figure 2b shows the 2D ^{1}H–^{15}N{^{15}N} spectrum for a $CDCl_3$ solution of **5**, recorded using a much smaller window (SW = 82 ppm). Again two sets of peaks are observed; however, only the peak at $\delta(^1\text{H})$ = 7.40 ppm shows a one-bond ^{31}P–^{15}N coupling [52 Hz; cf. $^1J(^{31}\text{P}–^{15}\text{N})$ for related compounds of 30–55 Hz[24]]. Thus, this resonance may be unequivocally assigned to H(N1), and the resonance at 12.73 ppm, which shows no ^{31}P–^{15}N coupling, can be assigned to H(N2).

Thermolysis of 4a. A solution of **4a** in freshly distilled THF was heated to reflux for several hours in an attempt to induce the elimination of Me_3SiCl from the complex. The reaction was monitored by ^{31}P NMR spectroscopy, which revealed the emergence of two predominant peaks at 67.0 ppm [$^1J(^{195}\text{Pt}–^{31}\text{PPh}_2)$ = 3789 Hz] and 4.9 ppm [$^1J(^{195}\text{Pt}–^{31}\text{PEt}_3)$ = 2956 Hz] in addition to a variety of minor phosphorus-containing resonances. These data suggest that, upon thermolysis of **4a**, the known compound *cis*-[Pt(PEt$_3$)(PPh$_2$NHC(4-CH$_3$C$_6$H$_4$)NH)]Cl (**5**) is generated. Indeed workup of the solution yields colorless crystals of **5**, whose identity was confirmed by ^{31}P and ^{1}H NMR studies.

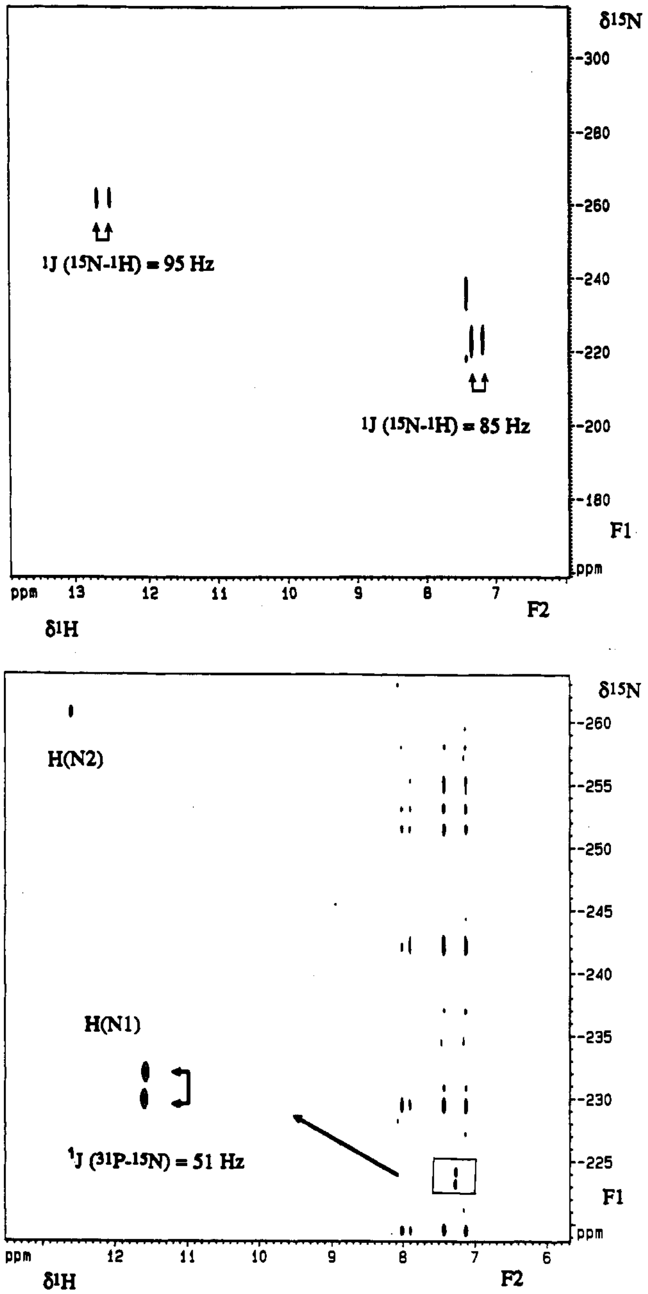

Figure 2. (a) Top: 2D ^{1}H–^{15}N HMQC spectrum of a $CDCl_3$ solution of **5**. The cross peaks separated by $^1J(^{15}\text{N}–^1\text{H})$ (F2 scale) are marked by arrows. (b) Bottom: 2D ^{1}H–^{15}N{^{15}N} HMQC spectrum of a $CDCl_3$ solution of **5**. The cross peak separated by $^1J(^{31}\text{P}–^{15}\text{N})$ (F1 scale) is enlarged for greater clarity. All other intensities are due to t_1 noise.

Thus, unexpectedly, it appears that **5** can be generated from **4a** by either reaction with PhECl (E = S, Se) or thermolysis.

A possible pathway for the thermolysis reaction is shown in Scheme II. It is likely that at elevated temperatures silyl 1,3-migration between the nitrogen sites is rapid[26,27] and that both **4a** and **4a′** are present in solution. It is possible that the less sterically hindered intermediate can chelate to the metal via the imino nitrogen more easily, thereby favoring this pathway. The chelated intermediates are thought to be extremely hydrolytically sensitive,[26] reacting rapidly with traces of moisture to produce **5** with the elimination of $(Me_3Si)_2O$. In contrast, the monodentate complex **4a** is stable in THF solution at ambient temperature for at least several hours.

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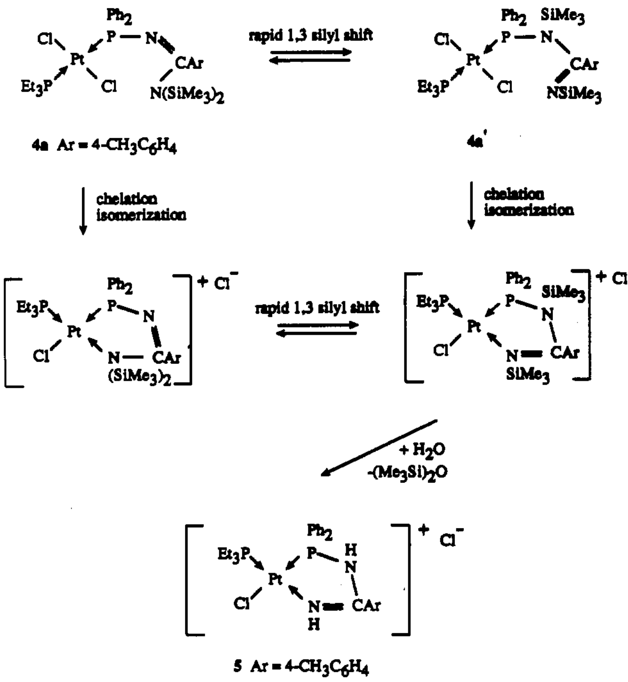
Scheme II. Possible Pathways for the Thermolysis of **4a** in THF Solution[a]



[a] Only species **5** could be isolated.

The reaction of **4a** with PhECl must occur via quite a different pathway, but in the absence of any mechanistic evidence, speculation on the details of this process is unwarranted.

Reactions of 4a and 4b with MBF$_4$ (M = Na, Ag). Efforts to prepare a rhodium derivative analogous to **5** via thermolysis of **4b** or reaction of **4b** with PhSeCl were unsuccessful. Consequently, an alternative method was employed. The reaction of 2 molar equiv of **3b** with [Rh(cod)Cl$_2$] in acetone solution in the presence of NaBF$_4$ yields NaCl and orange crystals of **6**. The ^{31}P NMR spectrum of **6** in acetone solution shows a doublet at 89.1 ppm [$^1J(^{103}$Rh–^{31}P) = 169 Hz, which suggests chelate ring formation.[3,28] An ^{1}H NMR spectrum of **6** reveals two broad, poorly resolved resonances at 8.65 and 9.12 ppm due to the presence of two different NH groups. This interpretation is supported by infrared spectroscopic data and D$_2$O-exchange studies, and an X-ray structural analysis confirms the identity of **6** as [Rh(cod)(PPh$_2$NHC(4-CH$_3$C$_6$H$_4$)NH)]BF$_4$.

Suprisingly it was discovered that NaBF$_4$ was not sufficiently powerful to remove a chloride group from **4a**. However, the reaction of AgBF$_4$ with **4a** produces a mixture of both *cis*-[PtCl(PEt$_3$)(PPh$_2$NHC(4-CH$_3$C$_6$H$_4$)NH)]Cl (**5**) and *trans*-[PtCl(PEt$_3$)(PPh$_2$NHC(4-CH$_3$C$_6$H$_4$)NH)]BF$_4$ [**7**; δ(PPh$_2$) = 69.5 ppm (d), $^1J(^{195}$Pt–^{31}P) = 2563 Hz, $^2J(^{31}$P–^{31}P) = 435 Hz; δ(PEt$_3$) = 18.5 ppm (d), $^1J(^{195}$Pt–^{31}P) = 2554 Hz, $^2J(^{31}$P–^{31}P) = 435 Hz)] and a number of unidentified species. The $^2J(^{31}$P–^{31}P) and $^1J(^{195}$Pt–^{31}P) values observed for **7** are very similar to those found for *trans*-Pt(PEt$_3$)[PPh$_2$NC(4-CH$_3$C$_6$H$_4$)N(SiMe$_3$)$_2$]Cl$_2$ (**4a**), as expected. A pure sample of **7** was not isolated.

Crystal and Molecular Structure of 6. Figure 3 is an ORTEP diagram showing the important features of **6**, together with the atomic numbering scheme. Selected bond lengths and bond angles are given in Table VI. The complex contains Rh(I) in an approximately square planar environment, with the PPh$_2$NHC(4-CH$_3$C$_6$H$_4$)NH ligand chelating to Rh via N(2) and P(1), forming a five-membered ring. The bond distances and bond angles within the chelated ligand are almost identical to those found in the analogous platinum complex **5**. In contrast, neither H(N1) or H(N2) in **6** show any apparent hydrogen-bonding interaction with the BF$_4^-$ anion. Difficulties were encountered in obtaining a 2D ^{1}H–^{15}N NMR HMQC specrum for 6 due to the poor resoluton of the NH resonances.

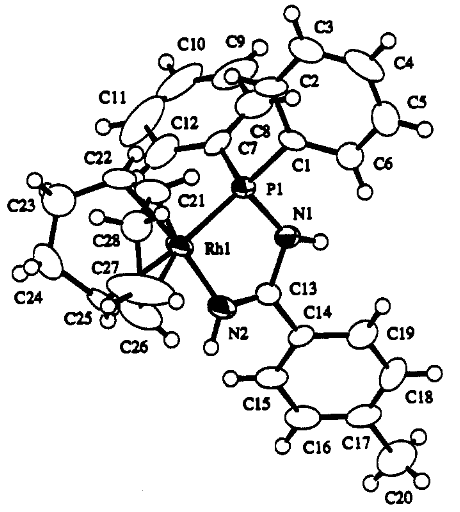


Figure 3. ORTEP plot for [Rh(cod)(PPh$_2$NHC(4-CH$_3$C$_6$H$_4$)NH)]BF$_4$ (**6**) with the acetone and BF$_4^-$ groups omitted.

Table VI. Selected Bond Distances (Å) and Bond Angles (deg) for [Rh(cod)(PPh$_2$NHC(4-CH$_3$C$_6$H$_4$)NH)]BF$_4$·(CH$_3$)$_2$CO (**6**·(CH$_3$)$_2$CO)

P(1)–Rh	2.238(3)	N(2)–Rh	2.066(9)
C(21)–Rh	2.134(13)	C(22)–Rh	2.150(12)
C(25)–Rh	2.227(13)	C(26)–Rh	2.238(16)
C(13)–N(1)	1.377(12)	C(13)–N(2)	1.291(14)
N(2)–Rh–P(1)	80.7(3)	C(21)–Rh–P(1)	100.5(3)
C(21)–Rh–N(2)	163.2(6)	C(22)–Rh–P(1)	96.8(4)
C(22)–Rh–N(2)	161.2(6)	C(22)–Rh–C(21)	35.6(6)
C(25)–Rh–P(1)	164.5(8)	C(25)–Rh–N(2)	95.9(5)
C(25)–Rh–C(21)	87.1(6)	C(25)–Rh–C(22)	81.5(5)
C(26)–Rh–P(1)	161.2(7)	C(26)–Rh–N(2)	93.3(5)
C(26)–Rh–C(21)	80.3(6)	C(26)–Rh–C(22)	94.5(7)
C(26)–Rh–C(25)	33.1(8)	N(1)–P(1)–Rh	101.4(3)
C(13)–N(1)–P(1)	116.8(7)	C(13)–N(2)–Rh	121.5(7)
N(2)–C(13)–N(1)	118.2(9)		

Reaction of [Rh(CO)$_2$Cl]$_2$ with 3c. The reaction of 2 molar equiv of **3c** with [Rh(CO)$_2$Cl]$_2$ in freshly distilled THF solution results in the loss of 1 mol of CO to form the chelate complex Rh(CO)(PPh$_2$NHC(4-CH$_3$C$_6$H$_4$)NH)Cl (**8**) as a yellow solid. Monitoring of the reaction by ^{31}P NMR spectroscopy demonstrates the presence of several unstable intermediates. A ^{31}P NMR spectrum of the crude THF solution after approximately 30 min of stirring at −78 °C shows two doublets at 56.9 and 100.1 ppm with $^1J(^{103}$Rh–^{31}P) values of 130 and 175 Hz, respectively. The former signal is due to a monodentate rhodium species [cf. **4b**: δ(PPh$_2$) = 60.3 ppm (d), $^1J(^{103}$Rh–^{31}P) = 157 Hz], while the latter indicates that chelation of the ligand has occurred [cf. **6**: δ(PPh$_2$) = 89.1 ppm (d), $^1J(^{103}$Rh–^{31}P) = 169 Hz]. The solution was allowed to warm to ambient temperature and stirred for 30 min. After such time, the ^{31}P NMR spectrum is much more complex, showing two major resonances at 89.8 (d)[$^1J(^{103}$Rh–^{31}P) = 125 Hz] and 100.1 ppm (d) [$^1J(^{103}$Rh–^{31}P) = 175 Hz], in addition to small quantities of two monodentate species and at least two more chelated species. The reaction mixture was stirred for a further 1 h under a slow stream of Ar gas, resulting in the precipitation of **8** [δ(PPh$_2$) = 105.7 ppm (d) $^1J(^{103}$Rh–^{31}P) = 175 Hz] from solution.

The ^{13}C NMR spectrum of **8** shows a resonance due to a single CO group at 189.4 ppm (dd) with $^1J(^{103}$Rh–^{13}C) and $^2J(^{31}$P–^{13}C) values of 68 and 17 Hz, respectively. This suggests that the CO

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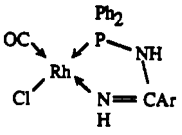
(28) Katti, K.; Cavell, R. G. *Organometallics* **1988**, *7*, 2236.



8 Ar = 4-$CH_3C_6H_4$

group is *cis* to the PPh_2 moiety,[28,29] and this is further supported by the observation of a ν_{CO} stretch in the infrared spectrum at 1991 cm^{-1}. ^1H NMR and infrared spectroscopic and microanalytical data are consistent with the structure illustrated.

The numerous monodentate and chelated intermediates observed during the course of this reaction suggest that a pathway similar to that described in Scheme II may be in operation.

Conclusion

The complexes $ML_2[PPh_2NC(4\text{-}CH_3C_6H_4)N(SiMe_3)_2]Cl$ (**4a**, M = Pt, L = PEt_3, Cl; **4b**, M = Rh, L = cod) can be prepared by the reaction of the appropriate chloride-bridged metal dimer with 4-$CH_3C_6H_4C[N(SiMe_3)_2](NPPh_2)$ (**3c**). Reaction of *trans*-$Pt(PEt_3)[PPh_2NC(4\text{-}CH_3C_6H_4)N(SiMe_3)_2]Cl_2$ (**4a**) with 2 molar equiv of PhECl (E = S, Se) or the thermolysis of **4a** generates *cis*-$[PtCl(PEt_3)(PPh_2NHC(4\text{-}CH_3C_6H_4)NH)]Cl$ (**5**). The application of HMQC NMR techniques provided decisive information for the solution structure of **5**. The analogous rhodium complexes $[Rh(cod)(PPh_2NHC(4\text{-}CH_3C_6H_4)NH)]BF_4$ (**6**) and $Rh(CO)(PPh_2NHC(4\text{-}CH_3C_6H_4)NH)Cl$ (**8**) are obtained from the reactions of **3c** with the appropriate rhodium(I) reagent. Thus all attempts to prepare chelated complexes of **3c** resulted in the isolation of compounds in which the bidentate ligand $PPh_2NHC(Ar)NH$ is coordinated to the metal, presumably as a result of a facile silyl 1,3-shift followed by hydrolysis.

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Supplementary Material Available: Tables of X-ray experimental details, bond distances and angles, anisotropic thermal parameters, and hydrogen positional parameters (22 pages). Ordering information is given on any current masthead page.

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(29) Katti, K.; Cavell, R. G. *Organometallics* **1989**, *9*, 2147.