groups in **4** and **5** are unremarkable. In summary, the overall structures of **4** and **5** appear to be those of cyclic sulfur diimides with almost planar conformations enforced by the bulky groups on phosphorus.

Preparation and Spectroscopic Characterization of Cr(CO)$_5$-[P(Me$_3$SiNR)NSNSNR'] (3e, R = R' = SiMe$_3$; 3f, R = R' = H). Recently, we reported a high yield synthesis of the P^{V}N$_3$S$_2$ ring,[42] which exploited an earlier discovery by Appel and Halstenberg[43] of the double 1,4-cycloaddition reaction of a P=N bond in a λ^5-iminophosphine with S$_4$N$_4$. In this investigation, we have used this synthetic approach for the preparation of metal carbonyl complexes of the P^{III}N$_3$S$_2$ ring **1** in its protonated form. The Cr(CO)$_5$ complex of Me$_3$SiN=P—N(SiMe$_3$)$_2$ is obtained as a viscous green liquid by treatment of Cr(CO)$_5$(THF) with the λ^3-iminophosphine.[22] The 1,4-cycloaddition reaction of the complex so obtained with S$_4$N$_4$ in a 2:1 molar ratio proceeds slowly at 23 °C in methylene dichloride and is complete after 4 days to give one major phosphorus-containing product (Scheme I). The crude product **3e** was obtained in ca. 80% yield as a viscous yellow oil, which could be purified by sublimation only with great difficulty. Treatment of this product with Pr^{i}OH produced orange crystals of **3f**. The IR and spectroscopic data for **3f**, which are compared with the corresponding data for **3a–c** in Table III, indicate the presence of nonequivalent N–H groups, one endocyclic and one exocyclic. This conclusion was confirmed by the X-ray structural determination of **3f**.[44]

A variety of λ^3-iminophosphines, RP=NR', are available,[45] and we have investigated briefly the extension of the synthetic approach illustrated in Scheme I to the preparation of the free ligand, **1**, as its N-protonated or N-alkylated derivative. The reactions of S$_4$N$_4$ with RP = NR' (R = (Me$_3$Si)$_2$N, R' = SiMe$_3$; R = Pr$^i_2$N, R = ^{t}Bu) in toluene at 0 °C give dark red solutions containing a mixture of at least five products (^{31}P NMR spectra). In view of the ambident reactivity of RP = NR', it is likely that nucleophilic degradation of S$_4$N$_4$ by the phosphorus(III) reagent[46] competes with the 1,4-cycloaddition reaction. Thus the success of this route to **1** is dependent on the prevention of nucleophilic degradation by coordination of the phosphorus lone pair to a metal center.

Conclusions. The reaction of Cr(CO)$_5$(RPCl$_2$) with 2 mol of NSO$^-$ produces binuclear complexes of the novel ligand, **2** (E = PR). Both cis (R = ^{t}Bu) and trans (R = Pr$^i_2$N) isomers of these complexes have been structurally characterized. The eight-membered P$^{III}_2$N$_4$S$_2$ rings in these complexes adopt almost planar conformations as a result of the bulky groups on phosphorus. A rational synthesis of the protonated form of the P^{III}N$_3$S$_2$ ring, as a complex with Cr(CO)$_5$, has been discovered. This new approach is not suitable for the preparation of the free ligand **1**, as an N-protonated or N-alkylated derivative, but it can probably be extended to other complexes of type **3**. The structural parameters for Cr(CO)$_5$ complexes of the ligands **1**, in its protonated form, and **2** (E = PR) are indicative of localized –N=S=N– units in the cyclophospha(III)thiazene rings.

Supplementary Material Available: Tables listing crystal data, atom coordinates, thermal parameters, bond distances, bond angles, and torsion angles for **4** and **5** (22 pages); tables of calculated and observed structure factors for **4** and **5** (36 pages). Ordering information is given on any current masthead page.

(42) Chivers, T.; Dhathathreyan, K. S.; Liblong, S. W.; Parks, T. *Inorg. Chem.* **1988**, *27*, 1305.

(43) Appel, R.; Halstenberg, M. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 696.

(44) The structure of **3f** is very similar to that reported for **3a**.[11] The P^{III}N$_3$S$_2$ ring in **3f** adopts a half-boat conformation with two short (1.560 (6) and 1.571 (7) Å) and two long (1.654 (7) and 1.684 (6) Å) S–N bond lengths and bond angles of 119.4 (4) and 107.6 (3)° at the two sulfur atoms. Chivers, T.; Fait, J. F.; Lensink, C. *Acta Crystallogr.*, in press.

(45) Niecke, E.; Gudat, D.; Schoeller, W. W.; Rademacher, P. *J. Chem. Soc., Chem. Commun.* **1985**, 1050 and references cited therein.

(46) Bojes, J.; Chivers, T.; Cordes, A. W.; MacLean, G.; Oakley, R. T. *Inorg. Chem.* **1981**, *20*, 16.

Contribution from The Ohio State University,
Department of Chemistry, Columbus, Ohio 43210

Syntheses and Characterization of Trigonal-Bipyramidal Rhodium(I) Complexes of Tris(2-(diphenylphosphino)ethyl)phosphine and Determination of a Spectroscopic Trans-Influence Series by ^{31}P{^{1}H} NMR Spectroscopy[1]

Jeffrey J. Gambaro, William H. Hohman,[2] and Devon W. Meek*,†

A series of low-spin, five-coordinate rhodium(I) complexes of the tripod ligand tris(2-(diphenylphosphino)ethyl)phosphine, PP$_3$, were synthesized and characterized by elemental analyses, infrared spectra, and ^{31}P{^{1}H} NMR spectra. The complexes have trigonal-bipyramidal geometries in which the PP$_3$ ligand occupies four of the five sites of C_{3v} symmetry and the variable fifth ligand is monodentate. The ^{31}P NMR spectral patterns are consistent with AMX$_3$ and AKMX$_3$ spin systems. The NMR spectra permit a determination of the trans influence of the fifth ligand on the rhodium–phosphorus apical coupling constant and the chemical shifts of the apical and equatorial phosphorus atoms of PP$_3$.

Introduction

The synthesis and characterization of new five-coordinate complexes and the coordination properties of chelating polydentate ligands such as tris(2-(diphenylphosphino)ethyl)phosphine, P-(CH$_2$CH$_2$PPh$_2$)$_3$ (PP$_3$), continue to be active areas of research.[3–9] The chelating tetradentate ligand PP$_3$ is ideally suited for synthesis of low-spin, trigonal-bipyramidal complexes with C_{3v} symmetry;

^{31}P{^{1}H} NMR studies on those resultant complexes should permit an evaluation of the electronic and steric properties of the variable

---

†Deceased December 7, 1988. Address correspondence to Dr. Bruce E. Bursten, Department of Chemistry, The Ohio State University.

(1) Presented at the 189th National Meeting of the American Chemical Society, Miami Beach, FL, 1985; see Abstract INOR 208. Abstracted from the M.S. thesis of J.J.G., The Ohio State University, 1985.

(2) On a sabbatical leave from Marietta College, Marietta, OH, 1983–84.

(3) Meek, D. W. Polydentate Ligands and Their Effects on Catalysis. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; pp 257–296.

(4) Gray, L. R.; Hale, A. L.; Levason, W.; McCullough, F. P.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1984**, 47.

fifth ligand, which would be located along the d_{z^2} orbital of the metal and which would be located trans to the central phosphorus atom of PP_3.

When the metal has a magnetic nucleus (e.g., ^{103}Rh or ^{195}Pt), both the $^1J_{M-P}$ coupling constant and the chemical shift of the central phosphorus atom of PP_3 provide excellent indicators of the bonding nature of the fifth ligand. Such spectroscopic information has been obtained in this study to determine a trans-influence series in five-coordinate, trigonal-bipyramidal complexes, specifically in two series of neutral and cationic rhodium(I) complexes. The results are compared to trends previously observed for four-coordinate, planar complexes of Rh(I)[10] and Pt(II).[11,12]

Experimental Section

Reagents and Chemicals. The chemicals were of reagent grade and were used without further purification unless stated otherwise. Dimethylphenylphosphine ($PPhMe_2$), triethylphosphine (PEt_3), and trimethyl phosphite [$P(OMe)_3$] were obtained from Strem Chemical Co., Danvers, MA. The tripod ligand tris(2-(diphenylphosphino)ethyl)-phosphine (PP_3) was purchased from Pressure Chemical Co., and $AgBF_4$ and 15-crown-5 were purchased from Aldrich Chemical Co. $RhBr_3$·$3H_2O$ and $RhCl_3$·$3H_2O$ used as starting materials were obtained from Johnson Matthey, Inc. $IrCl_3$·$3H_2O$ was purchased from Engelhard Industries. Standard literature procedures were used to prepare [RhCl-$(C_8H_{12})]_2$[13] and [IrCl(C_8H_{12})]$_2$.[14] Reagent grade solvents were purified by standard methods.[15] Spectral grade absolute ethanol and methanol were used as received.

Instrumentation. Infrared spectra of the solid complexes were measured on either a Perkin-Elmer 337 (4000–400 cm^{-1}) or a Perkin-Elmer 283B (4000–200 cm^{-1}) grating spectrophotometer as pressed potassium bromide pellets or as solutions by using a matched set of potassium bromide infrared cells with an approximate path length of 0.2 mm. The infrared peaks of the complexes were calibrated against the sharp peak (1601.4 cm^{-1}) of polystyrene film.

A Bruker HX-90 spectrometer operating at 36.43 MHz was used to collect most of the Fourier-mode, broad-band, proton-noise-decoupled ^{31}P NMR spectra. Also, several ^{31}P and ^{1}H NMR spectra were obtained on either a Bruker MSL-300 or a Bruker AM-500 spectrometer. The ^{31}P NMR spectra were obtained on the Bruker HX-90 instrument on solutions in a 10-mm tube fitted with a coaxial insert containing deuterated acetone for the deuterium lock and trimethyl phosphate for a secondary standard (1.59 ppm relative to the 85% H_3PO_4 standard). Spectra from the 300- and 500-MHz instruments were obtained with 5-mm tubes and standardized with external 85% H_3PO_4 and internal TMS. All samples were run at room temperature unless noted otherwise. Positive chemical shifts are downfield from the 85% H_3PO_4 standard. Proton magnetic resonance spectra were collected on the Bruker 80-MHz spectrometer with the residual protons of the deuterated solvent (referenced to TMS) as the internal standard.

Computer simulations of experimental spectra were performed with the PANIC program, which is a modification of Laocoon-III, provided by Bruker Instruments, Inc.

General Procedures. Standard techniques for manipulation of air-sensitive materials were used, and all reactions were carried out under an atmosphere of high-purity nitrogen by using standard Schlenk techniques and an inert-atmosphere box; transfers between glass vessels were made with syringes purged with nitrogen or with a stainless-steel cannula. Solvents were either freshly distilled under N_2 or purged with a N_2 stream for approximately 30 min prior to use.

Elemental analyses were performed by M.H.W. Laboratories, Phoenix, AZ. Satisfactory C, H, and X microanalyses were obtained for the complexes reported; the data for the new complexes are included as supplementary material.

Syntheses of the Complexes. Two general synthetic methods were used; method A involved metathesis and substitution reactions, and method B involved the preparation of the [Rh(PP$_3$)S]$^+$ cation as starting material, where S = acetone or THF.

Method A for [RhX(PPh$_3$)] (X = Cl$^-$, Br$^-$, I$^-$). These compounds were prepared by an adaptation of the method reported in the literature for preparing [RhCl(QP)].[16] A mixture of $Rh_2X_2(COD)_2$ (0.5 mmol) and PP_3 (1.0 mmol) was stirred in 30 mL of EtOH in a Schlenk flask. The resultant heterogeneous mixture was refluxed for 2 h and then allowed to stir at room temperature overnight. The resultant red-orange or orange microcrystals were collected on a Schlenk frit under N_2, washed in sequence with EtOH and Et_2O, and dried in vacuo; yields were 72.8%, 60.1%, and 45.0%, respectively. Our [RhCl(PP$_3$)] complex had the same ^{31}P{^{1}H} NMR spectrum as that reported in the literature.[8a]

[Rh(PP$_3$)PR$_3$]AsF$_6$ (PR$_3$ = P(OMe)$_3$, PEt$_3$). A slight excess (0.05 mL) of the monodentate phosphorus ligand was added via a syringe to a stirred mixture of RhCl(PP$_3$) (0.185 mmol) in 20 mL of MeOH. To the resultant yellow mixture was added a slight excess of LiAsF$_6$ (0.2 mmol). The color of the solution slowly changed to yellow-orange, and the mixture was stirred overnight at room temperature. The bright yellow or orange-yellow crystals, respectively, were collected on a frit, washed with MeOH and Et_2O, and dried in vacuo; yields 59.7% and 70.0%, respectively. The infrared spectra of the solids showed peaks characteristic of the monodentate phosphorus ligand and the AsF$_6^-$ anion. Attempts to prepare the corresponding P(C_6H_5)$_3$ derivative by this method were unsuccessful.

[RhBr$_2$(PP$_3$)]Br. This compound was prepared by the method adapted from the preparation of [RhCl$_2$(NP$_3$)]Cl.[17] A 1:1 molar mixture of RhBr$_3$·$3H_2O$ (1 mmol) and PP_3 (1 mmol) in 70 mL of EtOH was heated at reflux for 5 h. After cooling, yellow microcrystals were collected on a Schlenk frit, washed with EtOH, and dried in vacuo. This yellow solid was [RhBr$_3$(η^3-PP$_3$)] (II). The yellow filtrate was evaporated to dryness isothermally. The resultant yellow-tan solid was identified as [RhBr$_2$-(PP$_3$)]Br (I). The ^{31}P{^{1}H} NMR spectra of I and II were consistent with the proposed formulations.

[RhH(PP$_3$)]. A suspension of NaBH$_4$ (0.1 g, 2.5 mol excess) in 10 mL of EtOH was added via a dropping funnel to a solution of I (1.00 mmol) in 30 mL of EtOH. An orange solid formed on mixing. After all the NaBH$_4$ was added, the mixture was heated at 40 °C for 6 h. The bright yellow solid was separated by filtration from the yellow-orange solution. The yellow microcrystals were dried in vacuo for 2.5 h. Both ^{1}H NMR and ^{31}P NMR spectroscopies indicate the presence of a Rh–H bond, with no bridging hydride. The infrared Rh–H frequency, ν_{Rh-H} = 1730 cm^{-1}, and the ^{31}P and ^{1}H NMR spectral data of this compound were identical with those reported for RhH(PP$_3$).[9] If the mixture was allowed to stir overnight before filtration, formation of the orange solid [RhBr(PP$_3$)] resulted. However, addition of 0.10 g of NaBH$_4$ and heating at 45 °C for 3 h resulted in re-formation of the bright yellow solid [RhH(PP$_3$)].

Attempts to prepare [RhH(PP$_3$)] from solutions of II in EtOH resulted in the preparation of [RhBr(PP$_3$)]. The yield was 72.9%.

[Rh(PP$_3$)CO]BF$_4$. To a Schlenk flask were added [RhBr(PP$_3$)] (0.12 mmol) and NH$_4$BF$_4$ (0.12 mmol) in 10 mL of isopropyl alcohol. Carbon monoxide gas was bubbled through the mixture for 1 min, and the mixture was stirred for 45 min. The orange solid dissolved slowly. Addition of CO(g) was repeated twice. The mixture was then stirred overnight at room temperature. The resultant dull yellow microcrystals were collected on a frit, washed with i-PrOH and Et_2O, and dried in vacuo. The infrared carbonyl stretching frequencies of the solid were at 1985 and 2010 cm^{-1}; in addition, peaks characteristic of the BF$_4^-$ anion were present.

Attempted Synthesis of [Rh(PP$_3$)CO]BF$_4$ from [RhH(PP$_3$)]. A procedure analogous to that using [RhBr(PP$_3$)] was used except that [RhH(PP$_3$)] was used as the starting material. The bright yellow microcrystals that resulted had infrared carbonyl frequencies at 1985 and 2010 cm^{-1}, but there was an additional peak at 1792 cm^{-1}. This solid appeared

(5) Cecconi, F.; Ghilardi, C. A.; Innocenti, P.; Mealli, C.; Midollini, S.; Orlandini, A. *Inorg. Chem.* **1984**, *23*, 922.

(6) Mealli, C.; Midollini, S.; Moneti, S.; Albright, T. A. *Helv. Chim. Acta* **1983**, *66*, 557.

(7) Cecconi, F.; Midollini, S.; Orlandini, A. *J. Chem. Soc., Dalton Trans.* **1983**, 2263.

(8) (a) Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Zanobini, F. *Organometallics* **1987**, *6*, 2453. (b) Bianchini, C.; Meli, A.; Peruzzini, M.; Ramirez, J. A.; Vacca, A.; Vizza, F.; Zanobini, F. *Organometallics* **1989**, *8*, 337. (c) Bianchini, C.; Laschi, F.; Ottaviani, M. F.; Peruzzini, M.; Zanello, P.; Zanobini, F. *Organometallics* **1989**, *8*, 893.

(9) (a) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1987**, *109*, 5548. (b) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 6411.

(10) Blum, P. R. A Phosphorus-31 NMR Study of a Series of Square-Planar, Polyphosphine Rhodium(I) Complexes and Their Sulfur Dioxide Adducts, Ph.D. Dissertation, The Ohio State University, 1977.

(11) (a) Tau, K. D. A Phosphorus-31 NMR Study of a Series of Square-Planar, Platinum(II) Complexes of ttp, Ph.D. Dissertation, The Ohio State University, 1978. (b) Tau, K. D.; Meek, D. W. *Inorg. Chem.* **1979**, *18*, 3574.

(12) Meek, D. W.; Mazanec, T. J. *Acc. Chem. Res.* **1981**, *14*, 266.

(13) Chatt, J.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 4735.

(14) Winkhaus, G.; Singer, H. *Chem. Ber.* **1966**, *99*, 3610.

(15) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R., *Purification of Laboratory Chemicals*; Pergamon Press: New York, 1966.

(16) Higginson, B. R.; McAuliffe, C. A.; Venanzi, L. M. *Helv. Chim. Acta* **1975**, *58*, 1261.

(17) DiVaira, M.; Peruzzini, M.; Zanobini, F.; Stoppioni, P. *Inorg. Chim. Acta* **1983**, *69*, 37.

to be a mixture of [Rh(PP₃)CO]BF₄ and an additional compound, which was also indicated by the ³¹P{¹H} NMR spectrum. The additional compound in this mixture had a ³¹P{¹H} NMR spectrum identical with that of the (PP₃)Rh fragment at 173 K reported recently.[9a]

Method B, Synthesis of the Complexes [RhX(PP₃)] (X = Cl⁻, CN⁻, NO₂⁻, NCS⁻). [Rh(PP₃)(acetone)]BF₄ + NaX → [RhX(PP₃)] + Acetone. To a Schlenk flask containing an excess of NaX (40 mg) and acetone (10 mL) was added a solution of [Rh(PP₃)(acetone)]BF₄ via a stainless-steel cannula. In the cases of NaCN and NaNO₂, 15-crown-5 (0.2 mL) was added to enhance the solubility of the sodium salts in acetone. The ammonium salt, NH₄NCS, was used for X = NCS⁻. The resulting solution was stirred until precipitation was complete, overnight for the chloro and thiocyanato complexes, 30 min for the cyano complex, and 2 min for the nitro complex. The orange, yellow, orange-yellow, and orange solids, respectively, were collected on a frit, washed with EtOH and Et₂O, and dried in vacuo. Yields were 69%, 75%, 81%, and 77%, respectively. Infrared spectra indicated the presence of the cyano group with the C≡N stretching frequency at 2097 cm⁻¹, the NO₂⁻ group with the NO₂ bending frequency at 818 cm⁻¹ and the NO₂ symmetric stretching frequency at 1325 cm⁻¹, and the NCS⁻ group with ν_{CN} at 2105 cm⁻¹. Our [RhCN(PP₃)] complex has the same ³¹P{¹H} NMR spectrum and IR spectrum as is in the literature.[8c]

[Rh(PP₃)CH₃CN]BF₄. To a Schlenk flask containing [Rh(PP₃)(acetone)]BF₄ and acetone (10 mL) was added an excess of acetonitrile (ca. 1 mL). The solution was stirred for 3 h; a yellow solution resulted. The volume of solution was reduced to 5-7 mL, and Et₂O was added to precipitate a dark yellow solid. The solid was collected on a filter frit under nitrogen, washed with Et₂O, and dried in vacuo. Yield: 0.243 g, 65%.

[Rh(PP₃)py]BF₄. To a Schlenk flask containing [Rh(PP₃)(acetone)]BF₄ and acetone (10 mL) was added an excess of pyridine (1 mL). The solution was stirred overnight; a dark burgundy-colored solution resulted. The volume of solution was reduced to approximately 5 mL, and Et₂O was added to precipitate a red solid. The resulting bright red powder was collected on a filter frit under nitrogen, washed with Et₂O, and dried in vacuo. Yield: 0.272 g, 70%.

[Rh(PP₃)CO]BF₄. Carbon monoxide gas was bubbled for 5 min into a solution of [Rh(PP₃)(acetone)]BF₄. The color of the solution changed slowly from dark red to yellow. The solution was stirred for another 30 min under a CO atmosphere, with no additional color change apparent. The volume of solvent was reduced under vacuum to approximately 5-7 mL, and diethyl ether was added to precipitate a yellow solid. The resulting yellow precipitate was collected on a filter frit, washed with degassed EtOH and Et₂O, and dried in vacuo. The presence of the CO group was indicated by its infrared spectrum, with ν_{CO} peaks at 1985 and 2010 cm⁻¹. Yield: 0.267 g, 73%.

[Rh(PP₃)(PPhMe₂)]BF₄. To a Schlenk flask containing a solution of [Rh(PP₃)(acetone)]BF₄ was added a slight excess of degassed PPhMe₂ (0.62 mL, 0.450 mmol). The color of the solution changed slowly from dark red to tan. The solution was stirred overnight at room temperature. The solvent volume was reduced under nitrogen to approximately 5-7 mL, and addition of diethyl ether caused a yellow solid to form along with a brown oil. The dense nature of the brown oil allowed the yellow powder to be separated from the mixture by decanting the liquid and powder under nitrogen onto a filter frit. The yellow solid was then washed with Et₂O and dried in vacuo. Yield: 0.176 g, 43%.

[Rh(PP₃)(PEt₃)]BF₄. To a Schlenk flask containing [Rh(COD)-(acetone)₂]BF₄ (1.22 mmol) in acetone (10 mL) was added PEt₃ (0.58 mL, 4.88 mmol). The solution was stirred for 30 min; the resulting orange solution was transferred to a flask containing dried Celite 545. The resultant suspension was dried in vacuo, transferred to a column packed with Celite, and then washed with hexane and toluene to remove excess PEt₃. The product was eluted with 10 mL of acetone, and the resulting [Rh(PEt₃)₄]BF₄ was a red oil.

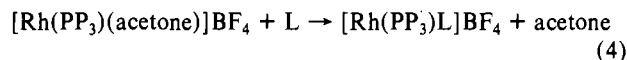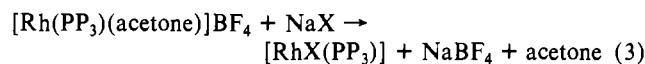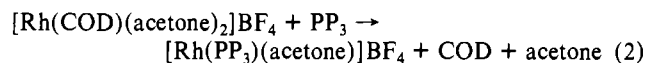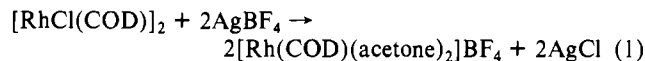A solution of [Rh(PEt₃)₄]BF₄ (0.275 g, 0.414 mmol) in acetone (5 mL) was added to a solution of PP₃ (0.278 g, 0.414 mmol) in acetone (5 mL) via a stainless-steel cannula. The resultant solution was stirred for 30 min, during which the solution color changed from orange to yellow. The volume of solvent was then reduced to approximately 5-7 mL, and Et₂O was added to cause precipitation of a yellow solid. The solid was collected under nitrogen on a filter frit, washed with diethyl ether, and dried in vacuo. Yield: 0.255 g, 63%.

Results and Discussion

Syntheses and Properties of the Complexes. The syntheses of trigonal-bipyramidal rhodium(I) complexes containing the tripod ligand P(CH₂CH₂PPh₂)₃, PP₃, by method A are essentially metathesis reactions where either an anion or a neutral molecule replaces a halide ion. The syntheses proved successful in most instances; however, sometimes reflux conditions and stirring for

long time periods (i.e., overnight) were involved. In addition, displacement of the halide ion by some neutral and anionic ligands (e.g., PPh₃ and CN⁻) was unsuccessful.

Method B involves a different synthetic route that is patterned after work by Schrock and Osborn.[18] They reported a procedure for in situ generation of a coordinatively unsaturated species [Rh(COD)Sₙ]⁺ (where n = 2 or 3 and S = a MeOH or acetone solvent molecule) from the chloro-bridged dirhodium complex [RhCl(COD)]₂. The solvated cation can then be treated easily with a variety of donor ligands to yield the corresponding four- or five-coordinate rhodium(I) complexes. The general reactions used for this study are given in eq 1-4.

$$[RhCl(COD)]_2 + 2AgBF_4 \rightarrow$$
$$2[Rh(COD)(acetone)_2]BF_4 + 2AgCl \quad (1)$$

$$[Rh(COD)(acetone)_2]BF_4 + PP_3 \rightarrow$$
$$[Rh(PP_3)(acetone)]BF_4 + COD + acetone \quad (2)$$

$$[Rh(PP_3)(acetone)]BF_4 + NaX \rightarrow$$
$$[RhX(PP_3)] + NaBF_4 + acetone \quad (3)$$

$$[Rh(PP_3)(acetone)]BF_4 + L \rightarrow [Rh(PP_3)L]BF_4 + acetone \quad (4)$$

Method B has several appealing advantages. First of all, the reactions were all performed at room temperature and were considered complete within 2 h, although some of the syntheses were allowed to stir overnight for convenience and to ensure completion of the reaction. Secondly, the precursor rhodium cation can be generated in situ prior to use. Finally, and most importantly, a wider variety of ligands can be reacted successfully with [Rh(PP₃)(acetone)]⁺ than with [RhX(PP₃)] (X = halide). Even weak ligands such as pyridine or acetonitrile can be treated with [Rh(PP₃)(acetone)]⁺ to give the corresponding five-coordinate complexes.

One explanation why [Rh(PP₃)(acetone)]⁺ is generally more useful than RhCl(PP₃) for synthesis of the five-coordinate complexes may depend on the ease of dissociation of the fifth ligand (acetone or chloride, respectively). For method A, dissociation of chloride would require breaking the Rh–Cl bond and separation of charge, whereas dissociation of the weak ligand acetone in method B does not involve separation of charge and should be facile. For bulky ligands (e.g., PEt₃ and PPh₃), even the [Rh-(PP₃)(acetone)]⁺ intermediate did not yield pentakis(phosphine) products. The latter result may be due to the small cavity remaining for the fifth ligand, as a result of the congested environment of the three equatorial diphenylphosphino groups. In order to test this steric hypothesis, we decided to invert the reaction sequence and add PP₃ to a preformed Rh–PEt₃⁺ species, i.e., [Rh(PEt₃)₄]⁺. This procedure gave the desired cation [Rh-(PP₃)(PEt₃)]⁺ in 63% isolated yield; that is, the chelating PP₃ ligand replaced three monodentate PEt₃ ligands, and the resulting [Rh(PP₃)(PEt₃)]⁺ cation was isolated.

Characterization of [Rh(PP₃)L]⁰,¹⁺ Complexes. The metal complexes were characterized by elemental analyses, infrared spectroscopy, and phosphorus-31 nuclear magnetic resonance spectroscopy. The most informative technique for this study was phosphorus-31 NMR spectroscopy.

Most of the [Rh(PP₃)L]⁰,¹⁺ complexes have simple first-order ³¹P{¹H} NMR splitting patterns, even at 36.43 MHz. When the monodentate, fifth ligand is not NMR active, the patterns indicate an AMX₃ spin system, which is consistent with the predicted trigonal-bipyramidal structure, C_{3v} symmetry. The spectra consist of a doublet of quartets for the apical phosphorus atom, resulting from being split into a quartet by coupling to three equivalent equatorial phosphorus atoms that are, in turn, split into a doublet due to coupling with the rhodium ($I = {}^1/_2$, 100% natural abundance) atom. Analogously, the equatorial phosphorus atoms are split into a doublet of doublets by the apical phosphorus atom and the rhodium atom. A typical spectrum, which illustrates this

(18) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397.

Table I. $^{31}P\{^1H\}$ NMR Data for the Trigonal-Bipyramidal $[Rh(PP_3)L]^{0,1+}$ Complexes

compd	coupling const, Hz					
	$^2J_{P_1-P_2}$	$^2J_{P_1-P_3}$	$^2J_{P_2-P_3}$	J_{Rh-P_1}	J_{Rh-P_2}	J_{Rh-P_3}
$[RhBr(PP_3)]$	16			148	128	
$[RhI(PP_3)]$	15			147	127	
$[RhCl(PP_3)]$	17			148	126	
$[Rh(PP_3)CH_3CN]BF_4$	18			143	117	
$[Rh(NCS)(PP_3)]$	19			146	117	
$[Rh(PP_3)py]BF_4$	16			145	112	
$[Rh(NO_2)(PP_3)]$	18			153	106	
$[RhCN(PP_3)]$	23			146	93	
$[Rh(PP_3)(PMe_2Ph)]BF_4$	23	42	289	140	90	100
$[RhH(PP_3)]$	19			162	89	
$[Rh(PP_3)PEt_3]BF_4$	24	41	271	143	88	96
$[Rh(PP_3)P(OMe)_3]BF_4$	26	49	456	140	87	164
$[Rh(PP_3)CO]BF_4$	25			133	84	
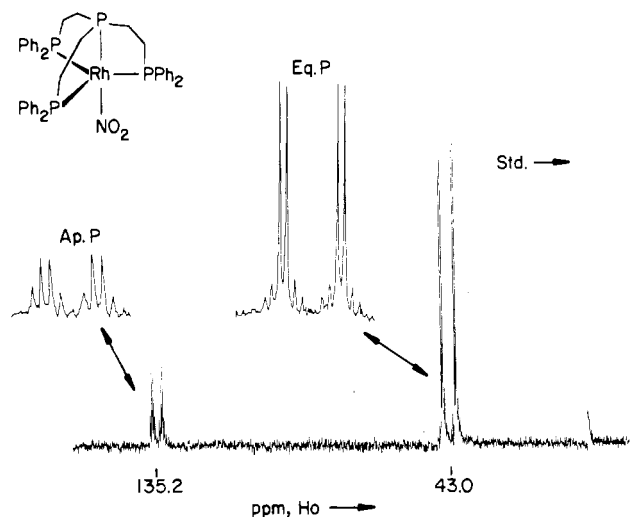
Figure 1. $^{31}P\{^1H\}$ NMR spectrum (36.43 MHz) of $Rh(NO_2)(PP_3)$ in CH_2Cl_2.

splitting, is shown in Figure 1, for $[Rh(NO_2)(PPh_3)]$. If the monodentate ligand is also NMR active (e.g., $[Rh(PP_3)(PEt_3)]BF_4$ and $[Rh(PP_3)(PPhMe_2)]BF_4$), then all the resonances described above will be split into additional doublets.

When the trans phosphorus ligand has a chemical shift close (L = phosphite) to that of the apical phosphorus atom, a second-order ABMX$_3$ splitting pattern is obtained. A 36.43-MHz $^{31}P\{^1H\}$ NMR spectrum of $Rh(PP_3)\{P(OMe)_3\}]AsF_6$ in CH_2Cl_2 is shown in Figure 2a. The corresponding computer-simulated spectrum is given in Figure 2b. The second-order nature of the three cobalt triad cations $[M(PP_3)\{P(OMe)_3\}]^+$ (M = Co, Rh, Ir) at 36.43 MHz decreases systematically as the central metal becomes heavier, i.e., Co > Rh > Ir. To better determine the splitting pattern of the $[Rh(PP_3)P(oMe)_3]AsF_6$ complex, a 121.497-MHz spectrum was obtained on a 300-MHz spectrometer. The spectrum in Figure 3 is almost a first-order AKMX$_3$ pattern that shows clearly the doublet of doublet of quartets for the apical phosphorus resonance, the doublet of doublet of quartets due to the monodentate phosphite ligand, and the doublet of doublet of doublets for the equatorial phosphorus atoms.

In general, the ^{31}P NMR chemical shift of a phosphine ligand is shifted downfield when it is coordinated to a metal, compared to the ^{31}P chemical shift of the free ligand; this shift is treated quantitatively as the coordination chemical shift, Δ, defined as $\delta(P(coordinated)) - \delta(P(free\ ligand))$.[19] The ^{31}P NMR data in Tables I and II show large Δ values, particularly for P_2, the apical phosphorus atom of PP_3. These large shifts result from the fact that phosphorus atoms that are incorporated into a five-membered chelate ring show larger coordination chemical shifts than do
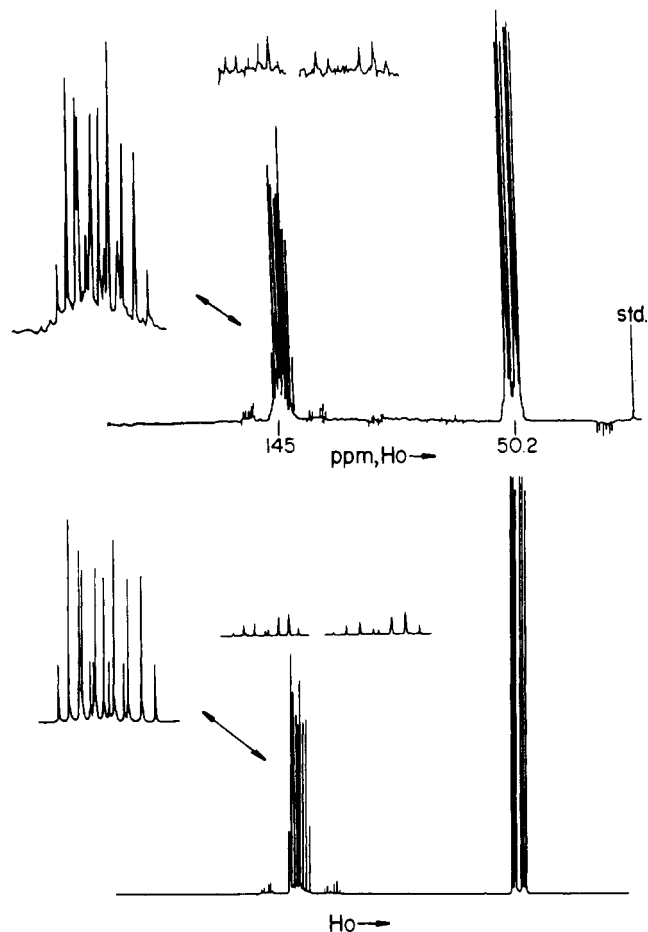
Figure 2. (a, Top) $^{31}P\{^1H\}$ NMR spectrum (36.43 MHz) of $[Rh(PP_3)\{P(OMe)_3\}]AsF_6$ in CH_2Cl_2. (b, Bottom) Computer-simulated spectrum for the six-spin $[Rh(PP_3)\{P(OMe)_3\}]^+$ cation.

monodentate PR_3 ligands or even four- or six-membered chelated phosphorus ligands.[20] Garrou[21] has described this behavior as an additional deshielding contribution to the chemical shift and has designated it Δ_R. The Δ values of the P_1 phosphorus atoms (equatorial ligands) in the five-membered chelate rings of PP_3 are approximately 55–65 ppm. It has been observed previously[12,22] that if a phosphorus atom is located at the bridgehead of two or three five-membered chelate rings, the Δ values for each chelate ring are nearly additive. Thus, the P_2 resonances show Δ values approximately 3 times as large as the P_1 Δ values, consistent with all three PPh_2 groups being chelated in these PP_3 complexes.

(19) (a) Mann, B. E.; Masters, C.; Shaw, B. L. *J. Chem. Soc. A* **1971**, 1104. (b) Mann, B. E.; Masters, C.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1972**, 704.

(20) Grim, S. O.; Briggs, W. L.; Barth, R. C.; Tolman, C. A.; Jesson, J. P. *Inorg. Chem.* **1974**, *13*, 1095.

(21) (a) Garrou, P. E. *Inorg. Chem.* **1975**, *14*, 1435. (b) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(22) King, R. B.; Cloyd, J. C. *Inorg. Chem.* **1975**, *14*, 1550.

Table II. $^{31}P\{^1H\}$ NMR Data for the Trigonal-Bipyramidal $[Rh(PP_3)L]^{0,1+}$ Complexes

compd	chem shift, ppm[a]			coord chem shift, ppm		
	$\delta(P_1)$	$\delta(P_2)$	$\delta(P_3)$	$\Delta(P_1)$[b]	$\Delta(P_2)$[c]	$\Delta(P_3)$[d]
$[RhBr(PP_3)]$	41.8	152.8		55.9	171.7	
$[RhI(PP_3)]$	43.7	160.0		57.8	178.9	
$[RhCl(PP_3)]$	40.3	146.7		54.4	165.6	
$[Rh(PP_3)CH_3CN]BF_4$	45.0	136.8		59.1	155.6	
$[Rh(NCS)(PP_3)]$	42.7	141.8		56.8	160.7	
$[Rh(PP_3)py]BF_4$	48.0	143.6		62.1	162.4	
$[Rh(NO_2)(PP_3)]$	43.0	135.2		57.1	154.1	
$[Rh(CN)(PP_3)]$	50.6	152.2		64.7	171.1	
$[Rh(PP_3)(PMe_2Ph)]BF_4$	45.8	143.7	1.1	59.9	162.6	47.1
$[RhH(PP_3)]$	64.5	159.2		78.6	178.1	
$[Rh(PP_3)PEt_3]BF_4$	44.4	140.8	13.4	58.5	159.3	32.3
$[Rh(PP_3)P(OMe)_3]BF_4$	50.2	145.9	139.1	64.3	164.8	1.1
$[Rh(PP_3)CO]BF_4$	60.9	152.5		59.1	155.6	

[a] Chemical shifts are relative to 85% H_3PO_4; (+) is downfield from H_3PO_4. [b] $\Delta(P_1) = \delta(\text{coordinated } P_1) - \delta(\text{free } P_1)$. [c] $\Delta(P_2) = \delta(\text{coordinated } P_2) - \delta(\text{free } P_2)$. [d] $\Delta(P_3) = \delta(\text{coordinated } P_3) - \delta(\text{free } P_3)$.
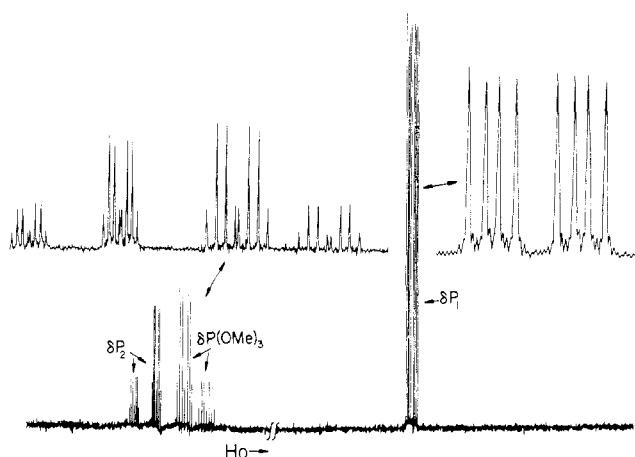

Figure 3. $^{31}P\{^1H\}$ NMR spectrum (121.497 MHz) of $[Rh(PP_3)\{P-(OMe)_3\}]AsF_6$ in CH_2Cl_2/CD_2Cl_2.

The Trans Influence. The trans influence of a ligand in a metal complex was described by Pidcock et al.[23] in 1966 as the extent to which that ligand weakens the bond trans to itself in the equilibrium ground state of that complex. Several experimental techniques (e.g., infrared and NMR spectroscopy and X-ray crystal structure determinations) have been employed to monitor the trans influence of a ligand.

To date, phosphorus NMR studies on rhodium complexes have generally dealt with planar systems. The ligand used in the present study, $P(CH_2CH_2PPh_2)_3$ (PP_3), is ideally suited for an investigation into the trans influence of trigonal-bipyramidal complexes, since this geometry is maintained throughout the series of rhodium–PP_3 complexes. Also, the constancy of the cis ligands, which PP_3 provides, is crucial to the study so that any change in J_{Rh-P_2}, where P_2 is trans to the variable fifth ligand L, can indeed be attributed to ligand L and not to changes of the cis ligands. The NMR spectral data, in particular the rhodium–phosphorus spin–spin coupling constant involving the apical phosphorus atom, can be used to probe the nature of the σ bonding within the complex.

Direct coupling between two heavy nuclei (A and B) having $I = ^1/_2$ is thought to be dominated by the Fermi contact term,[24] and to a first approximation it is given by eq 5.

$$J_{A-B} \approx \gamma_A\gamma_B\alpha_A^2\alpha_B^2|\psi_{A(ns)}{}^{(0)}|^2|\psi_{B(ns)}{}^{(0)}|^2((^3\Delta E)^{-1}) \quad (5)$$

Applying eq 5 to metal–phosphine complexes, the trans influence is apparently determined by the ligand's effectiveness in competing for the metal orbital's s-character.[23] This point can be understood by examining a series of closely related metal complexes where all the factors in eq 5 can be considered constant

except for α_M^2 and $|\psi_{M(ns)}{}^{(0)}|^2$. As with the platinum systems described earlier,[11,12] any changes in J_{Rh-P_2} must be due to variations in α_{Rh}^2. Thus, an increase in J_{Rh-P_2} should reflect a rehybridization of the rhodium center so that more s-character is used in the rhodium hybrid orbital bonding with P_2.

The complexes reported in Table I are listed in the order of decreasing J_{Rh-P_2}. The higher values of J_{Rh-P_2} indicate a weaker influence by the trans ligand L; that is, the ligand is not competing as well with P_2 for rhodium s-orbital character. If one lists the anionic ligands in order of decreasing J_{Rh-P_2}, the following series is obtained: $Br^- \approx I^- \approx Cl^- > NCS^- > NO_2^- > CN^- > H^-$. This order is roughly the reverse of that of the σ-donating ability of the ligand. As none of these anionic ligands displays any significant π-acid properties (with the possible exception of CN^-), this order of J_{Rh-P_2} values apparently reflects the relative trans-influence ability of the ligand.[10] Support for the assumption that variations in J_{Rh-P_2} are due to the influence of the trans ligand and not to some property of the molecule as a whole is the fact that the J_{Rh-P_1} values remain relatively constant. The lone exception to this trend is the abnormally high value of J_{Rh-P_1} for H^-. This aberration can be explained in terms of a synergistic effect, since a decrease in the s-character of the apical (trans) rhodium–phosphorus bond causes an increase in the s-character of the equatorial (cis) rhodium–phosphorus bonds. Similar results have been reported in square-planar complexes, in which a σ-donating ligand with a large trans influence has a small cis influence.[25]

The neutral ligands produce the following order of decreasing values of J_{Rh-P_2}: $CH_3CN > py > PPhMe_2 > PEt_3 > P(OMe)_3 > CO$. Some interesting questions arise from this series of neutral ligands. For example, the two ligands with the highest trans influence, CO and $P(OMe)_3$, are also relatively strong π-acids. If π-bonding makes a significant contribution to the M–L bond strengths, these ligands should not accurately reflect the trans influence, since NMR coupling constants should reflect directly only the σ-bonding character. The rhodium–phosphorus coupling constant for the equatorial (cis) phosphines is unusually small; a similar reduction has also been observed for the cis Rh–P coupling in the planar complex $[Rh(ttp)CO]PF_6$.[10] The low cis rhodium–phosphorus coupling in both cases may be explained by the fact that the CO ligand is generally considered to be a good π-acceptor. If the rhodium–phosphorus interactions have any dependence on formation of π-back-bonding with the rhodium atom, removal of π-electron density by the carbonyl ligands would affect all the Rh–P bonds, including the cis bonds. It should also be noted that the π-acidity of ligands L can, in principle, affect the σ-bonding by P_2. If P_2 is weakly π-acidic, its σ-donor ability will be enhanced. In this case, competition from a ligand such as CO could have the effect of reducing the π-back-donation to P_2, slightly lengthening the Rh–P_2 bond, and decreasing J_{Rh-P_2}.

The ligand cone angle is another important factor to consider when the trends for the neutral ligands are examined. The cone

(23) Pidcock, A.; Richards, R. E.; Venanzi, L. M. *J. Chem. Soc. A* **1966**, 1707.
(24) Pople, J. A.; Santry, D. P. *Mol. Phys.* **1964**, *8*, 1.

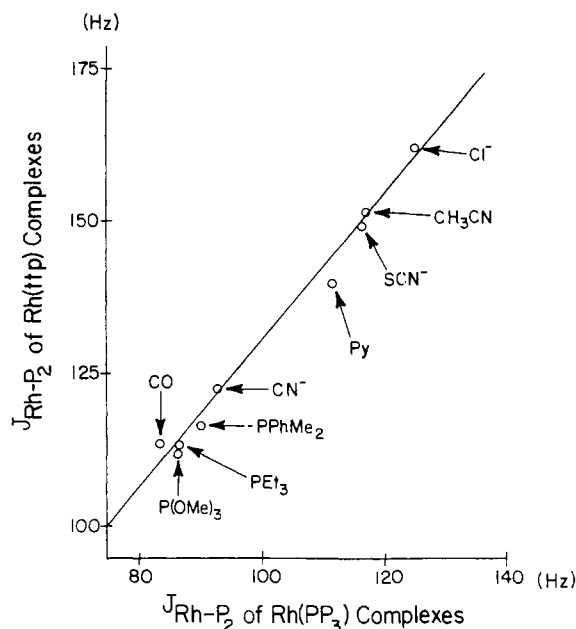(25) Mason, R.; Towl, A. D. C. *J. Chem. Soc. A* **1970**, 1601.

Figure 4. Plot of Rh–P coupling constants involving the central phosphorus atoms of ttp and PP_3 in planar and trigonal-pyramidal Rh(I) complexes, respectively.

angles of CO ($\approx 95°$) and $P(OMe)_3$ (107°) are significantly smaller than those of py (119°), $PPhMe_2$ (122°), and PEt_3 (132°).[26] The axial position, where the monodentate ligands coordinate, is sterically congested by the phenyl rings on the cis phosphorus atoms, and any increase in the cone angle would decrease the ligand's bonding effectiveness, owing to steric interactions. Consequently, the effective orbital overlap between the metal and the monodentate ligand is reduced, as the cone angle of the ligand increases.

Figure 4 shows a plot of J_{Rh-P_2} for the trigonal-bipyramidal $[Rh(PP_3)L]^{0,1+}$ complexes versus J_{Rh-PPh} for the planar $[Rh(ttp)L]^{0,1+}$ complexes (ttp = the tridentate ligand PhP-$(CH_2CH_2CH_2PPh_2)_2$).[10] Figure 4 reflects the constancy in the trans influence in both trigonal-bipyramidal and planar rhodium complexes. This is indicated by the linear plot (correlation = 0.995). It is clear that the mechanism of Rh–P coupling is similar for both series of complexes. For planar complexes, ideally one can consider 25% s-character (dsp^2 hybridization), whereas in trigonal-bipyramidal systems the metal orbital system would have 20% s-character (dsp^3); therefore, the expected trans influence in the $[Rh(ttp)L]^{0,1+}$ complexes should be greater than that in the $[Rh(PP_3)L]^{0,1+}$ complexes. This effect is reflected by the observed slope of 1.24.

The data in this study support the hypothesis that variations in the J_{Rh-P_2} values reflect variations in the amount of s-character of the hybrid orbital used in the rhodium–phosphorus bond. Ligands of high trans influence tend to use orbitals of high s-character in their bonds to rhodium; consequently, less s-character is available for use in the rhodium–phosphorus bond. Thus, a lower J_{Rh-P} value is observed.

Hohman et al.[27] have examined the effect of trans ligands on the chemical shifts of the central phosphorus atom in $[Co(PP_3)L]^{0,1+}$ and $[Ni(PP_3)L]^{1+,2+}$ complexes. A comparison of the

(26) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(27) Hohman, W. H.; Kountz, D. J.; Meek, D. W. *Inorg. Chem.* **1986**, *25*, 616.

Table III. Effect of the Trans Ligand on the Chemical Shift of the Central (Bridgehead) Phosphorus Atom, i.e., Influence on the Position of δ(P_2) (Hz)

compd	chem shift
$[Co(PP_3)L]^{0,1+}$ series	I⁻ < H⁻ < CN⁻ < Br⁻ < CO < 184.5 182.8 172.6 171.9 170.7 $P(OMe)_3$ < PF_2OMe < PPh_2OMe < 168.7 162.1 159.9 NCS⁻ < $PPhMe_2$ < PEt_3 158.7 152.3 147.2
$[Ni(PP_3)L]^{1+,2+}$ series	CO < I⁻ < H⁻ < CN⁻ < Br⁻ < 178.6 167.1 160.4 155.2 151.9 $P(OCH_2CF_3)_3$ < $P(OMe)_3$ < $P(OEt)_3$ < 151.2 147.5 142.8 Cl⁻ 140.9
$[Rh(PP_3)L]^{0,1+}$ series	I⁻ < H⁻ < Br⁻ < CO < 160.0 159.2 152.8 152.5 CN⁻ < Cl⁻ < $P(OMe)_3$ < $PPhMe_2$ < 152.2 146.7 145.9 143.7 NCS⁻ < PEt_3 < NO_2⁻ 141.8 138.3 135.2

^{31}P resonances of the central phosphorus atom (trans to the variable ligand L) in these cobalt and nickel complexes with the corresponding resonance in the $[Rh(PP_3)L]^{0,1+}$ series is given in Table III. Although the trends observed in Table III appear to be generally consistent for each metal series, there is no obvious quantitative relationship between the ^{31}P chemical shifts of the P_2 atom and the observed J_{Rh-P_2} values in the rhodium complexes.

Conclusions

The PP_3 ligand proved ideal for a study of AMX_3 and $AKMX_3$ spin systems in transition-metal complexes and of the trans influence, as it fixed the geometry of all the ligands in each complex. The ^{31}P NMR data show that J_{Rh-P} values apparently reflect accurately the percent s-character of the hybrid orbital of rhodium used in the rhodium–phosphorus bond. Finally, the influence of a ligand on the s-character of the hybrid orbital of the metal is the same in trigonal-bipyramidal complexes and planar complexes; even changing from rhodium to platinum[11] seemingly does not change the ligand's relative position in the trans-influence series.