trends are demonstrated qualitatively by the selection of vibrational frequencies shown in Table II. It is noted that the observed frequencies for Re-Re, which occur over a narrow range,[1] do not include any fully bridged molecules without axial ligands. A detailed examination of these effects should be a fruitful area for future application of molecular mechanics to the study of dimetal systems.

Acknowledgment. I am grateful to Professor F. A. Cotton for the hospitality extended while this work was carried out in his laboratory and for alerting me to many of the problems treated here and also to the University of the Witwatersrand for granting me a year's sabbatical leave.

Registry No. Cr, 7440-47-3; Mo, 7439-98-7; W, 7440-33-7; Re, 7440-15-5.

Contribution from the Department of Chemistry, Tulane University, New Orleans, Louisiana 70118

Synthesis of New Hybrid Phosphine Amine and Phosphine Amide Compounds. Preparation of a Series of New Phosphine Amido Chelate Complexes of Palladium(II) and Platinum(II) and Their Reactions with Bases and Brønsted Acids

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Received March 15, 1985

The phosphine amine and phosphine amide compounds *o*-$Ph_2PC_6H_4NHCH_2Ph$ (PNHBz), *o*-$Ph_2PC_6H_4CH_2NHPh$ (PCNHPh), *o*-$Ph_2PC_6H_4NHC(O)Ph$ (PNH(CPhO)), and *o*-$Ph_2PC_6H_4C(O)NHPh$ (P(CO)NHPh) have been synthesized and characterized. The reaction of PNH(CPhO) or P(CO)NHPh with $PtCl_4^{2-}$ or $PdCl_4^{2-}$ gives *trans*-$PtCl_2L_2$ or -$PdCl_2L_2$ (L = PNH(CPhO) or P(CO)NHPh)) where L is bonded monodentately through phosphorus. Treatment of these complexes with bases can be used to synthesize the N-bonded amido complexes *cis*- and *trans*-$M(P(CO)NPh)_2$ (M = Pd, Pt) and *cis*-$Pt(PN(CPhO))_2$. The amido complexes react with HCl to give $MCl_2(PNH(CPhO))_2$ and $MCl_2(P(CO)NHPh)_2$ (M = Pd, Pt). Structures are deduced by a combination of IR, ^1H NMR, and $^{31}P\{^1H\}$ NMR techniques.

The coordination chemistry of chelate ligands having mixed functionality types has received extensive study. An important aspect of this work is the development of hybrid ligands where one arm of the chelate is a tertiary phosphine that will selectively coordinate to group 8-10[22] elements of the second- and third-row transition metals.[1] These functionalized phosphines have been used as chelate ligands in complexes where it is desirable to have a hinging chelate arm available for ready substitution.[2] Alternatively the concept has been used to complex functional groups that usually only poorly coordinate[3] or to assemble hybrid ligands for the synthesis of heterobimetallics.[4] With this intramolecular effect, "chelate-assisted oxidative addition" has been induced with C-H,[5] Si-H,[6] N-H,[7] and C-C[8] bonds. In general, these reactions can be considered to be analogous to the well-known ortho-metalation reactions, where the close proximity between the ortho hydrogen and the transition-metal center enhances the reactivity.[9]

The feasibility of effecting O-H or N-H cleavage by these intramolecular-assisted reactions with functionalized phosphines was apparent after the synthesis of *o*-(diphenylphosphino)phenol[10] and *o*-(diphenylphosphino)aniline.[11] If we pursue the analogy that the ortho-metalation reaction is a good model for N-H activation, we will facilitate the insertion of a metal center into the N-H bond if the amino group has bulky substituents incorporated into the amide or secondary amine.[12] This paper describes the synthesis of our new hybrid phosphine amine and phosphine amide ligands and also the preparation of the phosphine amide complexes with platinum(II) and palladium(II). In addition to the characterization of the amide complexes, this first paper of ours from the project describes the reaction chemistry of the amide and amido complexes with external bases and acids, to effect the interconversion between complexed-amido and free-amide functionalities.

The secondary-amide- and amine-functionalized tertiary phosphines described in this paper are functionalized triphenylphosphines. The syntheses take full advantage of the properties of triarylphosphines, which can be easily modified by known synthetic procedures. Every attempt has been made to develop methods that allow for facile modification of the R substituent in *o*-$Ph_2PC_6H_4NHR$ while the integrity of the remainder of the

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molecule is retained. The choice of triaryl- over trialkylphosphines simply reflects our preference for using organophosphorus compounds that have the highest oxidative stability at phosphorus.

Experimental Section

Physical Measurements. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. IR spectra (4000–600 cm^{-1}) were recorded on a Perkin-Elmer Model 383 spectrometer as Nujol mulls. ^1H NMR spectra were obtained on a Nicolet NTC-200 spectrometer at 200 MHz as $CDCl_3$ solutions using with internal Me_4Si reference. $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were obtained at 15.03 and 24.15 MHz, respectively, on a JEOL FX60 spectrometer as $CDCl_3$ solutions. ^{13}C NMR spectra were referenced to internal Me_4Si ($\delta = 0.00$) or $CDCl_3$ ($\delta = 77.0$). ^{31}P NMR spectra were referenced to 85% H_3PO_4 in acetone-d_6 by substitution. All NMR shifts are referenced as high frequency positive. Combustion analyses were performed by Galbraith Laboratories Inc.

Materials. Tetrahydrofuran was dried by refluxing over purple sodium/benzophenone in a nitrogen atmosphere, a freshly distilled sample being collected immediately prior to each use. Pyridine was sequentially dried and distilled from powdered KOH and CaH_2 and then stored under a nitrogen atmosphere over activated 3A molecular sieves. Benzoyl chloride was vacuum distilled and used immediately. Acid-free benzaldehyde was obtained by washing a 50-mL portion with 10-mL portions of 10% aqueous sodium carbonate until CO_2 evolution ceased. The organic portion was dried over $MgSO_4$ and collected by vacuum distillation. The compounds *o*-(diphenylphosphino)aniline,[11] *o*-(diphenyloxophosphoranyl)aniline,[11] *o*-(diphenylphosphino)benzaldehyde[13] and *o*-(diphenylphosphino)benzoic acid[13] were prepared as described previously. *o*-Dinitrobenzene was either prepared according to the literature method or was purchased from Aldrich Chemical Co. *n*-Butyllithium (2.3 M) (Alfa Inorganics) was standardized by titration with 3,5-dimethoxybenzyl alcohol. All other commercially obtained reagents were used as supplied. The syntheses of phosphorus-containing compounds were carried out in deoxygenated solvents under a nitrogen atmosphere. Once isolated as pure solids, all new phosphine compounds are relatively air-stable and precautions for their storage are unnecessary. In manipulations requiring reduction of solvent volume a rotary evaporator was used.

***o*-(Diphenyloxophosphoranyl)-*N*-benzylaniline (*o*-$Ph_2P(O)C_6H_4NHCH_2Ph$) (P(O)NHBz).** *o*-(Diphenyloxophosphoranyl)aniline (2.12 g, 7.3 mmol), acid-free benzaldehyde (0.77 g, 7.3 mmol), and $PtCl_2$ (50 mg) were placed in a 100-mL single-neck round-bottom flask containing absolute ethanol (50 mL) and a magnetic stir bar. The flask was fitted to a Brown hydrogenator and the system purged with nitrogen for 30 min. The system was activated, and the reaction continued until the theoretical volume of an aqueous solution of $NaBH_4$ (1–2 M) had been consumed. The suspension was vacuum-filtered through Celite, and the solids were washed with absolute ethanol (4 × 25 mL). After reduction of the filtrate volume to *ca* 5 mL, addition of aqueous KOH (10% solution) gave a white oil. The solids were extracted with diethyl ether (4 × 25 mL), and the combined extracts were dried over $MgSO_4$. After filtration, the solvent was removed to give a yellow oil. Unreacted benzaldehyde was removed by trap-to-trap distillation. Vacuum distillation (1 torr) of the residue gave the product as a white solid, which was collected over the temperature range 250–260 °C. Yield 1.62 g (60%). The compound can be recrystallized as needles by adding water to the cloud point of an acetone solution and cooling the solution at −10 °C for 24 h. The filtered product was dried in vacuo for 48 h at 80 °C; mp 114–115 °C. Anal. Calcd for $C_{25}H_{22}NOP$: C, 78.3; H, 5.78; N, 3.65; P, 8.08. Found: C, 78.1; H, 5.84; N, 3.54; P, 8.24. The hydrogenation step can be carried out by using a Parr hydrogenation apparatus, but significant scale up of the synthetic procedure results in decreased yield.

***o*-(Diphenylphosphino)-*N*-benzylaniline (*o*-$Ph_2PC_6H_4NHCH_2Ph$) (PNHBz).** *o*-(Diphenyloxophosphoranyl)-*N*-benzylaniline (12.4 g, 32.3 mmol) and diphenylsilane (5.96 g, 32.3 mmol) were placed in a 100-mL single-neck round-bottom flask. The flask was connected to a gas buret via Tygon tubing and then placed in a sand bath at 180 °C. After evolution of the calculated quantity of hydrogen (800 mL at 298 K), a process requiring about 8 h, the flask was removed from the sand bath and the gas buret connection replaced with a connection to a nitrogen bubbler. After the reaction was cooled to ambient temperature, the white residue was extracted with deoxygenated methanol (10 × 50 mL). Methanol removal yielded a yellow oil. The yellow impurity was removed by passing the oil through a Florisil plug (4 cm × 10 cm) and eluting with toluene. Removal of the toluene followed by recrystallization of the resulting oil from a minimum volume of boiling ethanol gave the crystalline solid: yield 8.9 g (75%); mp 87–88 °C. Anal. Calcd for $C_{25}H_{22}NP$: C, 81.7; H, 6.04; N, 3.81; P, 8.43. Found: C, 81.5; H, 6.24; N, 3.54; P, 8.27.

***o*-(Diphenylphosphino)-*N*-phenylbenzylamine (*o*-$Ph_2PC_6H_4CH_2NHPh$) (PCNHPh).** *o*-(Diphenylphosphino)benzaldehyde (16.9 g, 58 mmol) and freshly distilled aniline (5.42 g, 58 mmol) were dissolved with stirring in absolute ethanol (200 mL). After 1 h, during which time some precipitate had formed, excess sodium borohydride (4 g) was added in portions. The mixture was stirred for 1 h. Filtration gave an orange solid. The solid was washed with methylene chloride (100 mL in portions), leaving a white residue. Removal of the solvent (CH_2Cl_2) gave an orange solid. Crystallization of this solid from a minimum volume of boiling ethanol gave the product as a white powder, yield 12.9 g (60%). Final purification to white crystalline needles was achieved by addition of hexane to a solution of the compound in a minimum volume of CH_2Cl_2. The compound was dried in vacuo at 25 °C for 24 h; mp 135–137 °C. Anal. Calcd for $C_{25}H_{22}NP$: C, 81.7; H, 6.04; N, 3.81; P, 8.43. Found: C, 81.7; H, 5.95; N, 3.73; P, 8.37.

***o*-(Diphenylphosphino)-*N*-benzoylaniline (*o*-$Ph_2PC_6H_4NHC(O)Ph$) (PNH(CPhO)).** *o*-(Diphenylphosphino)aniline (2.46 g, 8.9 mmol) and dry pyridine (2.12 g, 26.7 mmol) were dissolved in dry THF (10 mL) contained in a 25-mL two-neck round-bottom flask fitted with a septum, an oil bubbler connected to a nitrogen source, and a magnetic stir bar. Benzoyl chloride (1.25 g, 8.9 mmol) was rapidly added to the stirred solution via syringe. The suspension containing py·HCl was stirred for 2 h. The precipitate was filtered and washed with dry THF (20 mL in portions). Solvent removal left a viscous oil. The oil was washed with water (6 × 25 mL) and then dissolved in dichloromethane (15 mL) and the solution dried over $MgSO_4$. The filtered solution was reduced in volume to 3 mL, hexane (100 mL) was added, and the cloudy solution was stored at −10 °C. The resulting white needles were collected by filtration, lightly washed with hexane 10 mL), and dried in vacuo at 25 °C for 24 h: yield 2.81 g (83%), mp 107–108 °C. Anal. Calcd for $C_{25}H_{20}NOP$: C, 78.7; H, 5.29; N, 3.67; P, 8.12. Found: C, 78.8; H, 5.47; N, 3.67; P, 8.22. This procedure can be scaled up 10-fold without loss of purity or yield.

***o*-(Diphenylphosphino)-*N*-phenylbenzamide (*o*-$Ph_2PC_6H_4C(O)NHPh$) (P(CO)NHPh).** *o*-(Diphenylphosphino)benzoic acid (6.12 g, 20 mmol) and freshly distilled aniline (0.93 g, 20 mmol) were dissolved with stirring in $CHCl_3$ (40 mL) contained in a 250-mL two-neck round-bottom flask fitted with a 125-mL dropping funnel and a nitrogen bubbler. The dropping funnel was charged with a solution of *N,N'*-dicyclohexylcarbodiimide (4.12 g, 20 mmol) in $CHCl_3$ (50 mL). The flask was placed in an ice bath and allowed to cool. The diimide was added dropwise over 30 min. The mixture was stirred for 2 h as it warmed to ambient temperature. *N,N'*-Dicyclohexylurea was removed by filtration, and solvent removal from the filtrate gave a yellow oil. The oil was chromatographed on silica gel (230–400 mesh, 6 cm × 40 cm column, CH_2Cl_2 eluant). The lead eluant was P(CO)NHR. Solvent removal gave P(CO)NHR (3.41 g) as a white powder in 56% yield. Final purification was by recrystallization from CH_2Cl_2/hexane. The white needles were filtered and dried in vacuo at 25 °C for 24 h; mp 179–180 °C. Anal. Calcd for $C_{25}H_{20}NOP$: C, 78.7; H, 5.29; N, 3.67; P, 8.12. Found: C, 78.8; H, 5.34; N, 3.66; P, 8.06.

Isolation by vacuum distillation (255–260 °C (1 mm)) gives the other rotational isomer. Anal. Calcd for $C_{25}H_{20}NOP$: C, 78.7; H, 5.29; N, 3.67; P, 8.12. Found: C, 78.6; H, 5.35; N, 3.64; P, 7.99. This isolation procedure is not the one of choice for this compound if isomer selectivity is not required since thermal decomposition during the distillation results in lowered yield.

***trans*-$PtCl_2(PNH(CPhO))_2$ (1).** K_2PtCl_4 (400 mg, 0.96 mmol) was dissolved in H_2O/CH_3CN (4 mL/12 mL) in a 100-mL round-bottom flask fitted with a magnetic stir bar. The flask was equilibrated to the oil bath temperature (60 °C). To the solution was added PNH(CPhO) (735 mg, 1.93 mmol) dissolved in CH_3CN (20 mL) dropwise over 5 min. Stirring for 1 h caused the solution color to change from red to yellow as a yellow precipitate formed. The flask was removed from the oil bath and allowed to cool to room temperature. The filtered product was washed with water (3 × 10 mL), ethanol (3 × 10 mL), and then pentane (3 × 5 mL), followed by drying in vacuo. Yield 931 mg (94%); mp 270–275 °C dec. Anal. Calcd for $C_{50}H_{40}Cl_2N_2O_2P_2Pt$: C, 58.4; H, 3.92; N, 2.72; P, 6.02; Cl, 6.89. Found: C, 58.5; H, 4.00; N, 2.89; P, 6.29; Cl, 6.90.

***trans*-$PtCl_2(P(CO)NHPh)_2$ (2).** Using a procedure analogous to that for **1** with K_2PtCl_4 (400 mg, 0.96 mmol) and P(CO)NHPh (735 mg, 1.9 mmol) gave **2** (920 mg, 93% yield) as a pale yellow powder, mp 250–253 °C dec. Anal. Calcd for $C_{50}H_{40}Cl_2N_2O_2P_2Pt$: C, 58.4; H, 3.92; P, 6.02. Found: C, 58.6; H, 4.04; P, 5.94.

***cis*-$Pt(PN(CPhO))_2$ (3). Method A.** Complex **1** (250 mg, 0.24 mmol) was suspended in CH_3CN/Et_3N (19 mL/1 mL) and the mixture

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refluxed with stirring for 60–90 min. The reaction mixture was cooled, and the yellow-green solution was filtered. Reduction in filtrate volume to ca. 2 mL gave a pale yellow powder, which was shown by ^{31}P NMR spectroscopy to be impure **3**. Preparative-scale TLC (silica gel 60 F_{254}, 2-mm layer thickness or 20 cm × 20 cm plates; EM Reagents, MC/B Inc.) using acetonitrile as eluant with the complexes applied to the plate as a solution in dichloromethane gave one broad band. The material was extracted with dichloromethane (2 × 100 mL) and the filtered extracts were combined and reduced in volume to 2 mL. Dropwise addition of diethyl ether (20 mL) precipitated pure **3** as yellow translucent crystals, which were filtered and dried in vacuo. Anal. Calcd for $C_{50}H_{38}N_2O_2P_2Pt$: C, 62.8; H, 4.00; P, 6.48. Found: C, 62.3; H, 4.27; P, 6.38.

Method B. Complex **1** (150 mg, 0.14 mmol) and excess sodium *tert*-butoxide (200 mg, 2.0 mmol) were suspended in dry acetonitrile (25 mL) under nitrogen. After 48 h the suspension was filtered, and the filtrate was evaporated to dryness. The yellow-green solid was recrystallized from CH_2Cl_2/Et_2O to give **3**, yield 95 mg (68%).

***cis*-$PtCl_2(PNH(CPhO))_2 \cdot 0.25CH_2Cl_2 \cdot Et_2O$ (4).** Complex **3** (50 mg, 0.05 mmol) was dissolved in CH_2Cl_2 (2 mL). Hydrogen chloride was bubbled through the solution for 5 min, causing the color of the solution to change from yellow-green to pale yellow. Excess hydrogen chloride was removed by purging the solution with a vigorous stream of nitrogen. Dropwise addition of diethyl ether (20 mL) precipitated the product. The solids were isolated by filtration, washed with diethyl ether (10 mL), and dried in vacuo: yield 50 mg (80%); mp >300 °C. A recrystallization from dichloromethane and diethyl ether was necessary for the isolation of pure material. Anal. Calcd for $C_{54.25}H_{50.5}Cl_{2.5}N_2O_3P_2Pt$: C, 58.0; H, 4.52; N, 2.49; Cl, 7.88. Found: C, 58.0; H, 4.14; N, 2.56; Cl, 8.79.

***trans*-$Pt(P(CO)NPh)_2$ (5).** Complex **2** (100 mg, 0.097 mmol) and excess sodium methoxide (200 mg, 3.7 mmol) were suspended in dry acetonitrile (20 mL). The mixture was stirred in a dry atmosphere for 3 days. The solution was filtered, and the remaining solids were washed with dichloromethane (50 mL). The combined filtrate was evaporated to leave a yellow solid. Recrystallization from dichloromethane and hexane gave a yellow powder, which was washed with hexane and dried in vacuo; yield 85 mg (89%). Anal. Calcd for $C_{50}H_{38}N_2O_2P_2Pt$: C, 62.8; H, 4.00; P, 6.48. Found: C, 61.9; H, 4.34; P, 6.22.

***cis*-$Pt(P(CO)NPh)_2$ (6).** Complex **2** (100 mg, 0.097 mmol) and excess Dabco (200 mg, 18 mmol) were suspended in acetonitrile (50 mL), and the mixture was refluxed for 1 h under nitrogen. After the reaction was cooled to room temperature, the solvent was removed to give a yellow-green residue. This solid was dissolved in dichloromethane (10 mL), filtered, and extracted with aqueous NaCl (4 × 40 mL of 10% NaCl) to remove excess base. The organic layer was dried over anhydrous $MgSO_4$, reduced in volume to ca. 2 mL, and treated with diethyl ether dropwise (40 mL) to precipitate **6** as a pale yellow powder. The complex was filtered, washed with diethyl ether (10 mL), and dried in vacuo; yield 63 mg (68%). Anal. Calcd for $C_{50}H_{38}N_2O_2P_2Pt$: C, 62.8; H, 4.00. Found: C, 61.9; H, 4.51.

***cis*-$PtCl_2(P(CO)NHPh)_2$ (7).** Complex **6** (107 mg, 0.11 mmol) was dissolved in dichloromethane (5 mL) and the solution treated with HCl(g) for 5 min as the yellow-green solution changed to pale yellow. Excess HCl was removed by a nitrogen purge, and the filtered solution was reduced in volume to ca. 2 mL. Addition of diethyl ether (20 mL) gave the complex as pale yellow microcrystals, which were filtered, washed with diethyl ether, and dried in vacuo: yield 82 mg (72%); mp 217–220 °C. Anal. Calcd for $C_{50}H_{40}Cl_2N_2O_2P_2Pt$: C, 58.4; H, 3.92. Found: C, 58.3; H, 4.19.

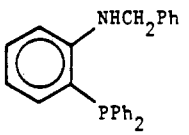
$PdCl_2(PNH(CPhO))_2$ (8). Sodium tetrachloropalladate(II) (203 mg, 0.69 mmol) was dissolved in acetonitrile (15 mL) and the solution filtered. A solution of PNH(CPhO) (526 mg, 1.38 mmol) in acetonitrile (40 mL) was then rapidly added to the stirred Na_2PdCl_4 solution. After 15 min, the yellow precipitate was filtered and washed successively with methanol (3 × 5 mL) and diethyl ether (3 × 5 mL). The complex was dried in vacuo: yield 512 mg (79%); mp 239–241 °C. Final purification was by recrystallization from CH_2Cl_2/MeOH. Anal. Calcd for $C_{50}H_{40}Cl_2N_2O_2P_2Pd$: C, 63.9; H, 4.29; N, 2.98. Found: C, 63.7; H, 4.31; N, 2.95.

$PdCl_2(P(CO)NHPh)_2$ (9). Using a procedure analogous to that for **8** with Na_2PdCl_4 (400 mg, 1.35 mmol) and P(CO)NHR (1.04 g, 2.7 mmol) gave 1.15 g (90%) of the complex as a light orange powder. The complex can be recrystallized in small batches (<50 mg) from CH_2Cl_2/Et_2O; mp 191–193 °C dec. Anal. Calcd for $C_{50}H_{40}Cl_2N_2O_2P_2Pd$: C, 63.9; H, 4.29; N, 2.98. Found: C, 63.7; H, 4.50; N, 2.84.

***cis*-$Pd(P(CO)NPh)_2$ (10).** A mixture of **9** (830 mg, 0.88 mmol) and Dabco (500 mg, 4.5 mmol) was placed in acetonitrile (100 mL) and the orange suspension stirred for 1 day. Solvent removal gave an orange solid. The solid was suspended in dichloromethane (20 mL) and then extracted with water (3 × 40 mL). The orange organic layer was dried over anhydrous magnesium sulfate. The filtrate was reduced in volume to 5 mL and treated with diethyl ether (100 mL) to precipitate the product as a light orange powder. The complex was filtered, washed with diethyl ether (20 mL), and dried in air, yielding 651 mg (85%) of a light orange powder, mp 223–225 °C dec. The complex was recrystallized from CH_2Cl_2/Et_2O and dried in vacuo. Anal. Calcd for $C_{50}H_{38}N_2O_2P_2Pd$: C, 69.3; H, 4.56. Found: C, 69.0; H, 4.59.

***trans*-$Pd(P(CO)NPh)_2$ (11).** A mixture of **9** (147 mg, 0.16 mmol) and excess sodium *tert*-butoxide (150 mg, 3.6 mmol) was suspended in dry acetonitrile (40 mL). After the mixture was stirred for 24 h in a dry atmosphere, the suspension was filtered and the solids were washed with dry acetonitrile (50 mL). Removal of the combined solvents gave 113 mg of a yellow solid, which was a mixture of **10** and **11**. The isomers were separated by preparative-scale TLC using 25-mg portions of the mixture in dichloromethane solvent. Elution with a 1:1 mixture of hexane with THF was halted when the yellow bands separated. Extraction with acetonitrile followed by solvent evaporation gave **10** (35 mg; R_f 0.0) and **11** (70 mg; R_f 0.4).

Table I. Structural Formulas and Abbreviations for the Hybrid Ligands[a]



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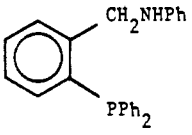
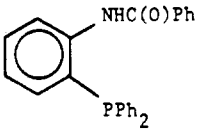
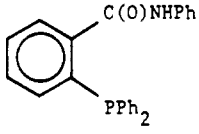


PCNHPh



PNH(CPhO)



P(CO)NHPh

[a] Anionic species denoted as PNBz, PCNPh, PN(CPhO), and P(CO)NPh.

Results and Discussion

Structural formulas and ligand abbreviations in both their free and N-deprotonated forms are given in Table I. In the abbreviation system, P and P(O) represent the respective phosphine and its oxide, C or CO between P and N denotes a methylene or carbonyl group bonded to nitrogen and the ortho aryl phosphine carbon, and the letters following N are terminal groups bonded to N, with CRO being an acyl group of the appropriate R substituent.

Characterization Methods. The $^{31}P\{^1H\}$ NMR spectra of the hybrid ligands show an expected single resonance in the range −10 to −30 ppm. The phosphine oxides show single resonances in the 20–30 ppm range. The $^{13}C\{^1H\}$ NMR spectra show phenyl carbons in the range 110–140 ppm, benzylamine methylene carbons in the region of 40–50 ppm, and amide carbons in the region of 165–175 ppm. The latter two show no coupling to ^{31}P.

The solvent- and concentration-dependent amide and aromatic amine resonances occur in distinct regions of the ^1H NMR spectrum at δ 6–9 and at δ 3–5, respectively. These resonances are quadrupolar broadened by coupling to ^{14}N.

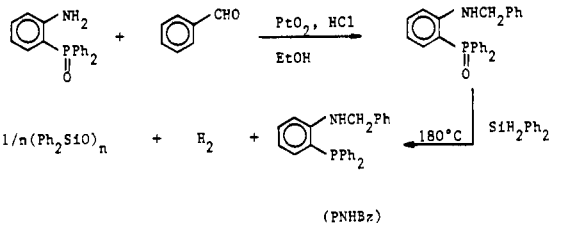
The methylene protons of PNHBz and PCNHPh are doublets; adding DCl (35% solution in D_2O) causes the amine resonances to disappear and the methylene signals to collapse to singlets. We assign this doublet splitting to $^3J_{HNCH}$. The amide proton resonance in P(CO)NHPh is unobserved but is found in its coordination complexes (vide infra).

Values of ν(NH) in the infrared spectra of aromatic amines are typically of medium intensity in the 3300–3500-cm^{-1} region,

Table II. Position of ν(NH) as a Function of Complex Stereochemistry and Hydrogen Bonding

	ν(NH), cm^{-1}	
isomer	H-bonded	non-H-bonded
E	3180–3140	3435–3385
Z	3320–3270	3480–3440

Scheme I

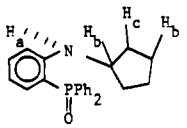


and PNHBz and PCNHPh follow this pattern. The expected weak bands for δ(NH) in the 1550–1650-cm^{-1} region are not observed. The aromatic ν(CN) band in PNHBz is readily assigned (ca. 1350 cm^{-1}), but the benzyl carbon–nitrogen stretching band (1000–1200 cm^{-1}) is in a complex spectral region and cannot be unambiguously assigned.[14]

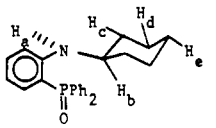
Secondary amides have four distinct infrared absorption bands, which are characteristic of the HNCO unit. The assignments and spectral ranges (cm^{-1}) are as follows: ν(NH), 3480–3140; amide I (primarily ν(CO)), 1700–1635; amide II and III (strongly coupled δ(NH) and ν(CN)), 1570–1510 and 1400–1300, respectively.[14] The values for ν(NH) and amide I bands are sensitive to the degree of intermolecular hydrogen bonding between amide molecules and also between amide and a polar solvent. The ν(NH) value is dependent on the rotational conformation of the amide (Table II). The amide II and III bands are relatively insensitive to environment.[15]

All four hybrid ligands prepared are crystalline solids with sharp melting points. The compounds are air-stable in the solid state but are slowly oxidized in solution. For each new hybrid ligand the IR and NMR spectral data are collected in Tables III and IV, and the values can be correlated with those expected from the general features discussed earlier in this section.

Ligand Syntheses. *o*-(Diphenylphosphino)-*N*-benzylaniline (PNHBz) is conveniently prepared from *o*-(diphenyloxophosphoranyl)aniline, P(O)NH$_2$,[11] in an overall 45% yield in a two-step synthesis (Scheme I). The reductive animation step gives the first intermediate in 60% isolated yield without hydrogenolysis of the benzylic C–N bond. If cyclopentanone or cyclohexanone are used in place of benzaldehyde, the products P(O)NH-c-C$_5$ and P(O)NH-c-C$_6$ can be isolated. Alternate approaches have



P(O)NH-c-C$_5$



P(O)NH-c-C$_6$

been considered. We could not successfully form a Schiff base by refluxing a mixture of benzaldehyde and either P(O)NH$_2$ or PNH$_2$, even though this reaction has been achieved between *o*-(diphenylphosphino)benzaldehyde and an aliphatic or an aromatic amine.[13] Apparently the substituted phosphorus substituent on the amine is sufficiently electron-withdrawing to render the ortho amine unreactive toward electrophiles, while this same substituent enhances the electrophilicity of an ortho carbonyl group. If the Schiff base route is desired, it can be achieved by template synthesis in the presence of nickel(II) salts. A template

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(15) Challis, B. C.; Challis, J. A. In "Comprehensive Organic Chemistry"; Barton, D. R. H., Ollis, W. D., Eds.; Pergamon Press: Oxford, England, 1979; Vol. 2, pp 990–991.

Table III. IR and ^{1}H NMR Spectral Data for New (P,N) Hybrid Ligands

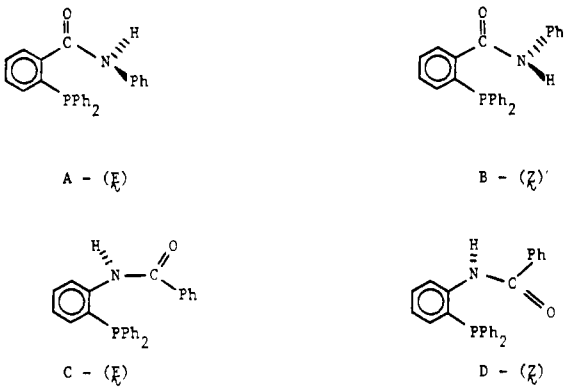
compd	IR, cm^{-1}	δ	*J*, Hz
P(O)NHPh	ν(NH) 3320	7.7–6.4 m (Ph, 19 H)	$^3J(CH_2NH)$ = 5.7
	ν(PO) 1175	5.3 br (NH, 1 H)	
		4.3 d (CH_2, 2 H)	
P(O)NH-c-C$_5$	ν(NH) 3310	8.0–6.8 m (Ph, 14 H)	
	ν(PO) 1180	5.3 br (H_a, 1 H)	
		3.7 m (H_b, 1 H)	
		1.8–1.2 br m (H_c and H_d, 8 H)	
P(O)NH-c-C$_6$	ν(NH) 3305	7.8–6.4 m (Ph, 14 H)	
	ν(PO) 1165	3.3 br m (H_b, 1 H)	
		1.8–1.1 (H_c, H_d, and H_e, 10 H)	
		H_a unobserved	
PNHBz	ν(NH) 3405	7.7–6.4 m (Ph, 19 H)	$^3J(CH_2NH)$ = 4.5
		5.1 br (NH, 1 H)	
		4.3 d (CH_2, 2 H)	
PCNHPh	ν(NH) 3410	7.6–6.4 m (Ph, 19 H)	$^3J(CH_2NH)$ = 1.4
		4.5 d (CH_2, 2 H)	
		3.8 br (NH, 1 H)	
PNH(CPhO)	ν(NH) 3350	8.80 br (NH, 1 H)	
	amide I 1680	8.83–8.45 m and 7.7–6.9 m (Ph, 19 H)	
	amide II 1510		
	amide III 1300		
P(CO)NHPh (A)	ν(NH) 3240	6.8–7.8 (Ph and NH, 20 H)	
	amide I 1650		
	amide II 1550		
	amide III 1330		
P(CO)NHPh (B)	ν(NH) 3360		

Table IV. ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR Data for New (P,N) Hybrid Ligands

	δ	
compd	^{31}P	^{13}C
PNHBz	−27.2 s	47.9 (CH_2), 110–140 m (Ph)
PCNHPh	−21.7 s	46.9 (CH_2), 112–147 m (Ph)
PNH(CPhO)	−26.8 s	165.1 br (CO), 120–135 m (Ph)
P(CO)NHPh	−16.4 s	167.0 br (CO), 110–140 m (Ph)

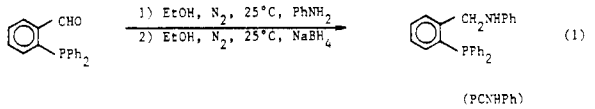
synthesis may be operative in the PtO_2-catalyzed coupling since the reductive amination products cannot be obtained by using a sodium borohydride method. The diphenylsilane method of Cooper[11] and Fritzsche[16] was successfully monitored by hydrogen

Chart I



evolution into a gas buret. The compound PNHBz could not be purified via a nickel(II) complex.[11] Attempted N-alkylation of PNH_2 gave products of P-alkylation, which were deactivated toward further reaction.

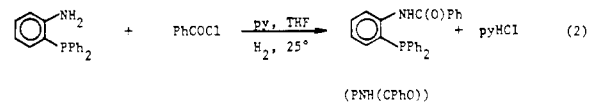
o-(Diphenylphosphino)-*N*-phenylbenzylamine (PCNHPh) was prepared by a two-step one-pot synthesis (eq 1). The first step



(1)

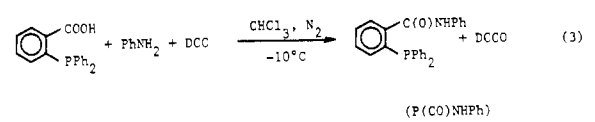
followed the procedure of Rauchfuss, except that the condensation reaction was achieved at ambient temperature. The intermediate Schiff base *o*-$Ph_2PC_6H_4CH{=}NPh$ (IR ν(CN) 1630 cm^{-1}; ^1H NMR δ 9.1 (CH, $^4J(PH)$ = 4.5 Hz); ^{31}P NMR δ 19.2) can be reduced by sodium borohydride in an ethanol suspension.

o-(Diphenylphosphino)-*N*-benzoylaniline (PNH(CPhO)) was obtained in 85% yield by the acylation of PNH_2 with benzoyl chloride in the presence of pyridine (eq 2).[17] The reductive



(2)

coupling of *o*-(diphenylphosphino)benzoic acid (P(COOH)) and aniline in the presence of *N,N'*-dicyclohexylcarbodiimide (DCC) gives *o*-(diphenylphosphino)-*N*-phenylbenzamide (P(CO)NHPh) in moderate yield (56%) (eq 3). The product was separated from PCOOH by chromatography on silica gel.



(3)

When the compound is isolated by high-temperature distillation the second rotational isomer B is isolated and is presumably the thermodynamically favored product.[15] The rotational isomers of PNH(CPhO) and P(CO)NHPh are shown in Chart I, the isomers being designated as either *E* or *Z*. Further isomerization is possible if there is slow rotation about either the C(O)–C(Ph) (A, B) or the N–C(Ph) (C, D) bond, maybe because of conjugation of the phenyl group with the O–C–N π-system or because of steric hindrance. The isomers in Chart I have the preferred configuration for P,N-chelation, but rotation by 180° about the C(O)–Ph carbon–carbon bond for P(CO)NHPh and the N–Ph carbon–carbon bond for *trans*-PNH(CPhO) gives compounds stereochemically ideal for P,O-chelation with the carbonyl oxygen.

Although differences in diamagnetic anisotropy of the amide carbonyl group cause changes in δ(NH), this method cannot be used for PNH(CPhO) and P(CO)NHPh because in the former only one isomer is obtained and in the latter δ(NH) is not observable in both isomers. We have therefore used IR spectroscopy

Figure 1. Amide–iminol tautomerization.

to assign isomers. The position of ν(NH) is a sensitive indicator of structure both in solution and in the solid state, the hydrogen-bonded E isomers having values at lower energies. The E isomers A and C have been used in the synthesis of the platinum and palladium complexes because they are in the correct configuration for P,N-chelation. For P(CO)NHPh the anilide rotational barrier is high enough for both compounds to be stable at room temperature, a fact which may be due to steric effects induced by the diphenylphosphine substituent. The value for ν(NH) in PNH(CPhO) is found at 3350 cm^{-1}. Comparison with the parent benzanilide also leads to a Z assignment for the compound. Sublimation at 220 °C (1 mm) causes no isomerization.

Complexes of Platinum(II) and Palladium(II)

Characterization Methods. These new hybrid phosphine amide ligands PNH(CPhO) and P(CO)NHPh coordinate to platinum(II) and palladium(II) in either a monodentate or a bidentate mode. In the former case coordination is via the phosphorus atom, while in the latter case both the phosphorus and the secondary nitrogen atom are coordinated. The various bonding modes and stereochemistries have been determined by a combination of $^{31}P\{^1H\}$ NMR, ^1H NMR, and IR spectroscopy. Coordination of a phosphine ligand to Pt(II) and Pd(II) usually results in a downfield shift of between 10 and 50 ppm in the ^{31}P NMR chemical shift.[18] For the platinum(II) complexes with $I = {}^1/_2$ for ^{195}Pt (33% abundance) nuclei, the values of ^1J(Pt–P) decrease as the trans influence of the ligand trans to the phosphorus increases. For phosphines trans to a ligand low in the trans-influence series, values of ^1J(PtP) are found in the 3100–3800-Hz range, whereas this range is 2400–2900 Hz for ligands high in the trans-influence series. Stereochemistry can also be determined in some cases from values of ^2J(PP) in the complexes since respective ranges of 0–50 and 100–600 Hz are found for mutually cis and trans phosphorus nuclei. An analysis of chemical shift positions (δ_P) must also take into account ring effects, since chelation significantly influences chemical shift.[19] This phenomenon is made semiquantitative by the calculation of Δ_R, which is the difference between δ_P of the chelated and monodentate phosphine ligand. For a 5-membered chelate ring, Δ_R ranges from +21 to +33 ppm and from −2 to −25 ppm for a 6-membered ring.

Structural characterization is also dependent on IR spectroscopy. Changes in the frequencies of the amide I, II, and III bands can be used to identify the mode of amide coordination. Complexation via oxygen will increase the contribution of the dipolar resonance form (eq 4), thereby shifting the amide I band to lower frequency. Coordination via amide nitrogen diminishes the contribution of the dipolar resonance form with a concomitant increase in amide I frequency. Third, coordination via a nitrogen atom of the iminol tautomer B (Figure 1) results in ν(CN) being found in the 1600–1650-cm^{-1} range and ν(CO) in the 1300–1400-cm^{-1} range. Coordination via an N-deprotonated amide causes a simplification of the IR spectrum since the ν(NH) and amide II bands disappear.

Coordination of a secondary amide via nitrogen results in a downfield shift of the NH resonance in the ^1H NMR spectrum. Nevertheless this criterion must not be used alone, since analogous shifts can be caused by intramolecular or solute–solvent hydrogen bonding. Throughout this paper chemical shift comparisons of δ(NH) between different compounds are only made for data measured in the same solvent.

(16) Fritzsche, H.; Hasserodt, U.; Korte, F. *Chem. Ber.* **1964**, *97*, 1988–1993.
(17) Wilson, M. W.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1978**, *100*, 2269–2270.
(18) Pregosin, P. S.; Kunz, R. W. "^{31}P and ^{13}C NMR of Transition Metal Complexes": Springer-Verlag: New York, 1979.
(19) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229–266.

Table V. $^{31}P\{^1H\}$ NMR, ^1H NMR, and IR Spectroscopic Data for the Platinum(II) and Palladium(II) Complexes

complex	$^{31}P\{^1H\}$ NMR, ppm (J, Hz)	^1H NMR, δ	IR, cm^{-1}
trans-$PtCl_2(PNH(CPhO))_2$ (**1**)	10.3 (^1J(PtP) = 2507)	9.1 (NH)	3340 ν(NH) 1660 (I); 1290 (III)
trans-$PtCl_2(P(CO)NHPh)_2$ (**2**)	15.4 (^1J(PtP) = 2607)		3275, 3285 ν(NH) 1680, 1685 (I); 1530 (II); 1310, 1320 (III)
cis-$Pt(PN(CPhO))_2$ (**3**)	9.5 (^1J(PtP) = 3241)		1600 (I); 1340 (III)
cis-$PtCl_2(PNH(CPhO))_2$ (**4**)	2.3 (^1J(PtP) = 3646)	9.7 (NH)	3330 ν(NH) 1670 (I); 1510 (II); 1300 (III)
trans-$Pt(P(CO)NPh)_2$ (**5**)	6.2 (^1J(PtP) = 2825)		1610 (I); 1350 (III)
cis-$Pt(P(CO)NPh)_2$ (**6**)	5.4 (^1J(PtP) = 3219)		1620 (I); 1345 (III)
cis-$PtCl_2(P(CO)NHPh)_2$ (**7**)	7.6 (^1J(PtP) = 3737)	9.6 (NH)	3320, 3295, 3260 ν(NH) 1688, 1685, 1670 (I); 1540 (II); 1320 (III)
$PdCl_2(PNH(CPhO))_2$ (**8**)	14.7	9.1 (NH)	3340 ν(NH) 1670 (I); 1295 (III)
$PdCl_2(P(CO)NHPh)_2$ (**9**)	19.2	9.4 (NH)	3380 ν(NH) 1655 (I); 1540 (II); 1325, 1335 (III)
cis-$Pd(P(CO)NPh)_2$ (**10**)	27.2		1605 (I); 1350 (III)
trans-$Pd(P(CO)NPh)_2$ (**11**)	9.3		1605 (I); 1350 (III)

Complexes of Platinum(II) with PNH(CPhO) and P(CO)NHPh. Addition of 2 equiv of L (L = PNH(CPhO), P(CO)NHPh) to an acetonitrile/water solution of K_2PtCl_4, or to an acetonitrile solution of $PtCl_2(PhCN)_2$, causes precipitation of *trans*-$PtCl_2L_2$ (**1**, L = PNH(CPhO); **2**, L = P(CO)NHPh) as a pale yellow powder (eq 4). The complexes are coordinated via

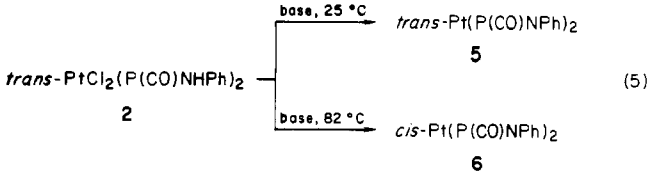
$$PtCl_4^{2-} + 2L \rightarrow PtCl_2L_2 + 2Cl^- \quad (4)$$

L = PNH(CPhO) (**1**), P(CO)NHPh (**2**)

phosphorus as evidenced by the downfield ^{31}P resonance (δ_P 10.3 (**1**) and 15.4 (**2**)), and trans stereochemistry is confirmed from ^1J(PtP) (2507 (**1**) and 2607 Hz (**2**)). The absence of any IR shifts in the amide I, II, and III bands eliminates a chelate structure $[PtL_2]Cl_2$, and the absence of a ν_{asym} band at 333 cm^{-1} eliminates a Magnus Green salt formulation, $[PtL_4][PtCl_4]$. No chelate complex $PtCl_2L$ has been prepared, and addition of only 1 equiv. of L results in a 50% yield of **1** or **2**. Subsequent reaction of **1** with $AgNO_3$ yields an insoluble product that has not been completely characterized.

Deprotonation of the uncoordinated nitrogen leads to the formation of an amido anion. Such an anionic functionality is a better ligand than a protonated amide, and halide substitution occurs. Complex **1** as a suspension in acetonitrile can be refluxed in the presence of triethylamine to give *cis*-$Pt(PN(CPhO))_2$ (**3**), which can be obtained as a yellow-green solid. $Et_3N{\cdot}HCl$ is also formed. The complex is a nonelectrolyte in dichloromethane solvent. The observation of a simple pseudotriplet in the ^{31}P NMR spectrum at δ 9.5 with ^1J(PtP) = 3241 Hz shows the complex to be monomeric with the phosphorus atoms mutually cis. The ^1H NMR spectrum shows the loss of the NH proton, and the amide I (1600 cm^{-1}) and amide III (1340 cm^{-1}) bands both show the expected frequency shifts.

A similar treatment of complex **2** with Brønsted base can be used to give either *trans*- or *cis*-$Pt(P(CO)NPh)_2$ (**5** and **6**, respectively), depending on the reaction conditions. Under ambient temperature conditions, a suspension of **2** in anhydrous acetonitrile solvent with either sodium *tert*-butoxide or sodium methoxide added gives *trans*-$Pt(P(CO)NPh)_2$ (**5**) in high yield, whereas refluxing a suspension of **2** and Dabco in the same solvent gives selectively *cis*-$Pt(P(CO)NPh)_2$ (eq 5). Both complexes are yellow



(5)

solids, which are slightly soluble in acetonitrile, very soluble in chlorinated aliphatic hydrocarbons, and insoluble in other organic solvents. The complexes can be recrystallized from dichloromethane solvent by addition of hexane. Again the complexes show no IR bands due to ν(NH) and amide II. The amide I and III bands are in the expected positions: amide I, 1610 (**5**) and 1620 cm^{-1} (**6**), amide III, 1350 (**5**) and 1345 cm^{-1} (**6**). Again the simple pseudotriplet patterns identify the complexes as monomeric. The data are as follows: δ_P 6.2 (**5**), 5.4 (**6**); J(PtP) = 2825 Hz (**5**), 3219 Hz (**6**). The isomer identification is based on ^1J(PtP). In this reaction the formation of **6** and **2** occurs with a trans to cis isomerization. No intermediates are observed. No interconversion occurs between **5** and **6** even under reflux conditions, hence the formation of **6** does not proceed via **5**.

An analogous chemistry is observed with $PdCl_4^{2-}$ and these ligands. High yields of $PdCl_2(PNH(CPhO))_2$ (**8**) and $PdCl_2(P(CO)NHPh)_2$ (**9**) can be obtained. The bright yellow powders are insoluble in all common solvents except chloroform and dichloromethane. Relevant spectroscopic data show δ_P 14.7 (**8**) and 19.2 (**9**), no shifts in the amide IR bands, and δ_{NH} 9.1 (**8**) and 9.4 (**9**).

The reaction of a suspension of **9** and sodium *tert*-butoxide in anhydrous acetone gives an approximately 1:1 mixture of *cis*-$Pd(P(CO)NPh)_2$ (**10**) and *trans*-$Pd(P(CO)NPh)_2$ (**11**). Complexes **10** and **11** can be separated by preparative-scale TLC using equal volumes of THF and hexane as eluant. The amide II and ν(NH) IR bands are absent in each complex, as is the resonance for δ(NH). The amide I and III bands shift as expected: amide I, 1605 cm^{-1}; amide III, 1350 cm^{-1}. The ^{31}P NMR spectra are singlets at δ 27.2 (**10**) and 9.3 (**11**). The stereochemical assignments are based on the empiricism that δ_P in complexes *cis*-PdX_2P_2 resonate at lower field than in complexes *trans*-PdX_2P_2.[18,20] Compound **10** is actually most conveniently prepared by the reaction of a suspension of **9** and excess Dabco in acetonitrile at ambient temperature; ^{31}P NMR spectroscopy indicates the absence of **11**. Amido complexes of the platinum group metals are rare.[21] These chelate-stabilized amido complexes are readily synthesized and isolated, and unlike the amido compounds of the high-valent early-transition-metal ions, they are stable to water. In view of their rarity, we have begun a study of the reaction chemistry of these d^8 amido complexes.

These chelate-stabilized bis(amido) complexes **3**, **5**, **6**, **10**, and **11** are readily protonated at nitrogen by HCl to give MCl_2L_2, where now the hybrid phosphine amide ligand is coordinated solely through phosphorus. This method can be used to prepare com-

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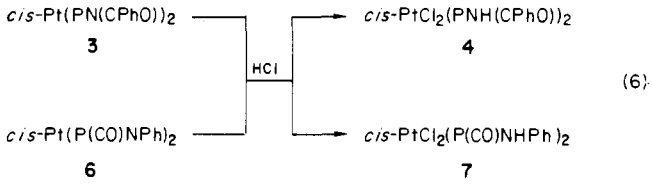
(22) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III 3 and 13.)

plexes *cis*-$PtCl_2(PNH(CPhO)_2$ (**4**) and *cis*-$PtCl_2(P(CO)NHPh)_2$ (**7**) (eq 6), and indeed this method of synthesis is the preferred



(6)

one for complex **7**. Complexes **3**, **5**, **6**, **10**, and **11** do not undergo substitution reactions by added chloride ion; therefore, the initial step in their reactions with HCl must involve protonation at nitrogen. For the platinum amido complexes the stereochemistry is retained, but the reaction of either the cis or the trans isomer of $Pd(P(CO)NPh)_2$ with HCl gives only a single product, $PdCl_2(P(CO)NHPh)_2$ **9** (δ_P 19.2). The spectral properties of **4** and **7** are respectively δ_P 2.3 (^1J(PtP) = 3646 Hz) and δ_P 7.6 (^1J(PtP) = 3737 Hz). NMR and IR spectral data for the complexes are collected in Table V.

Like the trans analogues **1** and **2**, the cis complexes **4** and **7** react with base to give the N-bonded amido complexes. In contrast, however, reaction of **4** or **7** with Dabco in acetonitrile solvent *rapidly* gives the amido complexes at ambient temperature. The respective products **3** and **6** are formed with retention of stereochemistry. This relative ease of intramolecular chloride ion substitution by the amido anion in the cis isomers over the trans ones is a consequence of the higher trans influence of the phosphine ligand.

Registry No. **1**, 91410-06-9; **2**, 98838-49-4; **3**, 91410-08-1; **4**, 91464-49-2; **5**, 98838-50-7; **6**, 98919-88-1; **7**, 98919-89-2; **8**, 91410-15-0; **9**, 98838-51-8; **10**, 98838-52-9; **11**, 98919-90-5; P(O)NHBz, 98821-87-5; PNHBz, 91410-00-3; PCNHPh, 91410-01-4; PNH(CPhO), 91409-99-3; P(CO)NHPh, 91410-02-5; P(O)NH-c-C_5, 98821-88-6; P(O)NH-c-C_6, 98821-89-7; *o*-$Ph_2PC_6H_4CH$=NPh, 98821-90-0; *o*-$Ph_2P(O)C_6H_4NH_2$, 23081-74-5; PhCHO, 100-52-7; Ph_2SiH_2, 775-12-2; *o*-$Ph_2PC_6H_4CHO$, 50777-76-9; $PhNH_2$, 62-53-3; *o*-$Ph_2PC_6H_4NH_2$, 65423-44-1; PhC(O)Cl, 98-88-4; *o*-$Ph_2PC_6H_4CO_2H$, 17261-28-8; K_2PtCl_4, 10025-99-7; Na_2PdCl_4, 13820-53-6.

Contribution from the Chemistry Departments, Ben-Gurion University of the Negev, Beer-Sheva, Israel, and Nuclear Research Center Negev, Beer-Sheva, Israel

Mechanism of Hydrolysis of the Metal-Carbon Bond in α-Hydroxyalkyl-Chromium(III) Complexes. Effect of Nonparticipating Ligands

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Received November 27, 1984

The specific rates of reaction of the free radicals $\cdot CH_2OH$, $\cdot CH(CH_3)OH$, and $\cdot C(CH_3)_2OH$ with $[Cr^{II}(edta)]^{2-}$, $[Cr^{II}(nta)]^-$, and *trans*-[(1,4,8,12-tetraazacyclopentadecane)$(H_2O)_2Cr^{II}]^{2+}$ are reported and compared with the analogous reactions with $Cr(H_2O)_6^{2+}$. The spectra of the α-hydroxyalkyl-chromium(III) complexes thus formed are reported and discussed. The rates of hydrolysis of the latter complexes are reported as well as that of *cis*-[(nta)$(H_2O)Cr^{III}$-$CH_3]^-$. The results point out that the electrophile in these hydrolysis reactions is a solvent water molecule and not a cis aqua ligand as earlier suggested. The effects of the pH of the solution and the addition of acetate on the hydrolysis reactions are reported and discussed.

The relative stability of alkyl-chromium(III) complexes in aqueous solutions allows the detailed study of their decomposition mechanisms.[2] The large range of stabilities of these complexes and variety of mechanisms of decomposition resulted in extensive studies[2] aimed at elucidating the factors affecting the mechanisms and rates of these reactions, which are model reactions to the decomposition of other complexes with σ metal-carbon bonds in protic media.

Pentaaqua(α-hydroxyalkyl)chromium(III) complexes were shown to decompose in acidic solutions via two pathways.

The first is a homolytic decomposition:[3]

$$[(H_2O)_5Cr^{III}\text{-}CR_1CR_2OH]^{2+} \underset{}{\overset{H_2O}{\rightleftharpoons}} Cr(H_2O)_6^{2+} + \cdot CR_1R_2OH \quad (1)$$

This mechanism is important only in the presence of scavengers of $Cr(H_2O)_6^{2+}$ and/or $\cdot CR_1R_2OH$, as $K_1 >> 1$.

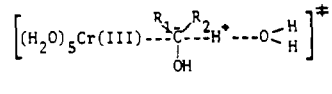
The second pathway is a heterocyclic hydrolysis reaction:[2,4]

$$[(H_2O)_5Cr^{III}\text{-}CR_1R_2OH]^{2+} \xrightarrow{H_2O} Cr^{III}_{aq} + HCR_1R_2OH \quad (2)$$

This reaction obeys in acidic solutions the rate law

$$-\frac{d[[(H_2O)_5Cr^{III}\text{-}CR_1R_2OH]^{2+}]}{dt} = (k_{H_2O} + k_{H_3O^+}[H_3O^+])[[(H_2O)_2Cr^{III}\text{-}CR_1R_2OH]^{2+}] \quad (3)$$

When the measurements were carried out in D_2O instead of H_2O it was found that both k_{H_2O} and d $k_{H_3O^+}$ have large kinetic H/D isotope effects.[5] For the $[H_3O^+]$-dependent term the following transition state is commonly accepted



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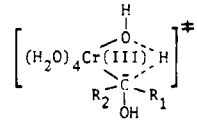
This transition state is in accord with the large kinetic isotope effect and with the observation that bulky R_1 and R_2 substituents decrease $k_{H_3O^+}$.[3]

For the [acid]-independent term, k_{H2O}, two different transition states were proposed.

1. It was suggested[2] that the attacking water molecule is the ligand bound to the chromium cis to the α-hydroxyalkyl ligand:



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