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Synthesis and Reaction Chemistry of Monomeric and Dimeric Amide Complexes of Platinum(II)

Soonheum Park, Arnold L. Rheingold, and D. Max Roundhill*

Departments of Chemistry, Tulane University, New Orleans, Louisiana 70118, and University of Delaware, Newark, Delaware 19711

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A series of complexes *trans*-$[PtH(NH_3)L_2]ClO_4$ (L = PPh_3, PEt_3, PCy_3), *trans*-$[PtMe(NH_3)L_2]ClO_4$ (L = PPh_3, PEt_3, $PMePh_2$, PCy_3), and $[PtMe(NH_3)dppe]ClO_4$ have been synthesized from *trans*-$PtH(ClO_4)L_2$, *trans*-$PtMe(ClO_4)L_2$, and $PtMe(ClO_4)dppe$ and ammonia, respectively. Reacting *trans*-$[PtH(NH_3)L_2]ClO_4$ (L = PPh_3, PEt_3) with $NaNH_2$ gives $[PtH(\mu\text{-}NH_2)L]_2$ as a mixture of anti and syn isomers. The complexes reductively eliminate ammonia. Reacting *trans*-$[PtMe(NH_3)L_2]ClO_4$ (L = PPh_3, PEt_3, $PMePh_2$) with $NaNH_2$ gives the stable complexes $[PtMe(\mu\text{-}NH_2)L]_2$ as mixtures of anti and syn isomers. For L = PPh_3, $PMePh_2$, PEt_3, the percentage anti isomer is 100, 75, and 50, respectively. For L = PEt_3, the intermediate complex *trans*-$PtMe(NH_2)(PEt_3)_2$ has been observed. Reacting $[PtMe(\mu\text{-}NH_2)L]_2$ with L (L = PPh_3, PEt_3) gives *cis*-$PtMe(NH_2)L_2$. Reacting *trans*-$[PtH(NH_3)(PCy_3)_2]ClO_4$, *trans*-$[PtMe(NH_3)(PCy_3)_2]ClO_4$, or *trans*-$[PtPh(NH_3)(PCy_3)_2]ClO_4$ with $NaNH_2$ gives *trans*-$PtH(NH_2)(PCy_3)_2$, *trans*-$PtMe(NH_2)(PCy_3)_2$, or *trans*-$PtPh(NH_2)(PCy_3)_2$. Reacting $[PtMe(\mu\text{-}Cl)PCy_3]_2$ with $AgClO_4$ then NH_3 gives $[PtMe(NH_3)_2PCy_3]ClO_4$. Treating $[PtMe(NH_3)_2PCy_3]$ with $NaNH_2$ gives an equimolar mixture of anti and syn isomers of $[PtMe(\mu\text{-}NH_2)PCy_3]_2$. The syn isomer, which has been isolated, converts to a mixture of syn and anti in the presence of tricyclohexylphosphine in $CDCl_3$ solution. The compound *anti*-$[PtMe(\mu\text{-}NH_2)PPh_3]_2$ crystallizes in the space group $C2/c$ with $a = 22.592$ (5) Å, $b = 11.844$ (3) Å, $c = 29.403$ (6) Å, $\beta = 116.43$ (2)°, and $Z = 8$. The two crystallographically independent molecules with Pt(1)–Pt(1A) and Pt(2)–Pt(2A) distances of 3.106 (1) and 3.117 (1) Å, respectively, are associated by Pt···H interactions. The complex *trans*-$PtMe(NH_2)(PCy_3)_2$ reacts with CF_3SO_3H to give *trans*-$[PtMe(NH_3)(PCy_3)_2]CF_3SO_3$. The complex *trans*-$PtPh(NH_2)(PCy_3)_2$ reacts with CF_3SO_3H and H_2O to give *trans*-$[PtPh(NH_3)(PCy_3)_2]CF_3SO_3$ and *trans*-$[PtPh(NH_3)(PCy_3)_2]OH$, respectively. *trans*-$PtPh(NH_2)(PCy_3)_2$ reacts with methyl iodide and allyl chloride to give *trans*-$PtPhI(PCy_3)_2$ and *trans*-$PtPhCl(PCy_3)_2$, respectively. Carbon dioxide reacts with *trans*-$PtPh(NH_2)(PCy_3)_2$ to give *trans*-$PtPh(NHCO_2H)(PCy_3)_2$ then *trans*-$PtPh(OCONH_2)(PCy_3)_2$.

Introduction

Although metal amide complexes are common for the early transition elements in high oxidation states, analogous complexes for the later transition-metal ions are still relatively uncommon.[1] Our research on amide complexes has focused on those of the later transition elements and particularly on those of platinum(II). This choice was made because we have the opportunity to synthesize coordinately unsaturated transition-metal amide complexes that may have weaker metal–nitrogen coordinate bonds than are present with the earlier transition-metal ions in a high oxidation state. This latter premise is based on the fact that the LUMO in complexes of platinum(II) have a high-energy $d_{x^2-y^2}$ orbital. Transfer of the lone electron pair on the complexed amide nitrogen to this $d_{x^2-y^2}$ orbital of platinum(II) to give a donor metal–nitrogen double bond is less favorable than for metal ions that have a low-energy LUMO.[2]

Monomeric amide complexes with the lone electron pair on nitrogen have a strong tendency to form dimers and oligomers. This feature, which is also prevalent for transition-metal hydroxides, alkoxides, and thiolates, is a consequence of a bimolecular substitution reaction where the electron pair on the coordinated ligand can act as a ligand to a second metal ion.[3] The tendency to undergo oligomerization is particularly acute for coordinatively unsaturated complexes. In these complexes each metal center has a vacant site available for coordination of a lone pair of electrons from a second metal amide, thereby facilitating oligomerization by an associative substitution pathway. Our synthetic strategy for the preparation of monomeric amides is to place the σ-donor hydride or methyl ligands trans to the amide ligand and to then block the cis coordination positions with tertiary phosphines. In this paper we describe the successful synthesis of monomeric amide hydride and methyl complexes of platinum(II), and we report the reactions of these complexes with several small molecules.

Experimental Section

Potassium tetrachloroplatinate was supplied either by Matthey Bishop Inc. or by Engelhard Inc. and used without prior purification. All manipulations of air-sensitive compounds were carried out on a Schlenk line by using a high-purity nitrogen atmosphere. Solvents were dried by refluxing over either sodium/benzophenone or $LiAlH_4$. Sodium amide and lithium dimethylamide were purchased from Aldrich and used as supplied. DABCO and DBN were purchased from Aldrich. The compounds PtMeCl(1,5-COD), PtPhCl(1,5-COD), *trans*-$PtHCl(PPh_3)_2$, *trans*-$PtHCl(PEt_3)_2$, and *trans*-$PtHCl(PCy_3)_2$ were prepared by literature procedures.[4] An alternative synthesis of PtPhCl(1,5-COD) has been developed that avoids the use of diphenylmercury, which gave us inconsistent results. This method involves converting $PtCl_2$(1,5-COD) into $PtPh_2$(1,5-COD) and then to PtPhCl(1,5-COD). The compounds *trans*-$PtRClL_2$ (R = Me, L = PPh_3, PEt_3, $PMePh_2$, PCy_3; R = Ph, L = PCy_3) were prepared from PtRCl(1,5-COD) and 2 equiv of L.[4] The ^1H, ^{31}P, ^{13}C, ^{19}F, and ^{195}Pt NMR spectra were measured on a Bruker AC200 spectrometer in $CDCl_3$ solvent unless otherwise noted. Deuterated solvents were purchased from Aldrich Chemical Co. Chemical shifts were obtained relative either to an internal standard or, in the case of ^1H, to TMS or to the residual protons in the deuterated solvent. The following references were used:

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^{1}H δ 7.24 ($CHCl_3$), δ 5.32 (CH_2Cl_2), δ 7.15 (C_6H_6); ^{31}P δ 0.0 (85% H_3PO_4); ^{13}C δ 77.0 ($CDCl_3$), δ 53.8 (CD_2Cl_2); ^{19}F δ −163.0(C_6F_6), δ −76.0 (CF_3CO_2H); ^{14}N δ 0.0 ($HCONH_2$); ^{195}Pt δ 0.0 (H_2PtCl_6). NMR simulations were carried out by using the PANIC simulation routine. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Infrared spectra were measured on a Perkin-Elmer Model 683 or Mattson Cygnus 100 spectrometer.

Safety Note. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

***trans*-Hydridoamminebis(triphenylphosphine)platinum Perchlorate, *trans*-[PtH(NH_3)(PPh_3)$_2$]ClO_4 (1).**[5] *trans*-Hydridochlorobis(triphenylphosphine)platinum (700 mg, 0.93 mmol) was dissolved in chloroform (30 mL). Silver perchlorate (193 mg, 0.93 mmol) in methanol (2 mL) was added dropwise to the stirred solution. The suspension was stirred for 30 min, when the AgCl was removed by vacuum filtration. Ammonia was then bubbled through the solution for 1 min. Addition of *n*-hexane (40 mL) to the solution gave a white solid, which was dissolved in dichloromethane (5 mL). Addition of diethyl ether (20 mL) to the solution gave a white precipitate, which was recrystallized by the addition of diethyl ether to a dichloromethane solution. Yield: 677 mg (87%). ^{1}H NMR: δ 7.1–7.9 (m, 30 H, phenyl), δ 2.17 (br, 3 H, NH_3; ^{2}J(PtH) = 26.0 Hz), δ −15.6 (t, 1 H, Pt*H*; ^{2}J(PH) = 12.7 Hz, ^{1}J(PtH) = 1039 Hz). ^{31}P{^{1}H} NMR: δ 30.5 (s: ^{1}J(PtP) = 2942 Hz).

***trans*-Hydridoamminebis(triethylphosphine)platinum Perchlorate, *trans*-[PtH(NH_3)(PEt_3)$_2$]ClO_4 (2).** A similar procedure as for complex 1 using *trans*-PtHCl(PEt_3)$_2$ (300 mg, 0.64 mmol), $AgClO_4$ (133 mg, 0.64 mmol), and excess ammonia gave the pure complex. Yield: 285 mg (81%). Anal. Calcd for $C_{12}H_{34}ClNO_4P_2Pt$: C, 26.3; H, 6.24; N, 2.55. Found: C, 26.5; H, 6.39; N, 2.51. IR: ν(NH) 3335, 3274, 3198 cm^{-1} (m, br); ν(PtH) 2198 cm^{-1} (s); ν(ClO_4) 1100 cm^{-1} (vs, br). ^{1}H NMR: δ 2.97 (br, 3 H, NH_3; ^{2}J(PtH) = 25.8 Hz), δ 1.7–2.0 (m, 12 H, CH_2), δ 1.0–1.2 (m, 18 H, CH_3), δ −17.7 (t, 1 H, Pt*H*; ^{2}J(PH) = 15.0 Hz, ^{1}J(PtH) = 1109 Hz). ^{31}P{^{1}H} NMR: δ 21.6 (s; ^{1}J(PtP) = 2662 Hz).

***trans*-Hydridoamminebis(tricyclohexylphosphine)platinum Perchlorate, *trans*-[PtH(NH_3)(PCy_3)$_2$]ClO_4 (3).** A similar procedure as for complex 1 using *trans*-PtHCl(PCy_3)$_2$ (500 mg, 0.63 mmol), $AgClO_4$ (131 mg, 0.63 mmol), and excess ammonia gave the pure complex. Yield: 468 mg (85%). Anal. Calcd for $C_{36}H_{70}ClNO_4P_2Pt$: C, 49.5; H, 8.08; N, 1.60. Found: C, 49.9; H, 8.28; N, 1.63. IR: ν(NH) 3340, 3273, 3186 cm^{-1} (w, br); ν(PtH) 2233 cm^{-1} (m); ν(ClO_4) 1100 cm^{-1} (vs, br). ^{1}H NMR: δ 2.83 (br, 3 H, NH_3; ^{2}J(PtH) = 26.2 Hz), δ 1.2–2.1 (m, 66 H, Cy), δ −18.5 (t, 1 H, Pt*H*; ^{2}J(PH) = 13.3 Hz, ^{1}J(PtH) = 1102 Hz). ^{31}P{^{1}H} NMR: δ 39.1 (s; ^{1}J(PtP) = 2715 Hz).

***trans*-Methylamminebis(triphenylphosphine)platinum Perchlorate, *trans*-[PtMe(NH_3)(PPh_3)$_2$]ClO_4 (4).** A similar procedure as for complex 1 using *trans*-PtMeCl(PPh_3)$_2$ (900 mg, 1.17 mmol), $AgClO_4$ (240 mg, 1.17 mmol), and excess ammonia gave the pure complex. Yield: 867 mg (87%). Anal. Calcd for $C_{37}H_{36}ClNO_4P_2Pt$: C, 52.2; H, 4.26; N, 1.65. Found: C, 52.6; H, 4.52; N, 1.77. IR: ν(NH) 3321, 3259, 3184 cm^{-1} (w, br); ν(ClO_4) 1100 cm^{-1} (vs, br). ^{1}H NMR: δ 7.4–7.7 (m, 30 H, phenyl), δ 1.91 (br, 3 H, NH_3; ^{2}J(PtH) = 24.5 Hz), δ 0.07 (t, 3 H, CH_3; ^{3}J(PH) = 7.0 Hz, ^{2}J(PtH) = 72.5 Hz). ^{31}P{^{1}H} NMR: δ 28.6 (s; ^{1}J(PtP) = 3053 Hz).

***trans*-Methylamminebis(triethylphosphine)platinum Perchlorate, *trans*-[PtMe(NH_3)(PEt_3)$_2$]ClO_4 (5).** A similar procedure as for complex 1 using *trans*-PtMeCl(PEt_3)$_2$ (450 mg, 0.93 mmol), $AgClO_4$ (192 mg, 0.93 mmol), and excess ammonia gave the pure complex. Yield: 445 mg (85%). Anal. Calcd for $C_{13}H_{36}ClNO_4P_2Pt$: C, 27.7; H, 6.44; N, 2.49. Found: C, 27.7; H, 6.53; N, 2.65. IR: ν(NH) 3327, 3273, 3194 cm^{-1} (w, br); ν(ClO_4) 1100 cm^{-1} (vs, br). ^{1}H NMR: δ 2.74 (br, 3 H, NH_3; ^{2}J(PtH) = 26.1 Hz), δ 1.7–1.9 (m, 12 H, CH_2), δ 1.0–1.2 (m, 18 H, CH_3), δ 0.19 (t, 3 H, PtCH_3; ^{3}J(PH) = 6.7 Hz, ^{2}J(PtH) = 75.8 Hz). ^{31}P{^{1}H} NMR: δ 16.7 (s; ^{1}J(PtP) = 2747 Hz).

***trans*-Methylamminebis(methyldiphenylphosphine)platinum Perchlorate, *trans*-[PtMe(NH_3)($PMePh_2$)$_2$]ClO_4 (6).** A similar procedure for complex 1 using *trans*-PtMeCl($PMePh_2$)$_2$ (500 mg, 0.77 mmol), $AgClO_4$ (160 mg, 0.77 mmol), and excess ammonia gave the pure complex. Yield: 459 mg (82%). Anal. Calcd for $C_{27}H_{32}ClNO_4P_2Pt$: C, 44.6; H, 4.44; N, 1.93. Found: C, 45.0; H, 4.62; N, 1.92. IR: ν(NH) 3325, 3261, 3183 cm^{-1} (w, br); ν(ClO_4) 1100 cm^{-1} (vs, br). ^{1}H NMR: δ 7.2–7.7 (m, 20 H, phenyl), δ 2.18 (pseudo t, 6 H, PCH_3; ^{2}J(PH) = 3.3 Hz, ^{3}J(PtH) = 35.6 Hz), δ 1.74 (br, 3 H, NH_3), δ 0.23 (t, 3 H, PtCH_3; ^{3}J(PH) = 7.3 Hz, ^{2}J(PtH) = 74.3 Hz).

***trans*-Methylamminebis(tricyclohexylphosphine)platinum Perchlorate, *trans*-[PtMe(NH_3)(PCy_3)$_2$]ClO_4 (7).** A similar procedure as for complex 1 using *trans*-PtMeCl(PCy_3)$_2$ (863 mg, 1.07 mmol), $AgClO_4$ (222 mg, 1.07 mmol), and excess ammonia gave the pure complex. Yield: 874 mg (92%). Anal. Calcd for $C_{37}H_{72}ClNO_4P_2Pt$: C, 50.1; H, 8.18; N, 1.58. Found: C, 49.7; H, 8.24; N, 1.46. ^{1}H NMR: δ 2.59 (br, 3 H, NH_3; ^{2}J(PtH) = 24.2 Hz), δ 1.2–2.2 (m, 66 H, Cy), δ 0.25 (t, 3 H, CH_3; ^{3}J(PH) = 5.6 Hz, ^{2}J(PtH) = 77.0 Hz). ^{31}P{^{1}H} NMR: δ 22.4 (s; ^{1}J(PtP) = 2731 Hz).

Methylammine(1,2-bis(diphenylphosphino)ethane)platinum Perchlorate, [PtMe(NH_3)dppe]ClO_4 (8). A similar procedure as for complex 1 using PtMeCl(dppe) (303 mg, 0.47 mmol), silver perchlorate (97.4 mg, 0.47 mmol), and excess ammonia gave the pure complex. Yield: 303 mg (89%). Anal. Calcd for $C_{27}H_{30}ClNO_4P_2Pt$: C, 44.7; H, 4.17; N, 1.93. Found: C, 44.5; H, 4.36; N, 1.35. IR: ν(NH) 3317, 3260, 3184 cm^{-1} (w, br); ν(ClO_4) 1100 cm^{-1} (vs, br). ^{1}H NMR: δ 7.3–7.7 (m, 20 H, phenyl), δ 3.46 (br, 3 H, NH_3; ^{2}J(PtH) = 40.9 Hz), δ 2.1–2.5 (m, 4 H, CH_2), δ 0.46 (dd, 3 H, CH_3; ^{3}J(P_{trans}H) = 6.8 Hz, ^{3}J(P_{cis}H) = 3.1 Hz, ^{2}J(PtH) = 55 Hz). ^{31}P{^{1}H} NMR: δ P_A(trans to methyl) 48.9 (s), δ P_B(trans to NH_3) 40.6 (s; ^{1}J(PtP_A) = 1741 Hz, ^{1}J(PtP_B) = 3927 Hz, ^{2}J(PP) + ^{3}J(PP) = 0 Hz).

Bis(hydrido(μ-amido)(triphenylphosphine)platinum), [PtH(μ-NH_2)PPh_3]$_2$ (9). Complex 1 and excess sodium amide were placed in a 5-mL two-necked flask. The inlet arm was connected to a supply of ammonia gas, and the outlet arm was connected to a U-type condenser containing dry ice and acetone. The suspension in liquid ammonia was stirred for 1 h. Evaporation of the ammonia under a nitrogen flow gave a colorless solid. This solid was dissolved in $CDCl_3$. The complex is thermally unstable, and $CDCl_3$ solutions decompose within 30 min at ambient temperature to give *cis*-$PtCl_2$(PPh_3)$_2$. Anti isomer: ^{1}H NMR (C_6D_6) δ 0.06 (br, NH_2), δ −15.08 (d, Pt*H*; ^{2}J(PH) = 22.6 Hz, ^{1}J(PtH) = 1117 Hz). Syn isomer: ^{1}H NMR (C_6D_6) δ −1.10 (br, NH_2), δ −15.11 (d, Pt*H*; ^{2}J(PH) = 21.8 Hz).

Bis(hydrido(μ-amido)(triethylphosphine)platinum), [PtH(μ-NH_2)PEt_3]$_2$ (10). A similar procedure as for complex 9 using 2 and excess $NaNH_2$ in liquid ammonia gave a solution containing the complex, as evidenced by NMR spectroscopy. Solutions in C_6D_6 are thermally unstable and decompose to give Pt(PEt_3)$_3$ and metallic platinum. Anti isomer: ^{1}H NMR (C_6D_6) δ −0.09 (br, NH_2), δ −16.10 (d, Pt*H*; ^{2}J(PH) = 25.5 Hz); ^{31}P{^{1}H} NMR (C_6D_6) δ 10.2 (^{3}J(PtP) = −26.8 Hz, ^{4}J(PP) = 7.3 Hz). Syn isomer: ^{1}H NMR (C_6D_6): δ −0.96 (br, NH_2), δ −15.94 (d, Pt*H*; ^{2}J(PH) = 23.4 Hz, ^{1}J(PtH) = 1098 Hz); ^{31}P{^{1}H} NMR (C_6D_6) δ 9.87 (^{3}J(PtP) = −22.0 Hz, ^{4}J(PP) = 0 Hz).

Bis(methyl(μ-amido)(triphenylphosphine)platinum), [PtMe(μ-NH_2)PPh_3]$_2$ (11). Complex 4 (300 mg, 0.39 mmol) and sodium amide (45 mg, 1.15 mmol) were placed in a 5-mL two-necked flask. The inlet arm was connected to a supply of ammonia gas, and the outlet arm was connected to a U-type condenser containing dry ice and acetone. The suspension in liquid ammonia was stirred for 1 h. Evaporation of the ammonia under a nitrogen flow gave a colorless solid. This solid was dissolved in benzene, and *n*-hexane was added to the filtered solution to give a colorless precipitate. Recrystallization from benzene and *n*-hexane gave the pure complex. Yield: 151 mg (79%). Anal. Calcd for $C_{19}H_{20}NPPt$: C, 46.7; H, 4.13; N, 2.87. Found: C, 46.1; H, 4.11; N, 2.88. IR: ν(NH) 3333, 3183 cm^{-1} (w, br). Anti isomer: ^{1}H NMR (C_6D_6) δ 6.9–7.8 (m, 30 H, phenyl), δ 0.55 (d, 6 H, CH_3; ^{3}J(PH) = 3.9 Hz, ^{2}J(PtH) = 73.9 Hz), δ −0.24 (br, 4 H, NH_2); ^{31}P{^{1}H} NMR (C_6D_6) δ 20.9 (^{1}J(PtP) = 3743 Hz, ^{3}J(PtP) = −20.0 Hz, ^{4}J(PP) = 4.9 Hz, ^{1}J(PtPt) = 292 Hz), δ −4.3 (s, resonance from free triphenylphosphine, which has an area of equal intensity to

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that of the complexed triphenylphosphine).

Bis(methyl(μ-amido)(triethylphosphine)platinum), [PtMe(μ-NH_2)PEt_3]$_2$ (12). A similar procedure as for complex 11 using complex **5** and excess $NaNH_2$ in liquid ammonia gave a colorless solid. Extraction of this solid with C_6D_6 gave a colorless solution that contained approximately equal quantities of the anti and syn isomers of the complex. The solution also contained approximately 10% of *trans*-PtMe(NH_2)(PEt_3)$_2$. Anti isomer: ^{1}H NMR (C_6D_6) δ −0.54 (br, NH_2), δ 0.58 (d, PtCH_3; ^3J(PH) = 3.6 Hz, ^2J(PtH) = 74.1 Hz); ^{31}P{^{1}H} NMR (C_6D_6) δ 5.8 (^1J(PtP) = 3550 Hz, ^3J(PtP) = −22.7 Hz, ^4J(PP) = 4.9 Hz). Syn isomer: ^{1}H NMR (C_6D_6) δ −1.40 (br, NH_2), δ 0.57 (d, PtCH_3; ^3J(PH) = 3.8 Hz, ^2J(PtH) = 70.2 Hz); ^{31}P{^{1}H} NMR δ 5.2 (^1J(PtP) = 3509 Hz, ^3J(PtP) = −28.6 Hz, ^4J(PP) = 0 Hz).

Bis(methyl(μ-amido)(methyldiphenylphosphine)platinum), [PtMe(μ-NH_2)$PMePh_2$]$_2$ (13). A similar procedure as for complex **11** using **6** and excess $NaNH_2$ in liquid ammonia gave a solution of the complex which had an anti/syn ratio of 3/1. Anti isomer: ^{1}H NMR (C_6D_6) δ −0.35 (br, NH_2), δ 0.57 (d, PtCH_3; ^3J(PH) = 4.2 Hz, ^2J(PtH) = 74.2 Hz); ^{31}P{^{1}H} NMR (C_6D_6) δ 2.06 (^1J(PtP) = 3665 Hz, ^3J(PtP) = −20.1 Hz, ^4J(PP) = 5.5 Hz). Syn isomer: ^{1}H NMR (C_6D_6) δ −1.81 (br, NH_2), δ 0.65 (d, PtCH_3; ^3J(PH) = 4.1 Hz, ^2J(PtH) = 72.4 Hz); ^{31}P{^{1}H} NMR δ 1.94 (^1J(PtP) = 3733 Hz, ^3J(PtP) = −18.0 Hz, ^4J(PP) = 0 Hz).

***cis*-Methylamidobis(triphenylphosphine)platinum, *cis*-PtMe(NH_2)(PPh_3)$_2$ (14).** Complex **11** (ca. 50 mg) and triphenylphosphine (10 equiv) were dissolved in benzene-d_6 in a 10-mm NMR tube. Complex **14** was slowly formed in solution, as evidenced by NMR spectroscopy. The conversion was 50% after 14 days. ^{1}H NMR (C_6D_6): δ 1.13 (dd, 3 H, CH_3; ^3J(P_{trans}H) = 7.2 Hz, ^3J(P_{cis}H) = 4.3 Hz, ^2J(PtH) = 64 Hz), δ 2.30 (br, 2 H, NH_2). ^{31}P{^{1}H} NMR (C_6D_6): δ P_A(trans to methyl) 27.3 (d), δ P_B(trans to NH_2) 18.6 (d; ^2J(PP) = 9.8 Hz, ^1J(PtP_A) = 1741 Hz, ^1J(PtP_B) = 3633 Hz).

***cis*-Methylamidobis(triethylphosphine)platinum, *cis*-PtMe(NH_2)(PEt_3)$_2$ (15).** To a solution of complex **12** in benzene-d_6 in a 10-mm NMR tube was added triethylphosphine (4 equiv). The complex was slowly formed, as evidenced by NMR spectroscopy. The reaction had proceeded to 24% completion after 2 days at ambient temperature. ^{1}H NMR (C_6D_6): δ 3.40 (2 H, NH_2). ^{31}P{^{1}H} NMR: δ P_A(trans to Me) 19.6 (d; ^1J(PtP) = 1792 Hz), δ P_B(trans to NH_2) 2.38 (d; ^1J(PtP) = 3391 Hz, ^2J(PP) = 12.2 Hz).

***trans*-Hydridoamidobis(tricyclohexylphosphine)platinum, *trans*-PtH(NH_2)(PCy_3)$_2$ (16).** A C_6D_6 solution of the complex was prepared by a similar procedure as for complex 11 using complex **3** and excess $NaNH_2$ in liquid ammonia. The complex was soluble in all organic solvents and could not be obtained analytically pure. ^{1}H NMR (C_6D_6): δ 1.2–2.2 (m, 66 H, Cy), δ 0.41 (br, 2 H, NH_2), δ −13.75 (t, PtH; ^2J(PH) = 16.2 Hz, ^1J(PtH) = 739 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 38.1 (s; (^1J(PtP) = 2951 Hz).

***trans*-Methylamidobis(tricyclohexylphosphine)platinum, *trans*-PtMe(NH_2)(PCy_3)$_2$ (17).** A C_6D_6 solution of the complex was prepared by a similar procedure as for complex **16** using complex **7** and excess $NaNH_2$ in liquid ammonia. The product was identified by NMR spectroscopy, and the complex was solution stable for 12 h. The complex was not isolated in the pure state because it was soluble in all organic solvents, and no effective purification procedure could be found. ^{1}H NMR (C_6D_6): δ 1.2–2.6 (m, 66 H, Cy), δ 0.38 (t, 3 H, PtCH_3; ^3J(PH) = 4.9 Hz, ^2J(PtH) = 62.7 Hz), δ −0.28 (br, 2 H, NH_2). ^{31}P{^{1}H} NMR (C_6D_6): δ 21.0 (s, ^1J(PtP) = 2929 Hz). ^{14}N{^{1}H} NMR (C_6D_6): δ 197.0.

***trans*-Phenylamminebis(tricyclohexylphosphine)platinum Perchlorate, *trans*-[PtPh(NH_3)(PCy_3)$_2$]$ClO_4 \cdot {}^1/_2CH_2Cl_2$ (18).** The complex *trans*-PtPhCl(PCy_3)$_2$ was prepared from PtPhCl(1,5-COD) by using the literature procedure.[4] The complex PtPhCl(1,5-COD) was either prepared by using this literature procedure with diphenylmercury or by an alternative route. The alternative route uses $PtCl_2$(1,5-COD) (1.00 g, 2.67 mmol) suspended in toluene (40 mL) in a Schlenk tube. To this stirred suspension was added dropwise phenyllithium (3.7 mL of 1.8 M solution, 6.7 mmol) over a period of 5 min. The dark reaction mixture was stirred for 1 h, filtered through alumina, and decolorized with charcoal. The solvent was removed in vacuo to give $PtPh_2$(1,5-COD) as an off-white solid. The complex $PtPh_2$(1,5-COD) (0.435 g, 0.95 mmol) was dissolved in dichloromethane (10 mL) and methanol (1 mL) added. Acetyl chloride (74 μL, 1.05 mmol) was added and the solution stirred for 10 min. Removal of the solvent in vacuo gave PtPhCl(1,5-COD) as a white solid. Yield: 379 mg (96%). A similar procedure as for complex **4** using *trans*-PtPhCl(PCy_3)$_2$ (700 mg, 0.81 mmol), $AgClO_4$ (168 mg, 0.81 mmol), and excess ammonia gave the pure complex. Yield: 731 mg (91%). Anal. Calcd for $C_{42.5}H_{75}Cl_2NO_4P_2Pt$: C, 51.5; H, 7.62; N, 1.41. Found: C, 51.9; H, 8.01; N, 1.71. IR: ν(NH) 3331, 3273, 3195 cm^{-1} (w, br); ν(ClO_4) 1100 cm^{-1} (vs, br). ^{1}H NMR: δ 6.8–7.5 (m, 5 H, phenyl), δ 2.74 (br, 3 H, NH_3), δ 1.0–1.8 (m, 66 H, Cy). ^{31}P{^{1}H} NMR: δ 17.7 (s; ^1J(PtP) = 2700 Hz).

***trans*-Phenylamidobis(tricyclohexylphosphine)platinum, *trans*-PtPh(NH_2)(PCy_3)$_2$ (19).** To a mixture of complex 18 (750 mg, 0.79 mmol) and $NaNH_2$ (70 mg, 1.79 mmol) was added dry THF (30 mL) via syringe. The suspension was stirred for 1 h under a nitrogen atmosphere. The solvent was then removed under vacuum. The resulting residue was dissolved in hot *n*-hexane (20 mL), and the solution was vacuum-filtered to give a pale yellow solution. After the solution was allowed to stand for 12 h at −5 °C, the complex was obtained as pale yellow crystals. Yield: 523 mg (78%). Anal. Calcd for $C_{42}H_{73}NP_2Pt$: C, 59.4; H, 8.67; N, 1.65. Found: C, 59.6; H, 8.79; N, 1.81. IR: ν(NH) 3351, 3277 cm^{-1}. ^{1}H NMR (C_6D_6): δ 6.9–8.0 (5 H, phenyl), δ 1.0–2.2 (66 H, Cy), δ 0.09 (2 H, NH_2). ^{31}P{^{1}H} NMR (C_6D_6): δ 17.0 (s; ^1J(PtP) = 2891 Hz).

***cis*-Methylbis(ammine)(tricyclohexylphosphine)platinum Perchlorate, *cis*-[PtMe(NH_3)$_2$$PCy_3$]$ClO_4$ (20).** A similar procedure as for complex **4** using [PtMe(μ-Cl)PCy_3]$_2$ (550 mg, 0.52 mmol), $AgClO_4$ (216 mg, 1.04 mmol), and excess ammonia gave the pure complex. Yield: 526 mg (81%). Anal. Calcd for $C_{19}H_{42}ClN_2O_4PPt$: C, 36.6; H, 6.78; N, 4.49. Found: C, 36.9; H, 6.87; N, 4.31. IR ν(NH) 3352, 3329, 3281 (sh), 3269, 3227, 3190 cm^{-1} (w, br); ν(ClO_4) 1100 cm^{-1} (vs, br). ^{1}H NMR: δ 2.98 (3 H, NH_3; ^3J(PH) = 2.6 Hz, ^2J(PtH) = 34.9 Hz), δ 2.48 (3 H, NH_3; ^2J(PtH) = 23.5 Hz) δ 1.1–1.9 (m, (33 H, Cy), δ 0.23 (d, 3 H, CH_3; ^3J(PH) = 2.1 Hz, ^2J(PtH) = 73.6 Hz). ^{31}P{^{1}H} NMR: 18.4 (s; ^1J(PtP) = 4145 Hz).

Bis(methyl(μ-amido)(tricyclohexylphosphine)platinum), [PtMe(μ-NH_2)PCy_3]$_2$ (21). A similar procedure as for complex 11 using complex **20** (300 mg, 0.48 mmol) and $NaNH_2$ (50 mg, 1.28 mmol) in liquid ammonia gave approximately equal amounts of anti and syn isomers of the complex. Yield: 173 mg (71%). Anal. Calcd for $C_{19}H_{38}NPPt$: C, 45.1; H, 7.56; N, 2.77. Found: C, 45.1; H, 7.62; N, 2.67. Anti isomer: ^{1}H NMR (C_6D_6) δ 1.1–2.2 (m, 66 H, Cy), δ 0.65 (d, 6 H, CH_3; ^3J(PH) = 2.5 Hz, ^2J(PtH) = 73.9 Hz), δ −0.29 (br, 4 H, NH_2); ^{31}P{^{1}H} NMR (C_6D_6) δ 19.0 (^1J(PtP) = 3618 Hz, ^3J(PtP) = −22.0 Hz). Syn isomer: ^{1}H NMR (C_6D_6) δ 1.1–2.2 (m, 66 H, Cy), δ 0.56 (d, 6 H, CH_3; ^3J(PH) = 2.5 Hz, ^2J(PtH) = 73.8 Hz), δ −0.39 (br, 4 H, NH_2); ^{31}P{^{1}H} NMR (C_6D_6) δ 17.9 s (^1J(PtP) = 3589 Hz, ^3J(PtP) = −31.7 Hz).

***trans*-Phenyl(carbamato-*N*)bis(tricyclohexylphosphine)platinum, *trans*-PtPh($NHCO_2H$)(PCy_3)$_2$ (22).** A solution of *trans*-PtPh(NH_2)(PCy_3)$_2$ (100 mg, 0.12 mmol) in benzene (5 mL) was purged with dry carbon dioxide for 2 min. During this time a white solid precipitated. The complex was filtered out and dried in vacuo for 12 h. Yield: 97 mg (92%). Anal. Calcd for $C_{43}H_{73}NO_2P_2Pt$: C, 57.8; H, 8.24; N, 1.57. Found: C, 57.8; H, 8.26; N, 1.44. IR: ν(CO) 1602 cm^{-1} (s); ν(NH + OH) 3351, 3318 cm^{-1} (w, br). ^{1}H NMR (CD_2Cl_2): δ 3.35 (br, 2 H, NH + OH; ^2J(PtH) = 24 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 17.6 (s; ^1J(PtP) = 2711 Hz). When this complex is dissolved in CD_2Cl_2, it is converted over a period of several hours into a second isomer, *trans*-PtPh($OCONH_2$)(PCy_3)$_2$, which was identified spectroscopically. IR: ν(CO) 1616 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 6.7–7.6 (m, 5 H, phenyl), δ 4.01 (s, 2 H, NH_2), δ 1.0–1.9 (m, 66 H, cyclohexyl). ^{31}P{^{1}H} NMR: δ 18.9 (s; ^1J(PtP) = 2927 Hz). ^{13}C {^{1}H} NMR: δ 162.5.

X-ray Structure Determination. Crystallographic data for [PtMe(μ-NH_2)PPh_3]$_2$ are summarized in Table I.[6] A colorless

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(6) The transformation matrix (100, 010, 101) will convert the *C*-centered cell we report to an *I*-centered cell with *a* and *b* unchanged, *c* = 27.993 (6) Å, and β = 109.85 (2)°. Except for the altered cell dimensions, nothing we report would have been changed had we chosen to use the more standard cell for data collection and processing.

Table I. Crystallographic Data for $[PtMe(\mu\text{-}NH_2)(PPh_3)]_2$

chem formula $C_{38}H_{40}N_2P_2Pt_2$	space group $C2/c$
fw 976.8	$T = 23$ °C
$a = 22.592$ (5) Å	$\lambda = 0.71073$ Å (Mo Kα)
$b = 11.844$ (3) Å	$P_{calcd} = 1.841$ g cm^{-3}
$c = 29.403$ (6) Å	$\mu = 84.7$ cm^{-1}
$\beta = 116.43$ (2)°	transm coeff 0.154–0.120
$V = 7046$ (6) Å^3	$R(F) = 4.04\%$
$Z = 8$	$R_w(F) = 4.86\%$

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å^2 $\times 10^3$) for $[PtMe(NH_2)PPh_3]_2$

	x	*y*	*x*	*U*[a]
Pt(1)	4261.3 (2)	2183.0 (3)	2391.1 (1)	28.5 (1)
Pt(2)	5040.3 (2)	5707.6 (3)	1984.5 (1)	32.9 (2)
P(1)	3313 (1)	1660 (2)	1763 (1)	30 (1)
P(2)	4399 (1)	6249 (2)	1200 (1)	35 (1)
N(1)	4838 (2)	2627 (7)	2011 (3)	32 (3)
N(2)	4341 (4)	5278 (7)	2263 (3)	39 (4)
C(1)	3892 (5)	1767 (10)	2899 (4)	47 (5)
C(2)	5858 (5)	6079 (11)	1865 (4)	53 (5)
C(11)	3006 (3)	549 (5)	827 (2)	43 (5)
C(12)	2961	495	339	51 (5)
C(13)	3174	1403	147	52 (5)
C(14)	3432	2365	444	47 (5)
C(15)	3477	2418	932	39 (4)
C(16)	3264	1510	1124	31 (4)
C(21)	3546 (3)	−570 (6)	2036 (3)	53 (6)
C(22)	3382	−1690	2075	66 (8)
C(23)	2727	−1985	1937	81 (9)
C(24)	2235	−1160	1760	65 (7)
C(25)	2398	−41	1722	54 (5)
C(26)	3054	255	1860	33 (4)
C(31)	2031 (3)	2502 (5)	1189 (2)	48 (5)
C(32)	1497	3203	1108	59 (6)
C(33)	1552	4008	1471	60 (6)
C(34)	2142	4112	1915	57 (6)
C(35)	2676	3412	1996	50 (5)
C(36)	2621	2607	1632	34 (4)
C(41)	3208 (4)	5452 (5)	1113 (3)	50 (5)
C(42)	2534	5490	981	56 (6)
C(43)	2168	6454	753	64 (6)
C(44)	2476	7381	655	66 (7)
C(45)	3150	7343	787	50 (5)
C(46)	3516	6379	1016	37 (4)
C(51)	4870 (3)	4464 (6)	829 (3)	55 (6)
C(52)	4886	3773	450	66 (8)
C(53)	4427	3932	−55	75 (8)
C(54)	3853	4782	−182	69 (7)
C(55)	3937	5474	197	59 (6)
C(56)	4396	5315	702	39 (5)
C(61)	4567 (4)	8016 (7)	602 (3)	60 (6)
C(62)	4653	9153	523	90 (9)
C(63)	4771	9940	907	94 (9)
C(64)	4803	9590	1370	71 (7)
C(65)	4717	8453	1450	64 (6)
C(66)	4599	7666	1066	44 (5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

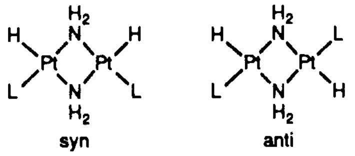
Table III. Selected Bond Distances and Angles in $[PtMe(\mu\text{-}NH_2)(PPh_3)]_2$

	Bond Distances (Å)		
Pt(1)–P(1)	2.205 (2)	Pt(2)–P(2)	2.204 (2)
Pt(1)–C(1)	2.070 (13)	Pt(2)–C(2)	2.077 (14)
Pt(1)–N(1A)	2.079 (7)	Pt(2)–N(2A)	2.085 (7)
Pt(1)–N(1)	2.127 (11)	Pt(2)–N(2)	2.139 (10)
Pt(1A)–N(1)	2.079 (7)	Pt(2A)–N(2)	2.085 (7)
Pt(1)–Pt(1A)	3.106 (1)	Pt(2)–Pt(2A)	3.117 (1)
P(1)–C(16)	1.840 (8)	P(2)–C(46)	1.827 (8)
P(1)–C(26)	1.829 (8)	P(2)–C(56)	1.832 (8)
P(1)–C(36)	1.822 (7)	P(2)–C(66)	1.826 (9)
	Bond Angles (deg)		
P(1)–Pt(1)–N(1)	102.9 (2)	P(2)–Pt(2)–N(2)	102.5 (2)
N(1)–Pt(1)–C(1)	167.7 (3)	N(2)–Pt(2)–C(2)	168.5 (3)
N(1)–Pt(1)–Pt(1A)	41.8 (2)	N(2)–Pt(2)–Pt(2A)	41.8 (2)
P(1)–Pt(1)–C(1)	89.1 (3)	P(2)–Pt(2)–C(2)	88.9 (3)
P(1)–Pt(1)–N(1A)	178.3 (3)	P(2)–Pt(2)–N(2A)	177.2 (2)
C(1)–Pt(1)–N(1A)	90.4 (4)	C(2)–Pt(2)–N(2A)	90.3 (4)
P(1)–Pt(1)–Pt(1A)	136.6 (1)	P(2)–Pt(2)–Pt(2A)	136.2 (1)
C(1)–Pt(1)–Pt(1A)	126.4 (2)	C(2)–Pt(2)–Pt(2A)	127.4 (3)
N(1)–Pt(1)–N(1A)	77.5 (4)	N(2)–Pt(2)–N(2A)	78.2 (3)
Pt(1A)–Pt(1)–N(1A)	43.0 (3)	Pt(2A)–Pt(2)–N(2A)	43.1 (3)
Pt(1)–N(1)–Pt(1A)	95.2 (4)	Pt(2)–N(2)–Pt(2A)	95.1 (3)

specimen (0.26 × 0.29 × 0.34 mm), affixed with epoxy cement to a glass fiber, was found to diffract adequately. The presence of 2-fold symmetry in each of two chemically identical but crystallographically independent molecules affirmed our choice of the centrosymmetric space group $C2/c$. The data were empirically corrected for absorption (six ψ-scan reflections, 216 data). Of 6660 room-temperature data collected (Nicolet R3m/μ, Mo Kα, 2θ(max) = 50°), 6198 were independent and systematically present ($R_{int} = 0.035$), and 4433 with $F_o \geq 3\sigma(F_o)$ were retained as observed data.

The Pt atoms were located by heavy-atom methods. The H atoms attached to N(1) and N(2) were found and isotropically refined. The remaining H atoms were treated as idealized contributions (d(CH) = 0.96 Å). All non-H atoms were anisotropically refined. The phenyl rings were refined as rigid, planar hexagons (d(CC) = 1.395 Å). At convergence, $R(F) = 4.04\%$, $R_w(F) = 4.86\%$ [all data, $R(F) = 6.50\%$, $R_w(F) = 5.71\%$], GOF = 1.051, Δ/σ = 0.08, $\Delta(\rho) = 1.2$ e Å^{-3} (0.92 Å from Pt(1)), $N_o/N_v = 13.0$. All computations used SHELXTL (5.1) software (G. Sheldrick, Nicolet SRD, Madison, WI). Atomic coordinates are given in Table II, and selected bond distances and angles in Table III.

Chart I



Results and Discussion

Synthesis and Reactions of Hydride Amide Platinum Complexes. A convenient starting complex for the synthesis of amide hydride complexes is the cationic ammine hydride complex *trans*-$[PtH(NH_3)(PPh_3)_2]ClO_4$ (1) (^{1}H NMR: δ −15.6 (t)). This complex has been prepared previously from the reaction between ammonia and *trans*-$PtH(ClO_4)(PPh_3)_2$.[5] We have successfully reproduced this synthesis. We find, however, that the ammine complex *trans*-$PtH(NH_3)(PPh_3)_2$ cannot be readily prepared by the direct reaction between *trans*-$PtHCl(PPh_3)_2$ and ammonia but must be synthesized via the perchlorate complex. Treating *trans*-$[PtH(NH_3)(PPh_3)_2]ClO_4$ with sodium amide or sodium 2,6-di-*tert*-butyl-4-methylphenoxide as a suspension in liquid ammonia gives the amide-bridged complex $[PtH(\mu\text{-}NH_2)(PPh_3)]_2$ (9) (eq 1).

$$\underset{\mathbf{1}}{trans\text{-}[PtH(NH_3)(PPh_3)_2]ClO_4} + B^- \rightarrow \tfrac{1}{2}\underset{\mathbf{9}}{[PtH(\mu\text{-}NH_2)PPh_3]_2} + BH + ClO_4^- \quad (1)$$

$$B^- = NH_2^-,\ 4\text{-Me-}2,6\text{-}t\text{-}Bu_2C_6H_2O^-$$

Extraction of this complex into $CDCl_3$ solvent shows that it is formed as a mixture of syn and anti isomers (Chart I) (^{1}H NMR: anti δ −15.08 (d); syn δ −15.11 (d)). The rationale behind this assignment is explained later in the paper. The complex is too unstable in solution to allow for its purification. The route to the synthesis of this bimetallic complex most likely involves the initial formation of the monomer *trans*-$PtH(NH_2)(PPh_3)_2$. For the case of the 2,6-di-*tert*-butyl-4-methylphenoxide anion as base, this initial step involves deprotonation of the complexed ammine ligand. The pK_a of free ammonia is 33, indicative of a very low acidity, but complexation to a cationic platinum(II) center has sufficiently increased the ammine acidity so that it can be deprotonated by this hindered phenoxide base. The increased acidity of ammonia upon complexation to a transition-metal ion is well documented in the literature.[7] For the amide anion we have not differentiated between pathways where NH_2^- acts as a base or as a substitution ligand. We propose that *trans*-$PtH(NH_2)(PPh_3)_2$ is the initial product because precedent suggests that it can readily undergo associative dimerization by triphenylphosphine substitution by the lone electron pair on the amide nitrogen (eq 2).[8] This bimetallic

$$trans\text{-}PtH(NH_2)(PPh_3)_2 \rightarrow \tfrac{1}{2}\underset{\mathbf{9}}{[PtH(\mu\text{-}NH_2)PPh_3]_2} + PPh_3 \quad (2)$$

complex is thermally unstable in a solution of $CDCl_3$ and undergoes reductive elimination of ammonia. This reaction can be followed from intensity changes in the ^1H NMR hydride resonances. The final product is *cis*-$PtCl_2(PPh_3)_2$, and its formation can be explained by the intermediate formation of the 14-electron complex $Pt(PPh_3)_2$. This two-coordinate intermediate is known to undergo chlorine atom abstraction from the $CDCl_3$ solvent to give *cis*-$PtCl_2(PPh_3)_2$ as the final product (eq 3).[9]

$$\tfrac{1}{2}\underset{\mathbf{9}}{[PtH(\mu\text{-}NH_2)PPh_3]_2} + PPh_3 \rightarrow Pt(PPh_3)_2 + NH_3$$

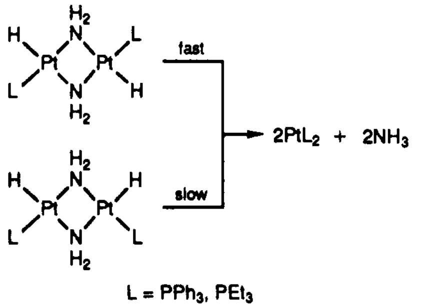
$$Pt(PPh_3)_2 \xrightarrow{CDCl_3} cis\text{-}PtCl_2(PPh_3)_2 \quad (3)$$

A similar chemistry is observed with the triethylphosphine complex *trans*-$[PtH(NH_3)(PEt_3)_2]ClO_4$ (**2**) (^1H NMR: δ −17.7 (t)), which has been prepared in a similar manner to the triphenylphosphine analogue. Again, by ^1H NMR spectroscopy, we observe the formation of a mixture of syn and anti isomers of the dimeric complex $[PtH(\mu\text{-}NH_2)PEt_3]_2$ (**10**) (^1H NMR: anti δ −16.10 (d); syn −15.94 (d)) from the reaction of *trans*-$[PtH(NH_3)(PEt_3)_2]ClO_4$ with sodium amide. Solutions of **10** in C_6D_6 slowly decompose. The stability is higher than is observed for $[PtH(\mu\text{-}NH_2)PPh_3]_2$, which correlates with the stronger donor PEt_3 ligand in **10** stabilizing the amide platinum(II) dimer to reductive elimination. Stoichiometry suggests that reductive elimination of ammonia should give the unobserved intermediate complex $Pt(PEt_3)_2$, which can then undergo ligand disproportionation to yield a mixture of $Pt(PEt_3)_3$ and metallic platinum (eq 4). The formation

$$\tfrac{1}{2}\underset{\mathbf{10}}{[PtH(\mu\text{-}NH_2)PEt_3]_2} + PEt_3 \rightarrow Pt(PEt_3)_2 + NH_3$$

$$Pt(PEt_3)_2 \rightarrow \tfrac{2}{3}Pt(PEt_3)_3 + \tfrac{1}{3}Pt \quad (4)$$

of $Pt(PEt_3)_3$ is verified by the observation of a singlet resonance in the $^{31}P\{^1H\}$ NMR spectrum at δ 42.3 ($^1J(PtP)$ = 4209 Hz) and a quartet resonance in the ^{195}Pt NMR spectrum at δ −4510.[10] Metallic platinum is formed as a black precipitate in the reaction. The formation of both syn and anti isomers of the intermediate $[PtH(\mu\text{-}NH_2)PEt_3]_2$ in C_6D_6 solution has been verified by both ^1H and $^{31}P\{^1H\}$ NMR spectroscopy ($^{31}P\{^1H\}$ NMR: anti δ 10.2; syn δ 9.87). The measurement of $^{31}P\{^1H\}$ NMR resonances is possible in this case because of the higher thermal stability of $[PtH(\mu\text{-}NH_2)PEt_3]_2$ as compared to $[PtH(\mu\text{-}NH_2)PPh_3]_2$. The assignment of the individual spectral lines to each isomer of $[PtH(\mu\text{-}NH_2)PEt_3]_2$ is based on the assumption that $^4J(PP)$ is greater for the anti isomer than it is for the syn; we observe the respective values of 7.3 and 0 Hz for $^4J(PP)$ for the $^{31}P\{^1H\}$ NMR resonances at δ 10.2 (anti) and δ 9.87 (syn).[11] Comparison of the ^1H NMR spectral data between the isomers of $[PtH(\mu\text{-}NH_2)PEt_3]_2$ and $[PtH(\mu\text{-}NH_2)PPh_3]_2$ now allows us to tentatively assign the ^1H NMR spectral parameters of the syn and anti isomers of $[PtH(\mu\text{-}NH_2)PPh_3]_2$. The assignments for *anti*- and *syn*-$[PtH(\mu\text{-}NH_2)PPh_3]_2$ are based on the observation that for complexes $[PtX(\mu\text{-}NH_2)L]_2$ (X = H, Me; L = tertiary phosphine) the ^1H NMR resonance of the bridging amide is further upfield in the syn than in the anti isomer. For the triphenylphosphine complex we observe hydride resonances at δ −15.08 (anti) and δ −15.11 (syn), and for the corresponding triethylphosphine complexes at δ −16.10 (anti) and δ −15.94 (syn). The reductive elimination of ammonia, as followed by the rate of loss of the hydride resonances in the ^1H NMR spectrum, is faster for the anti isomer than for the syn isomer (eq 5). This result can be



(5)

explained on the basis of the known chemistry of platinum(II) complexes. Generally, reductive elimination from platinum(II) is favored by the two ligands being in mutually cis coordination positions.[12] If the complex $[PtH(\mu\text{-}NH_2)L]_2$ follows an analogous pathway, we can expect that the elimination of ammonia is favored by the presence of mutually cis hydride and amide ligands at both platinum centers. This stereochemistry is found in the anti isomer.

Using an analogous synthetic procedure, we have synthesized the cationic complex *trans*-$[PtH(NH_3)(PCy_3)_2]ClO_4$ (**3**) (^1H NMR: δ −18.5 (t)). This complex, as a suspension in liquid ammonia, reacts with sodium amide to give the *monomeric* complex *trans*-$PtH(NH_2)(PCy_3)_2$ (**16**) (eq 6). The trans stereochemistry of this amide hydride

$$trans\text{-}\underset{\mathbf{3}}{[PtH(NH_3)(PCy_3)_2]ClO_4} + NaNH_2 \rightarrow trans\text{-}\underset{\mathbf{16}}{PtH(NH_2)(PCy_3)_2} + NH_3 + NaClO_4 \quad (6)$$

16 is verified by the observation of a triplet upfield hydride resonance at δ −13.75 ($^2J(PH)$ = 16.2 Hz).[13] This chemical shift value places the trans influence of the amide ligand close to that of iodide but larger than that of chloride (for *trans*-$PtHI(PCy_3)_2$, δ −13.9; for *trans*-$PtHCl(PCy_3)_2$, δ −18.8).[14] This monomeric hydride amide complex is

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[7] Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1967; p 33.

[8] Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *Inorg. Chem.* **1987**, *26*, 973–976. Alcock, N. W.; Bergamini, P.; Kemp, T. J.; Pringle, P. G. *J. Chem. Soc., Chem. Commun.* **1987**, 235–236.

[9] Kramer, A. V.; Labinger, J. A.; Bradley, J. S.; Osborn, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 7145–7147.

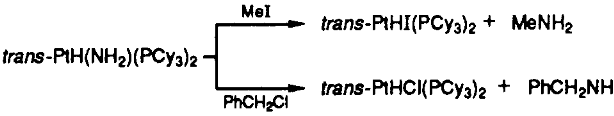
[10] Mann, B. E.; Musco, A. J. *J. Chem. Soc., Dalton Trans.* **1980**, 776–785.

[11] Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: New York, 1979.

[12] Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 1988; Chapter 6.

[13] Roundhill, D. M. *Adv. Organomet. Chem.* **1975**, *13*, 273–361.

thermally stable in benzene solution, even at reflux temperature. This monomeric complex is therefore stabilized against substitution dimerization because of the bulky tricyclohexylphosphine ligand and against reductive elimination because the hydride and amide ligands are mutually separated in the trans isomer. The isolation of the stable complex *trans*-$PtH(NH_2)(PCy_3)_2$ shows that amide hydride complexes can be isolated if sterically bulky substituents are attached to the supporting ligands. This complex is significant because monomeric amides of the later transition metals are very uncommon, especially examples of complexes having an unsubstituted NH_2 ligand.[1] The complex *trans*-$PtH(NH_2)(PCy_3)_2$ reacts with methyl iodide to give *trans*-$PtHI(PCy_3)_2$ and with benzyl chloride to give *trans*-$PtHCl(PCy_3)_2$ (eq 7). The product amine

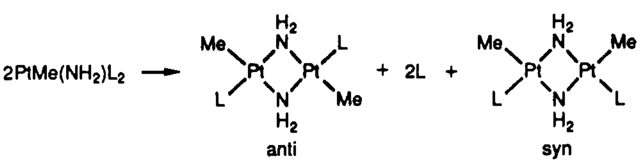


$$trans\text{-}PtH(NH_2)(PCy_3)_2 \begin{cases} \xrightarrow{MeI} trans\text{-}PtHI(PCy_3)_2 + MeNH_2 \\ \xrightarrow[PhCH_2Cl]{} trans\text{-}PtHCl(PCy_3)_2 + PhCH_2NH_2 \end{cases} \quad (7)$$

has not been detected either by ^1H NMR spectroscopy or by mass spectroscopy. The quantity of amine formed is expected to be only in the millimolar range, and efficient trapping by the excess alkylating agent will give the nonvolatile compounds $[Me_2NH_2]I$ and $[(PhCH_2)_2NH_2]Cl$. This complex *trans*-$PtH(NH_2)(PCy_3)_2$ is the expected product from the addition of ammonia to $Pt(PCy_3)_2$; both we and others have found that this addition reaction does not occur.[15] The isolation of *trans*-$PtH(NH_2)(PCy_3)_2$ suggests that the failure of $Pt(PCy_3)_2$ to react with ammonia is due to kinetic rather than thermodynamic factors. Indeed, even under reflux conditions in benzene solvent, we do not observe any reductive elimination of ammonia from *trans*-$PtH(NH_2)(PCy_3)_2$. Thermochemical data place the enthalpy of a Pt–H bond in the 60 kcal/mol range.[16] If we use the linear correlation diagram between H-NH_2 and Pt–NH_2, we arrive at an approximate value of 50 kcal/mol for the Pt–N bond enthalpy.[17] These rough estimates of the Pt–H and Pt–N bond enthalpies lead to the conclusion that the oxidative addition of ammonia, with a bond enthalpy of 107 kcal/mol, to platinum(0) is approximately thermoneutral.

Synthesis and Reactions of Methyl Amide Platinum Complexes. If transition-metal complexes are to be developed for use as homogeneous catalysts for the addition of N-H bonds to alkenes, it is useful to acquire information about the thermal stability of amide alkyl as well as amide hydride complexes.[18] We have therefore used a synthetic strategy similar to that of the amide hydrides to synthesize both *dimeric* and *monomeric* methyl amide complexes having the structures $[PtMe(\mu\text{-}NH_2)L]_2$ and *trans*-$PtMe(NH_2)L_2$, where L is a tertiary phosphine. The cationic precursor complexes *trans*-$[PtMe(NH_3)L_2]ClO_4$ (L = PPh_3 (**4**), PEt_3 (**5**), $PMePh_2$ (**6**), PCy_3 (**7**) (^1H NMR: δ 0.07 (t) (**4**), δ 0.19 (t) (**5**), δ 0.23 (t) (**6**), δ 0.25 (t) (**7**)) have been prepared by the reaction of ammonia with trans-$PtMe(ClO_4)L_2$ (eq 8). These complexes have been

Scheme I



$$trans\text{-}PtMe(ClO_4)L_2 + NH_3 \rightarrow trans\text{-}[PtMe(NH_3)L_2]ClO_4 \quad (8)$$

isolated, purified, and characterized by a combination of microanalytical methods and both ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The complexes have ^1H NMR resonances of equal intensity for the methyl and ammine ligands. The respective $^2J(PtH)$ values are approximately 75 Hz for the Pt–CH_3 group and 25 Hz for the Pt–NH_3 group. The cis complex $[PtMe(NH_3)dppe]ClO_4$ (**8**) (^1H NMR: δ 0.46 (dd)) has also been prepared, and the respective values of ^2J(PtH) for the methyl and ammonia resonances are now 55 and 40.9 Hz.

The complexes *trans*-$[PtMe(NH_3)L_2]ClO_4$ do not react with strong organic bases such as DABCO and DBN. Reaction with the amide ion does, however, result in the initial formation of the neutral complexes *trans*-$PtMe(NH_2)L_2$ (eq 9). For L = PCy_3 the reaction does not

$$trans\text{-}[PtMe(NH_3)L_2]ClO_4 + NaNH_2 \rightarrow trans\text{-}PtMe(NH_2)L_2 + NaClO_4 + NH_3 \quad (9)$$

proceed further. The complex *trans*-$PtMe(NH_2)(PCy_3)_2$ (**17**) (^1H NMR: δ 0.38 (t)) is stable in solution, and it undergoes no change when refluxed in benzene for several hours under an inert atmosphere. The complex *trans*-$PtMe(NH_2)(PCy_3)_2$ reacts with CF_3SO_3H to give *trans*-$[PtMe(NH_3)(PCy_3)_2]CF_3SO_3$. The reactions with methyl iodide and carbon monoxide lead to mixtures of products. The $^{31}P\{^1H\}$ NMR spectrum of the carbonylated solution shows multiple resonances due to the formation of a series of inseparable complexes. The ^1H NMR spectrum indicates that CO has inserted into both the Pt–Me and the Pt–NH_2 bonds, but we have been unable to find the experimental conditions that yield a single product.

For the case where L = PPh_3, PEt_3, and $PMePh_2$, the monomeric amide methyl complexes undergo subsequent substitution dimerization to yield a mixture of the syn and anti isomers of $[PtMe(\mu\text{-}NH_2)L]_2$ (Scheme I). For the case of L = PEt_3, the intermediate monomeric complex *trans*-$PtMe(NH_2)(PEt_3)_2$ is observed in the reaction solution. The following spectral data identify this intermediate monomeric complex: ^1H NMR (C_6D_6) δ 0.26 (t, 3 H, CH_3; $^3J(PH)$ = 6.1 Hz, $^2J(PtH)$ = 62.8 Hz), δ −0.16 (br, 2 H, NH_2); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 15.0 (s; $^1J(PtP)$ = 2937 Hz). For the final dimeric product the relative amounts of syn and anti isomer formed are dependent on the tertiary phosphine L. For the dimeric complexes $[PtMe(\mu\text{-}NH_2)L]_2$ the respective percentages of the anti isomer formed are 100%, 75%, and 50% for L being PPh_3 (**11**), $PMePh_2$ (**13**), and PEt_3 (**12**). These percentages were obtained by intergration of the individual NMR resonances, and the numerical values correlate with a steric argument. When the phosphine L is changed, the percentage of syn isomer, which has the tertiary phosphines L in closer proximity than does the anti isomer, is smaller for the bulkier ligands. We have been unable to separate and individually isolate the syn and anti isomers of complexes **12** and **13** because of their similar solubility in organic solvents.

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(14) Miyamoto, T. *J. Organomet. Chem.* **1977**, *134*, 335–362. Leviston, P. V.; Wallbridge, M. G. H. *J. Organomet. Chem.* **1976**, *110*, 271–279.

(15) Fornies, J.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1006–1009.

(16) Low, J. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1984**, *106*, 6928–6937.

(17) If we take the Pt–NMe_2 bond as 36 kcal/mol (see: Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444–1456. Park, S.; Pontier Johnson, M.; Roundhill, D. M. *Inorg. Chem.* **1990**, *29*, 2689–2697), we can estimate the Pt–NH_2 bond enthalpy to be 51 kcal/mol, on the basis of the difference of 15 kcal/mol between the N–H bond enthalpies of NH_3 and $NHMe_2$ (McMillen, D. P.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532.)

(18) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444–1456. Buckner, S. W.; Gord, F. R.; Freiser, B. S. *J. Am. Chem. Soc.* **1988**, *110*, 6606–6612.

Table IV. ^{1}H NMR Shift Data for the Methyl and Amide Resonances

	δ(Me)	δ(NH_2)
anti-$[PtH(\mu\text{-}NH_2)PPh_3]_2$ (*anti*-**9**)		0.06
syn-$[PtH(\mu\text{-}NH_2)PPh_3]_2$ (*syn*-**9**)		-1.10
anti-$[PtH(\mu\text{-}NH_2)PEt_3]_2$ (*anti*-**10**)		-0.09
syn-$[PtH(\mu\text{-}NH_2)PEt_3]_2$ (*syn*-**10**)		-0.96
anti-$[PtMe(\mu\text{-}NH_2)PEt_3]_2$ (*anti*-**12**)	0.58	-0.54
syn-$[PtMe(\mu\text{-}NH_2)PEt_3]_2$ (*syn*-**12**)	0.57	-1.40
anti-$[PtMe(\mu\text{-}NH_2)PMePh_2]_2$ (*anti*-**13**)	0.57	-0.35
syn-$[PtMe(\mu\text{-}NH_2)PMePh_2]_2$ (*syn*-**13**)	0.65	-1.81
anti-$[PtMe(\mu\text{-}NH_2)PCy_3]_2$ (*anti*-**21**)	0.65	-0.29
syn-$[PtMe(\mu\text{-}NH_2)PCy_3]_2$ (*syn*-**21**)	0.56	-0.39
anti-$[PtMe(\mu\text{-}NH_2)PPh_3]_2$ (**11**)	0.55	-0.24
cis-$PtMe(NH_2)(PPh_3)_2$ (**14**)	1.13	2.30
cis-$PtMe(NH_2)(PEt_3)_2$ (**15**)	*a*	3.40
trans-$PtH(NH_2)(PCy_3)_2$ (**16**)		0.41
trans-$PtMe(NH_2)(PCy_3)_2$ (**17**)	0.38	-0.28
trans-$PtPh(NH_2)(PCy_3)_2$ (**19**)		0.09
trans-$PtMe(NH_2)(PEt_3)_2$	0.26	-0.16

[a] Peak overlapped with those from triethylphosphine.

The ^{1}H NMR resonances for the complexed amide (NH_2) ligand are upfield shifted when compared with those resonances of the complexed ammine (NH_3) ligand in the complexes *trans*-$[PtMe(NH_3)L_2]ClO_4$ (L = PPh_3, PEt_3, $PMePh_2$, PCy_3). The chemical shift of the amide ligand is upfield by approximately 2–3 ppm from that in the ammine analogue complex. For example, the chemical shifts in the complexes *trans*-$[PtH(NH_3)L_2]ClO_4$ and *trans*-$[PtMe(NH_3)L_2]$ fall in the δ 1.74–3.46 range, whereas the chemical shifts in both the monomeric and dimeric amide complexes fall in the δ 0.41 to −1.81 range. For the amide-bridged complexes *trans*-$[PtMe(\mu\text{-}NH_2)L]_2$ (L = PEt_3, $PMePh_2$) the amide hydrogens are upfield shifted further for the syn isomer than for the anti isomer. The shift positions for the amide complexes are collected in Table IV, where it is apparent that the amide resonances are usually upfield of those observed for the complexed methyl ligand. The only exception is for *cis*-$PtMe(NH_2)L_2$ (L = PPh_3, PEt_3) where both the methyl and amide ligands are trans to phosphorus rather than being mutually trans to each other. These shift values of the amide ligand to high field correlate with that found for alkyl ligands. This trend is found for methylamine itself, since in C_6D_6 solvent the CH_3 and NH_2 resonances are found at δ 2.18 and 0.19, respectively.

Crystal Structure of *anti*-$[PtMe(\mu\text{-}NH_2)PPh_3]_2$ (11). The X-ray crystal structure of *anti*-$[PtMe(\mu\text{-}NH_2)PPh_3]_2$ (**11**) has been solved. The structure confirms the stereochemistry and the stoichiometry as a symmetric dimer. The asymmetric unit consists of two independent but chemically identical half molecules on sites with a common 2-fold rotation axis. The two crystallographically independent molecules of *anti*-$[PtMe(\mu\text{-}NH_2)PPh_3]$ are associated by Pt···H interactions (Figures 1 and 2). The crystallographic data are collected in Table I, and atomic coordinates, selected bond distances, and selected bond angles are collected in Tables II–IV. The presence of two separate molecules in the crystal results in there being two sets of distances. The respective Pt(1)–Pt(1A) and Pt(2)–Pt(2A) distances are 3.106 (1) and 3.117 (1) Å, which are longer than expected for any significant Pt–Pt bonding. The Pt(1)–C(1) and Pt(2)–C(2) distances are 2.070 (13) Å and 2.077 (14) Å respectively, values which correspond with those expected for a single Pt–C bond. The Pt–N–Pt bridge distances are slightly unsymmetrical. The observed distances are the following: Pt(1)–N(1), 2.127 (11) Å; Pt(1A)–N(1), 2.079 (7) Å; Pt(2)–N(2), 2.139 (10) Å; Pt(2A)–N(2), 2.085 (7) Å. The angles within the bridge are as follows: N(1)–Pt(1)–Pt(1A), 77.5 (4)°; N(2)–Pt(2)–N(2A), 78.2 (3)°; Pt(1)–N(1)–Pt(1A), 95.2 (4)°; Pt(2)–N(2)–Pt(2A), 95.1 (3)°.

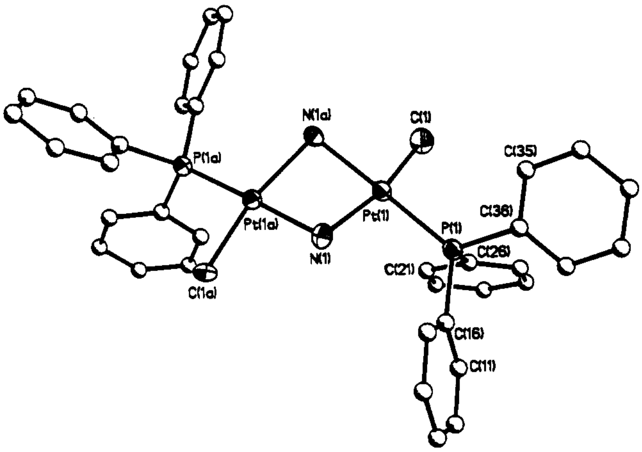

Figure 1. Molecular structure and labeling scheme for one molecule of two crystallographically independent molecules of $[PtMe(\mu\text{-}NH_2)PPh_3]_2$ associated by Pt···H interactions (see Figure 2).

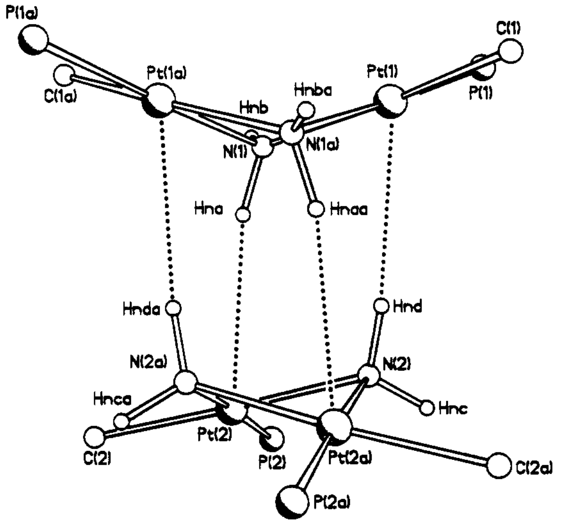

Figure 2. Association of the two crystallographically independent but chemically identical molecules of $[PtMe(\mu\text{-}NH_2)PPh_3]_2$ through the formation of 2.58- and 2.82-Å Pt···H interactions. The Pt(1)–Pt(1A) and Pt(2)–Pt(2A) vectors are in parallel planes with a 71.2° twist angle between these vectors when projected down the 2-fold crystallographic axis.

Reactions of Methyl Amide Platinum Complexes. The complexes $[PtMe(\mu\text{-}NH_2)L]_2$ (L = PPh_3, PEt_3) in C_6D_6 solution undergo bridge cleavage with added tertiary phosphines L to give solutions containing the monomeric complexes *cis*-$PtMe(NH_2)L_2$ (^{1}H NMR: δ 1.13 (dd) (L = PPh_3)) (eq 10). The reaction is very slow at room temperature, requiring up to 2 weeks to produce a solution containing predominantly the monomer, as evidenced by NMR integration. These monomeric cis complexes do not undergo reductive elimination of methylamine even though the stereochemistry makes this reaction potentially facile. The stereochemistry of this cleavage reaction corresponds to a substitution pathway whereby the large trans effect of the methyl group preferentially labilizes the Pt–N bridge bond opposite to it.[19] For the case of **11** (L = PPh_3), where

$$[PtMe(\mu\text{-}NH_2)L]_2 + 2L \rightarrow 2cis\text{-}PtMe(NH_2)L_2 \qquad (10)$$

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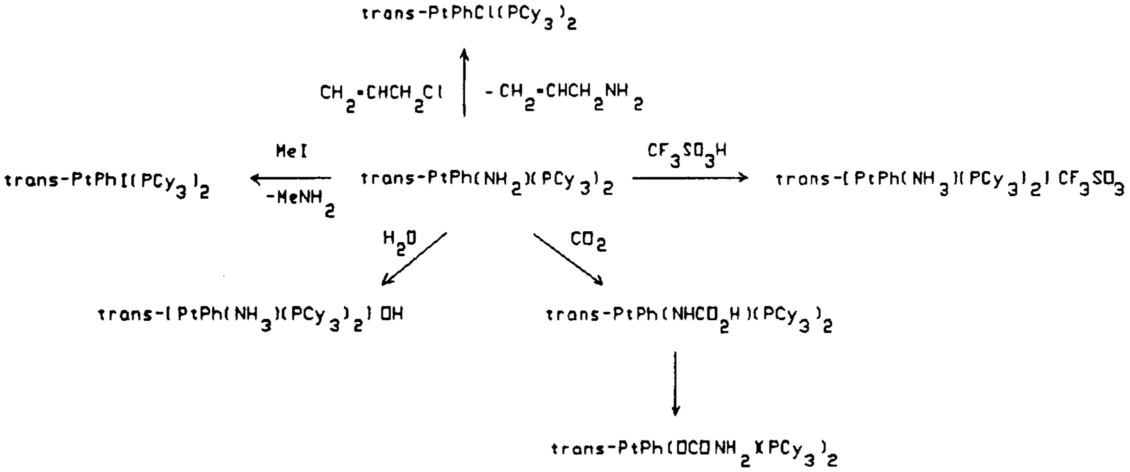
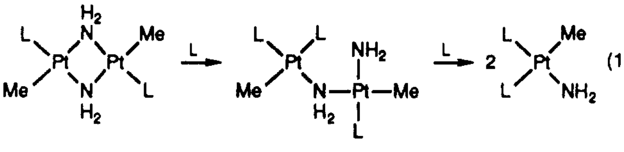
[19] Basolo, F.; Chatt, J.; Gray, H. B.; Pearson, R. G.; Shaw, B. L. *J. Chem. Soc.* **1961**, 2207–2215.

Scheme II

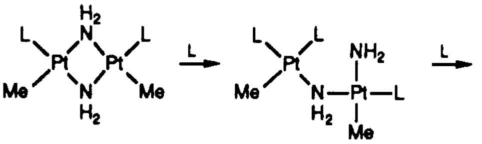


the percentage of the anti complex is 100%, *cis*-PtMe(NH_2)(PPh_3)$_2$ is the expected product for a stereoselective substitution reaction at each platinum center (eq 11). For


(11)

L = PPh_3

the case of 12 (L = PEt_3), where the solution contains equal amounts of the anti and syn isomers, stereoselective substitution trans to the methyl group should give *cis*-PtMe(NH_2)(PEt_3)$_2$ and *trans*-PtMe(NH_2)(PEt_3)$_2$ in a 3/1 ratio. This prediction is a consequence of *anti*-[PtMe(μ-NH_2)PEt_3]$_2$ giving only *cis*-PtMe(NH_2)(PEt_3)$_2$ (eq 11; L = PEt_3) and *syn*-[PtMe(μ-NH_2)PEt_3]$_2$ giving equal amounts of *cis*-PtMe(NH_2)(PEt_3)$_2$ and *trans*-PtMe(NH_2)(PEt_3)$_2$ (eq 12). This second step requires substi-



cis-PtMe(NH_2)L_2 + *trans*-PtMe(NH_2)L_2 (12)

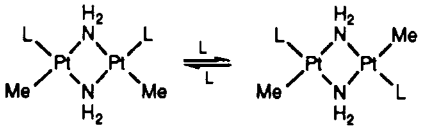
L = PEt_3

tution trans to triethylphosphine. Our observation that *cis*-PtMe(NH_2)(PEt_3)$_2$ ($^{31}P\{^1H\}$ NMR: δ P_A 19.6 (d), δ P_B 2.38 (d)) is the sole product implies that *trans*-PtMe(NH_2)(PEt_3)$_2$ isomerizes to cis, which is unlikely, or that *syn*-[PtMe(μ-NH_2)PEt_3]$_2$ can isomerize to *anti*-[PtMe(μ-NH_2)PEt_3]$_2$ and that the monomer is in equilibrium with the dimer. Our results with [PtMe(μ-NH_2)PCy_3]$_2$ discussed below show that the syn isomer can convert to the *anti* isomer, thereby validating the feasibility of the latter pathway.

The failure to observe bridged amide complexes with tricyclohexylphosphine under experimental conditions where complexes of the other phosphines yield dimers is likely due to the steric inhibition of substitution dimerization. In order to verify that tricyclohexylphosphine dimers are stable, we have explored an alternative route to amide dimers that have terminal tricyclohexylphosphine ligands. Treating [PtMe(μ-Cl)PCy_3]$_2$ with silver perchlorate followed by ammonia gas gives *cis*-[PtMe(NH_3)$_2$$PCy_3$]$ClO_4$ (**20**) (^1H NMR: δ 0.23). Complex **20** reacts with sodium amide to give the bridged complex [PtMe(μ-NH_2)PCy_3]$_2$ (**21**) (^1H NMR: anti δ 0.65 (d), syn δ 0.56 (d)) (eq 13) as a mixture of anti and syn isomers in

$$\underset{\mathbf{20}}{cis\text{-}[PtMe(NH_3)_2PCy_3]ClO_4} + NaNH_2 \rightarrow \tfrac{1}{2}\underset{\mathbf{21}}{[PtMe(\mu\text{-}NH_2)PCy_3]_2} + 2NH_3 + NaClO_4 \quad (13)$$

equal amounts. When the benzene solution of this isomeric mixture is allowed to stand for 12 h at ambient temperature, the syn isomer precipitates. This pure isomer is characterized by a single $^{31}P\{^1H\}$ NMR resonance in $CDCl_3$ solution at δ 17.9. When an excess of tricyclohexylphosphine is added to this solution, the complex isomerizes to a mixture of the syn and anti isomers containing approximately equal amounts of each (eq 14). This ratio


(14)

L = PCy_3

of syn/anti is the same as that obtained in the synthesis from *cis*-[PtMe(NH_3)$_2$$PCy_3$]$ClO_4$, strongly suggesting that this ratio is that of a mixture at equilibrium. After several days at ambient temperature, the bridge cleavage product *trans*-PtMe(NH_2)(PCy_3)$_2$ begins to be formed in the solution containing [PtMe(μ-NH_2)PCy_3]$_2$ and PCy_3. The formation of the trans isomer rather than the expected cis reflects the thermodynamic preference for the former isomer when the bulky tricyclohexylphosphine ligand is used.

Synthesis and Reactions of Phenyl Amide Platinum Complexes. In view of our failure to observe selective reaction chemistry with the methyl amide complexes, we have synthesized the phenyl analogues. The strategy behind this variation is based on the premise that the observed low selectivity in the reaction of the methyl amide complexes with small molecules may be a consequence of chemical reactions occurring at both the methyl and amide ligands. According to recent studies, a metal–phenyl bond is stronger than a metal–methyl bond.[20]

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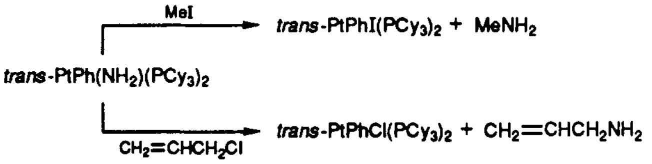
(20) Collman, J. P.; Hegedus, L. S.; Norton, F. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 102. On the contrary there is *kinetic* evidence that carbonyl insertion into a platinum–phenyl bond is faster than into a platinum–methyl bond (see: Anderson, G. K.; Cross, R. J. *Acc. Chem. Res.* **1984**, *17*, 67–74).

We have therefore prepared monomeric phenyl amide complexes of platinum(II) with tricyclohexylphosphine ligands in order to try and direct selectivity toward the Pt–NH_2 bond. Treating *trans*-$PtPhCl(PCy_3)_2$ with $AgClO_4$, followed by ammonia gas, gives *trans*-$[PtPh(NH_3)(PCy_3)_2]ClO_4$ (**18**) ($^{31}P\{^1H\}$ NMR: δ 17.7 (s)). This complex reacts with the amide ion to give *trans*-$PtPh(NH_2)(PCy_3)_2$ (**19**) ($^{31}P\{^1H\}$ NMR: δ 17.0 (s)) (eq 15).

$$\underset{\mathbf{18}}{trans\text{-}[PtPh(NH_3)(PCy_3)_2]ClO_4} + NaNH_2 \rightarrow \underset{\mathbf{19}}{trans\text{-}PtPh(NH_2)(PCy_3)_2} + NaClO_4 + NH_3 \quad (15)$$

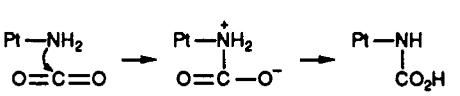
Treating *trans*-$PtPh(NH_2)(PCy_3)_2$ with trifluorosulfonic acid or water gives the ammine cation complexes *trans*-$[PtPh(NH_3)(PCy_3)_2]X$ (X = CF_3SO_3, OH). Treating *trans*-$PtPh(NH_2)(PCy_3)_2$ with methyl iodide or allyl chloride gives *trans*-$PtPhX(PCy_3)_2$ (X = I, Cl) (eq 16). The amine products have not been detected.



$$trans\text{-}PtPh(NH_2)(PCy_3)_2 \xrightarrow{MeI} trans\text{-}PtPhI(PCy_3)_2 + MeNH_2$$
$$trans\text{-}PtPh(NH_2)(PCy_3)_2 \xrightarrow[CH_2=CHCH_2Cl]{} trans\text{-}PtPhCl(PCy_3)_2 + CH_2{=}CHCH_2NH_2$$

(16)

Carbon dioxide reacts with *trans*-$PtPh(NH_2)(PCy_3)_2$ in benzene solvent with the precipitation of *trans*-$PtPh(NHCO_2H)(PCy_3)_2$ (**22**) (ν(CO) 1602 cm^{-1}, ν(NH + OH) 3351, 3318 cm^{-1}; ^1H NMR δ 3.35 (br, N*H*; ^2J(PtH = 24 Hz))).[21] This N-bonded carbamato complex is formed by electrophilic attack at the amide nitrogen by the carbon atom of carbon dioxide (eq 17). When this carbamato-*N*



$$\underset{O=C=O}{Pt{-}NH_2} \longrightarrow \underset{O=C{-}O^-}{Pt{-}\overset{+}{N}H_2} \longrightarrow \underset{CO_2H}{Pt{-}NH} \quad (17)$$

complex is dissolved in dichloromethane, isomerization to the O-bonded complex *trans*-$PtPh(OCONH_2)(PCy_3)_2$ (ν(CO) 1616 cm^{-1}; ^1H NMR δ 4.01 (s, NH_2); ^{13}C $\{^1H\}$ NMR δ 162.5) occurs.[22] This O-bonded isomer can be obtained in a single step by reacting *trans*-$PtPh(NH_2)(PCy_3)_2$ with carbon dioxide in dichloromethane solvent, when the N-isomer *trans*-$PtPh(NHCO_2H)(PCy_3)_2$ is observed as an intermediate in solution. These transformations are shown in Scheme II.

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Supplementary Material Available: Tables of atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, and H atom coordinates and isotropic thermal parameters (4 pages); a listing of F_o and F_c values (37 pages). Ordering information is given on any current masthead page.

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[21] Glueck, D. S.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* 1989, *111*, 2719–2721.

[22] Monodentate dimethylcarbamate ligands are known with ν(CO) in the 1630–1640-cm^{-1} range; see: Chisholm, M. H.; Extine, M. W. *J. Am. Chem. Soc.* 1977, *99*, 782–792.

Synthesis of Platinum(II) Hydroxycarbonyl Complexes and Related Species and Their Reactions with Hydrogen Peroxide: Existence of Organometallic Peroxy Acids

Ivana Torresan,[1a] Rino A. Michelin,[1b] Andrea Marsella,[1a] Andrea Zanardo,[1a] Francesco Pinna,[1a]
and Giorgio Strukul*,[1a]

Department of Chemistry, University of Venice, 30123 Venice, Italy,
and Institute of Industrial Chemistry, University of Padua, 35100 Padua, Italy

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The synthesis and characterization of a class of complexes of the type $P_2Pt(Rx)(COOH)$ (P_2 = $(PPh_3)_2$, $(PPh_2Me)_2$, dppe, diphoe, dppp; Rx = CF_3, Me, Ph) obtained by insertion of CO into the Pt–OH bond of the corresponding hydroxo complexes is reported, together with their reactivity toward MeOH, $P_2Pt(CF_3)(OH)$, and $P_2Pt(CF_3)(OOH)$ species (P_2 = diphosphine). The reaction between PtCOOH and PtOH complexes leads to the formation of CO_2-bridged dinuclear species. The reactions of all the carboxy compounds with hydrogen peroxide were studied with the aim of finding a synthetic route to organometallic peroxy acids. Spectroscopic studies suggest the existence of transient hydroperoxy species of the type $PtCOO_2H$; however, attempts to exploit their oxidizing properties in the oxidation of olefins resulted only in the catalytic oxidation of carbon monoxide.

Introduction

Hydrogen peroxide is a poor oxidant for organic synthesis, but it is a key starting material for the preparation of organic peroxy acids, which are very versatile reagents in a variety of organic oxidation reactions, including the synthesis of epoxides and glycols from olefins, sulfoxides and sulfones from sulfides, tertiary amine oxides from tertiary amines, and esters or lactones from ketones.[2] Organic peroxy acids are also employed in industry, for example in the Bayer–Degussa[3] and Propylox[4] processes

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[1] (a) University of Venice. (b) University of Padua.

[2] For general reviews of this argument see: (a) Plesnicar, B. In *Oxidation in Organic Chemistry*; part C; Trahanovsky, W. S., Ed.; Academic Press: New York, 1978; Part C, p 211. (b) Bouillon, G.; Lick, C.; Shank, K. In *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; Chapter 10, p 279.

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