$[RuH_2(PPh_3)_4]$ or $[OsH_4(PPh_3)_3]$ with *p*-tolyl isocyanate affords the formamidinato complexes $[MH(RN\overset{\cdots}{-}CH\overset{\cdots}{-}NR)(CO)(PPh_3)_2]$ (M = Ru and Os, respectively). The ruthenium complex is identical with an authentic specimen previously prepared from di-*p*-tolylcarbodiimide[4,5] and is shown by X-ray diffraction methods to possess stereochemistry IVa.[5] In contrast, the less labile osmium system retains the intermediate stereochemistry IVb rather than isomerizing to the thermodynamically preferred structure IVa. Spectroscopic data (Table II) are in accord with these stereochemical assignments. Formation of the formamidinate ligand clearly involves fragmentation of at least two isocyanate moieties. The stoichiometry of the overall reaction appears to be

$$RuH_2(PPh_3)_4 + 2RNCO \rightarrow RuH(RN\overset{\cdots}{-}CH\overset{\cdots}{-}NR)(CO)(PPh_3)_2 + PPh_3 + OPPh_3$$

or

$$OsH_4(PPh_3)_3 + 2RNCO \rightarrow OsH(RN\overset{\cdots}{-}CH\overset{\cdots}{-}NR)(CO)(PPh_3)_2 + OPPh_3 + H_2$$

At the request of a referee we append a note on the NMR spectra of the formamide and formamidinate ligands. As we have previously noted, chelate ligands of the form $X\overset{\cdots}{-}CH\overset{\cdots}{-}Y$ (X, Y = RN or S) usually show a proton resonance, τ_{CH} ca. −5 to +2, attributable to the ligand CH group. However, in several instances the position of this resonance is such that masking by the aromatic resonances of the PPh_3 ligand (τ_{Ph} 2.2–2.7) occurs. Masking has already been fully documented for one of the products mentioned in the present paper, $[RuH(RN\overset{\cdots}{-}CH\overset{\cdots}{-}NR)(CO)(PPh_3)_2]$, and the structure of this complex has been confirmed by X-ray diffraction methods.[5] Therefore the apparent absence of such resonances from the ^1H NMR spectra of the formamido and formamidinato complexes discussed above is not inconsistent with the proposed structures.

Registry No. I (M = Ru, X = Cl, R = *p*-Me-C_6H_4), 69372-56-1; I (M = Ru, X = Br, R = *p*-Me-C_6H_4), 69372-57-2; I (M = Os, X = Br, R = *p*-Me-C_6H_4), 71597-17-6; IIa (M = Ru, R = *p*-Me-C_6H_4), 69372-58-3; IIb (M = Os, R = *p*-Me-C_6H_4), 69427-90-3; III (M = Ru, R = *p*-Me-C_6H_4), 69403-53-8; III (M = Os, R = *p*-Me-C_6H_4), 69403-54-9; IVa (R = *p*-Me-C_6H_4), 60939-10-8; IVb (R = *p*-Me-C_6H_4), 71629-32-8; carbonylchlorohydridotris(triphenylphosphine)ruthenium, 16971-33-8; bromocarbonylhydridotris(triphenylphosphine)ruthenium, 16971-34-9; carbonyldihydridotris(triphenylphosphine)ruthenium, 25360-32-1; carbonyldihydridotris(triphenylphosphine)osmium, 12104-84-6; dihydridotetrakis(triphenylphosphine)ruthenium, 19529-00-1; tetrahydridotris(triphenylphosphine)osmium, 24228-59-9; bromocarbonylhydridotris(triphenylphosphine)osmium, 16971-32-7; *p*-tolyl isocyanate, 622-58-2.

References and Notes

(1) Part 17: C. J. Creswell, A. Dobson, D. S. Moore, and S. D. Robinson, *Inorg. Chem.*, **18**, 2055 (1979).

(2) S. D. Robinson and A. Sahajpal, *J. Organomet. Chem.*, **99**, C65 (1975); *Inorg. Chem.*, **16**, 2718 (1977).

(3) S. D. Robinson and A. Sahajpal, *J. Organomet. Chem.*, **111**, C26 (1976); *Inorg. Chem.*, **16**, 2722 (1977).

(4) S. D. Robinson and A. Sahajpal, *J. Organomet. Chem.*, **117**, C111 (1976).

(5) L. D. Brown, S. D. Robinson, A. Sahajpal, and J. A. Ibers, *Inorg. Chem.*, **16**, 2728 (1977).

(6) S. D. Robinson and A. Sahajpal, *J. Organomet. Chem.*, **164**, C9 (1979).

(7) S. Cenini and G. La Monica, *Inorg. Chim. Acta*, **18**, 279 (1976).

(8) N. Ahmad, S. D. Robinson, and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 843 (1972).

(9) S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 1912 (1973).

(10) A. Dobson, S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 370 (1975).

(11) K. R. Laing, S. D. Robinson, and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 1205 (1974).

(12) G. Chandra, A. D. Jenkins, M. F. Lappert and R. C. Srivastava, *J. Chem. Soc. A*, 2550 (1970).

(13) J. D. Wilkins, *J. Organomet. Chem.*, **67**, 269 (1974), and references therein.

(14) S. Cenini, M. Pizzotti, F. Porta, and G. La Monica, *J. Organomet. Chem.*, **88**, 237 (1975).

(15) W. Beck, W. Rieber, S. Cenini, F. Porta, and G. La Monica, *J. Chem. Soc., Dalton Trans.*, 298 (1974).

(16) J. A. J. Jarvis, B. E. Job, B. T. Kilburn, R. H. B. Mais, P. G. Owston, and P. F. Todd, *Chem. Commun.*, 1149 (1967), and references therein.

(17) M. Dekker and G. R. Knox, *Chem. Commun.*, 1243 (1967).

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

Platinum(II) Complexes of the Chelating Triphosphine Bis(3-(diphenylphosphino)propyl)phenylphosphine. Phosphorus-31 NMR Studies of the Cis and Trans Influence on These Model Compounds[1]

KWOLIANG D. TAU and DEVON W. MEEK*

Received September 22, 1978

A series of planar $[Pt(ttp)X]^+$ (ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$; X = Cl^-, NCS^-, NO_2^-, H^-, CH_3^-, CH_2CN^-, $COOCH_3^-$, $CH_2CH{=}CH_2^-$, and Ph^-) and $[Pt(ttp)Y]^{2+}$ (Y = $P(OMe)_3$ and PEt_3) complexes have been prepared and characterized by their elemental analyses, conductivity measurements, infrared spectra, and ^1H and ^{31}P NMR spectra. The σ-bonded carbon ligands (X = methyl, cyanomethyl, and allyl) were prepared by oxidative-addition reactions on the Pt(0) compounds $Pt(ttp)PPh_3$ and $Pt(ttp)CO$. The SO_2 complex $[Pt(ttp)Cl]Cl{\cdot}SO_2$ is unusual for a SO_2–metal complex, as the SO_2 molecule is sulfur bonded to the ionic chloride to give the SO_2Cl^- anion, instead of being bonded either to the metal or to one of its ligands. The magnitude of the one-bond platinum–phosphorus coupling constant obtained from phosphorus-31 NMR spectra produces the trans influence series $Ph^- \sim \sigma\text{-allyl}^- > COOCH_3^- > CH_3^- > H^- > CH_2CN^- > PEt_3 > P(OMe)_3 > NO_2^- > {-}NCS^- > Cl^-$. As the fourth ligand ($X^-$ or Y) is varied, the changes in the cis coupling constants, $^1J_{Pt-PPh_2}$, are smaller than the changes in the trans coupling constants, $^1J_{Pt-PPh}$. The σ-donor ligands that exert a large trans influence (e.g., CH_3^- and $CH_2CH{=}CH_2^-$) display a small cis influence, whereas those ligands that exert a small trans influence (e.g., Cl^-) produce a relatively large cis influence. The following cis influence series is deduced from the $^1J_{Pt-PPh_2}$ values: $P(OMe)_3 > NCS^- > Cl^- > PEt_3 > NO_2^- > CH_2CN^- > COOH_3^- > H^- > CH_3^- > Ph^- > \sigma\text{-allyl}^-$. The ^{31}P NMR spectra of several $[Pt(ttp)X]^+$ complexes (X = anionic ligand) demonstrate that the ^{195}Pt satellite patterns are not necessarily the same as the central resonance.

Introduction

A trans or cis influence is defined as the extent to which a ligand L weakens the bond trans or cis to itself, M–A, in the ground state of a metal complex.[2] Recent theoretical treatments explain satisfactorily the high trans influence of ligands such as hydride and σ-alkyl which have strong σ-donor

0020-1669/79/1318-3574$01.00/0

and virtually no π-acceptor properties.[2-4] However for ligands with strong π-acceptor properties (e.g., CO and $F_2C{=}CF_2$), the available data seem to indicate that the cis or trans influence may also depend, at least to some extent, on the metal → ligand π back-bonding.

Although the cis and trans influences can be measured directly via bond lengths, most of the investigations reported in the literature have used indirect methods (e.g., vibrational spectra and NMR spectra) as measurements.[6] Pidcock et al. have attempted to find a correlation between Pt–P bond lengths and the NMR coupling constants in trialkylphosphine complexes.[7] However, some recent publications have disagreed with the proposed correlation.[8-10] The failure may be attributed to the steric and electronic effects of the cis ligands. Since the overall bonding factors in a metal complex depend on the nature of the ligands and the metal coordination geometry, it is imperative that all of the factors be fixed, except for the one variable ligand, if one is to determine the cis or trans influence of a ligand. The chelating triphosphine $PhP(CH_2CH_2CH_2PPh_2)_2$, ttp, appears to be an ideal ligand for X-ray crystallography and ^{31}P NMR studies on planar metal complexes, as it fixes three of the four coordination positions into a constant environment. Also, physical measurements on its planar complexes yield simultaneously both the cis and trans influences of the fourth ligand; in addition, conformational flexibility of the trimethylene chain permits the P–M–P angles within each chelate ring to be ~90°. Herein, we report the preparation and characterization of several Pt(II) complexes of the types $[Pt(ttp)X]^+$ (X = anion) and $[Pt(ttp)Y]^{2+}$ (Y = neutral ligand) and their ^{31}P NMR studies to evaluate the cis and trans influences of the variable fourth ligand.

Experimental Section

Reagents and Chemicals. Triethylphosphine was obtained from Pressure Chemical Co., Pittsburgh, PA, and was used without further purification. Trimethyl phosphite (from Eastman Chemical Co.) was distilled from sodium under nitrogen. The $Pt(COD)Cl_2$ was prepared according to literature methods,[11] and ttp was prepared by modifying Nappier's[12,13] sequence. Solvents were dried and purified by standard literature methods.

Instrumentation and Characterization Measurements. Infrared spectra of solids were measured on a Perkin-Elmer Model 337 grating spectrophotometer from 400 to 4000 cm^{-1} as Nujol mulls or hexachlorobutadiene mulls between potassium bromide plates. A polystyrene film was used for calibration of the spectra.

Conductance measurements were made on approximately 10^{-3} M nitromethane solutions with an Industrial Instruments, Inc., conductivity bridge, Model RC 16B2, operating at 1000 Hz. The nitromethane was reagent grade and it was distilled from anhydrous $CaCl_2$ prior to use.

Proton magnetic resonance spectra were collected on either a Varian A60-A, a Varian HA-100, or a Bruker HX-90 spectrometer. Me_4Si was generally used as an internal reference or lock signal. In some cases, the solvent resonance was used as a reference and lock signal and corrected to be relative to Me_4Si; in other cases the residual proton signal from the deuterated solvent was used as an internal reference.

Fourier-mode, proton-noise-decoupled, phosphorus-31 NMR spectra were collected on a Bruker HX-90 spectrometer operating at 36.43 MHz with a Bruker B-NC 12 data system. The samples were run in 10-mm tubes, and deuterated solvents (10–20% of the sample volume) provided an internal deuterium lock. Generally, 85% phosphoric acid was used as an external reference by (1) obtaining a spectrum of the sample, (2) inserting a coaxial tube containing phosphoric acid into the sample tube and collecting 5–7 pulses for the reference spectrum, and (3) merging the two spectra together via the computer to obtain a standardized spectrum. *Positive chemical shifts are downfield from* H_3PO_4. In some cases the deuterated solvent and trimethyl phosphate (used as a secondary standard; $\delta = 58.09$ Hz relative to H_3PO_4) were contained in a 5-mm coaxial tube inside the sample tube throughout the collection of data.

Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ; carbon analyses were performed by using a V_2O_5 combustion catalyst.

Syntheses of the Platinum(II) and Platinum(0) Complexes of ttp. Generally, the AsF_6^- salts of the Pt(II) cations were prepared similarly. Thus, only the preparation of $[Pt(ttp)Cl]AsF_6$ is described in detail.

[Pt(ttp)Cl]Cl. A solution of $Pt(COD)Cl_2$ (1.7417 g) in benzene (40 mL) was treated with ttp (17 mL, 0.2936 M in toluene) and then refluxed for 3 h. The resultant precipitate was collected on a filter, washed with benzene (40 mL) and diethyl ether (50 mL) successively, and dried with air. Recrystallization from hot ethanol gave a white crystalline solid. This compound also was prepared by refluxing K_2PtCl_4 with ttp in a solution of $EtOH-H_2O$. The yield was 90% by the $PtCl_2(COD)$ route, whereas 80% yields were obtained by using K_2PtCl_4 directly.

[Pt(ttp)Cl]AsF₆. To a solution of [Pt(ttp)Cl]Cl (0.6375 g) in ethanol (30 mL) was added $NaAsF_6$ (0.3251 g). A crystalline white precipitate formed instantaneously and the resulting mixture was refluxed for 1 h to ensure completeness of reaction. After the mixture cooled to room temperature, the solid was separated by filtration, washed sequentially with distilled water, ethanol, and ether, and then dried with air; yield 0.6835 g.

Anal. Calcd for $C_{36}H_{37}AsClF_6P_3Pt$: C, 44.02; H, 3.81; Cl, 3.61; F, 11.61. Found: C, 43.86; H, 3.79; Cl, 3.78; F, 11.48.

The analogous complexes with BF_4^- and NO_3^- as nonbonded anions were prepared in a similar way.

[Pt(ttp)Cl]Cl·SO₂. A slow stream of SO_2 gas was bubbled through a solution of [Pt(ttp)Cl]Cl (0.7118 g) in dichloromethane (20 mL) for 1.5 h; then the solution was treated with diethyl ether (35 mL). Colorless crystals started to form gradually. The resulting mixture was allowed to sit in a freezer for 3 h before it was filtered. The crystals were collected on a filter, washed with diethyl ether, and dried in vacuo; yield 0.7209 g.

Anal. Calcd for $C_{36}H_{37}Cl_2O_2P_3PtS$: C, 48.43; H, 4.19; Cl, 7.94; S, 3.59. Found: C, 48.25; H, 4.08; Cl, 8.16; S, 3.69.

[Pt(ttp)NO₂]AsF₆. A solution of $NaNO_2$ (0.8591 g) in ethanol (30 mL) and distilled water (15 mL) was mixed with $[Pt(ttp)Cl]AsF_6$ (0.3956 g) and then refluxed for 2 h. The solvent was removed from the resulting mixture on a rotary evaporator, and the resultant white solid was collected on a filter, washed with distilled water and diethyl ether successively, and then air-dried; yield 0.3805 g.

Anal. Calcd for $C_{36}H_{37}AsF_6NO_2P_3Pt$: C, 43.56; H, 3.76; N, 1.41. Found: C, 43.53; H, 3.94; N, 1.22.

[Pt(ttp)NCS]NCS. A solution of [Pt(ttp)Cl]Cl (0.7549 g) and potassium thiocyanate (1.0 g) in absolute ethanol (35 mL) was refluxed for 40 min. The solvent was removed on a rotary evaporator, the residue was mixed with distilled water (100 mL), and the resulting solid was collected on a filter. The white solid was washed with hexane and ether and then air-dried; yield 0.6724 g.

Anal. Calcd for $C_{38}H_{37}N_2P_3PtS_2$: C, 52.22; H, 4.28; N, 3.21. Found: C, 52.49; H, 4.11; N, 3.11.

[Pt(ttp)NCS]AsF₆. Anal. Calcd for $C_{37}H_{37}AsF_6NP_3PtS$: C, 44.23; H, 3.72; N, 1.39. Found: C, 44.24; H, 3.54; N, 1.34.

[Pt(ttp)H]Cl. To a solution of [Pt(ttp)Cl]Cl (1.0275 g) in absolute ethanol (40 mL) was added dropwise 99–100% hydrazine hydrate (2 mL). The resulting mixture was refluxed for 2 h, treated with distilled water (25 mL), and then heated on a hot plate to evaporate the ethanol. When the volume of solution had been reduced to ca. 30 mL, pale white crystals precipitated. After the mixture was cooled in a refrigerator for 1 h, a solid was collected on a filter, washed with distilled water and ether, and then dried in vacuo; yield 0.8800 g.

Anal. Calcd for $C_{36}H_{38}ClP_3Pt$: C, 54.44; H, 4.83; Cl, 4.46. Found: C, 54.59; H, 4.99; Cl, 4.56.

[Pt(ttp)H]AsF₆. Anal. Calcd for $C_{36}H_{38}AsF_6P_3Pt$: C, 45.62; H, 4.05; F, 12.03. Found: C, 45.73; H, 3.97; F, 11.88.

[Pt(ttp)CH₃]AsF₆. To a solution of $Pt(ttp)PPh_3$ (0.5621 g) was added CH_3FSO_3 (0.3 mL, 95%). The resulting mixture was refluxed for 1 h and then cooled to room temperature. The white precipitate was collected on a filter, washed with benzene (35 mL) and then hexane (40 mL), and dried in vacuo; yield ~0.50 g. This solid (0.426 g) was extracted with hot ethanol (40 mL) and the extract was then added into a clear solution of $NaAsF_6$ (0.2363 g) in absolute ethanol (25 mL) to give white needles. After filtration, the crystals were washed with distilled water and diethyl ether and dried in vacuo; yield 0.4192 g.

Anal. Calcd for $C_{37}H_{40}AsF_6P_3Pt$: C, 46.21; H, 4.20; F, 11.85. Found: C, 45.87; H, 4.35; F, 11.67.

[Pt(ttp)CH₂CN]AsF₆. A solution of $Pt(ttp)(PPh_3)$ (0.9826 g) in benzene (30 mL) was treated with $ClCH_2CN$ (ca, 0.1 mL) and then

Table I. Infrared and ^{1}H NMR Data for [Pt(ttp)H] Cl and [Pt(ttp)H] AsF_6

compd	ν_{Pt-H},[a] cm^{-1}	δ_{Pt-H}[b]	$^1J_{Pt-H}$, Hz	J_{PPh_2-H}, Hz	J_{PPh-H}, Hz
[Pt(ttp)H] Cl	2040	12.3	912	10	156
[Pt(ttp)H] AsF_6	2043	12.2	914	10	156

[a] Nujol mull. [b] Spectra were run in CD_3NO_2.

refluxed for 0.5 h. The white precipitate was collected on a filter, washed with benzene and diethyl ether, and then air-dried. This solid (0.7824 g) was dissolved in ethanol (35 mL) and treated with $NaAsF_6$ (0.2950 g). A white precipitate formed immediately. The resulting mixture was refluxed for 0.5 h and then cooled to room temperature. The white crystalline solid was separated by filtration, washed with distilled water and diethyl ether, and then air-dried. Recrystallization from hot ethanol gave white microcrystals; yield 0.6576 g.

Anal. Calcd for $C_{38}H_{39}AsF_6NP_3Pt$: C, 46.25; H, 3.99; F, 11.55. Found: C, 46.21; H, 4.19; F, 11.27.

[Pt(ttp)$CH_2CH{=}CH_2$]Cl. A solution of Pt(ttp)CO (0.8379 g) in benzene (30 mL) was treated with allyl chloride (0.4 mL) and then refluxed for 0.5 h. The resulting white precipitate was collected in a Schlenk filter, washed with hexane (40 mL), and dried in vacuo.

Anal. Calcd for $C_{39}H_{42}ClP_3Pt$: C, 56.14; H, 5.09; Cl, 4.25. Found: C, 55.90; H, 5.04; Cl, 4.53.

[Pt(ttp)$CH_2CH{=}CH_2$]AsF_6. Anal. Calcd for $C_{39}H_{42}AsF_6P_3Pt$: C, 47.42; H, 4.29; F, 11.54. Found: C, 47.42; H, 4.42; F, 11.67.

[Pt(ttp)Ph]Cl. To a solution of Pt(COD)(Ph)Cl[14] (0.1484 g) in benzene (20 mL) was added ttp (1.8 mL, 0.2255 M in benzene). After the solution was stirred for 2 h, the resulting white precipitate was removed by filtration, washed with benzene and diethyl ether, and then dried in vacuo.

Anal. Calcd for $C_{42}H_{42}ClP_3Pt$: C, 57.96; H, 4.87; Cl, 4.07. Found: C, 57.82; H, 4.82; Cl, 4.20.

[Pt(ttp)$COOCH_3$]AsF_6. A solution of [Pt(ttp)Cl]Cl (0.4400 g) in methanol (35 mL) was treated with CO gas for 5 min and then treated with $AgAsF_6$ (97%, 0.3387 g in 10 mL of methanol). A white solid formed instantly. The resulting mixture was then refluxed for 1.5 h with additional CO gas bubbling. After the mixture cooled to room temperature, it was filtered through a pad of Celite filter-aid on a sintered glass frit and the solid was extracted with dichloromethane (ca. 100 mL). The filtrate and the CH_2Cl_2 extract were combined and concentrated to ca. 20 mL on a rotary evaporator. The resultant white precipitate was collected on a filter, washed with diethyl ether, and air-dried. Recrystallization from CH_2Cl_2 and diethyl ether gave a white solid; yield 0.3876 g.

Anal. Calcd for $C_{38}H_{40}AsF_6O_2P_3Pt$: C, 45.38; H, 4.02; F, 11.34. Found: C, 45.44; H, 4.17; F, 11.51.

[Pt(ttp)Br]Br. A solution of Pt(ttp)(PPh_3) (0.326 g) in benzene (30 mL) was treated with 2-bromopropane (1.2 mL) and refluxed for 4 h. The light yellow precipitate was collected, washed with ether and hexane, and then air-dried.

Anal. Calcd for $C_{36}H_{37}Br_2P_3Pt$: C, 47.12; H, 4.07; Br, 17.42. Found: C, 47.33; H, 4.15; Br, 17.15.

[Pt(ttp)P$(OMe)_3$][AsF_6]$_2$. To a solution of [Pt(ttp)Cl]Cl (0.7757 g) in methanol (30 mL) was added P$(OMe)_3$ (0.8 mL). After the solution was refluxed for 1 h, $NaAsF_6$ (0.3956 g) was added and a white solid formed immediately. The mixture was refluxed for another 2 h and then the solid was collected on a Schlenk filter. The solid was washed with benzene and then dried in vacuo. Recrystallization from dichloromethane and diethyl ether gave a white solid.

Anal. Calcd for $C_{39}H_{46}As_2F_{12}O_3P_4Pt$: C, 37.18; H, 3.69; F, 18.10. Found: C, 37.05; H, 3.59; F, 18.27.

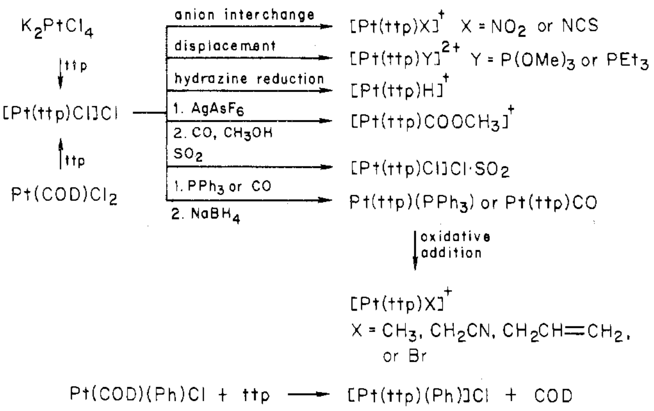
[Pt(ttp)(PEt_3)][AsF_6]$_2$. To a solution of [Pt(ttp)Cl]Cl (0.4235 g) and PEt_3 (0.25 mL) in absolute ethanol (30 mL) was added $TlAsF_6$ (0.5176 g). A white solid precipitated immediately and the resulting mixture was refluxed for 3 h. After all the solvent was removed under reduced pressure, the white solid residue was extracted with dichloromethane (50 mL). Removal of the dichloromethane gave a white solid which was then recrystallized from dichloromethane and benzene, washed with diethyl ether, and dried with air.

Anal. Calcd for $C_{42}H_{52}As_2F_{12}P_4Pt$: C, 40.23; H, 4.19; F, 18.19; P, 9.88. Found: C, 40.43; H, 4.17; F, 17.94; P, 10.09.

Pt(ttp)(PPh_3). To a solution of [Pt(ttp)Cl]Cl (1.056 g) in absolute ethanol (50 mL) and distilled water (15 mL) was added PPh_3 (0.4013 g). The resulting mixture was stirred for 20 min and then treated with solid $NaBH_4$ (0.1448 g) in small portions. A bright yellow solid precipitated immediately. After the reaction mixture had been stirred for 0.5 h at room temperature, the yellow solid was collected on the frit of a Schlenk filter, washed with distilled water (50 mL) and hexane in sequence (30 mL), and dried in vacuo.

Anal. Calcd for $C_{54}H_{52}P_4Pt$: C, 63.58; H, 5.15. Found: C, 63.42; H, 5.31.

Scheme I



Pt(ttp)CO. A solution of [Pt(ttp)Cl]Cl (1.0589 g) in absolute ethanol (50 mL) and distilled water (15 mL) was treated with a stream of CO gas and with simultaneous addition of solid $NaBH_4$ (0.1502 g) in small portions. Hydrogen gas bubbles were evolved and gradually the solution turned to a light yellow; then a solid precipitated. The CO bubbles were continued for another 0.5 h. The resulting light yellow solid was collected on the frit of a Schlenk filter, washed with distilled water (60 mL) and absolute ethanol (40 mL) successively, and dried in vacuo. Recrystallization from a mixture of benzene and absolute ethanol gave light yellow needles; yield 0.8370 g.

Anal. Calcd for $C_{37}H_{37}OP_3Pt$: C, 56.55; H, 4.76; P, 11.83. Found: C, 56.41; H, 4.50; P, 12.01.

Results and Discussion

Characterization of the Complexes. In this study a series of $[Pt(ttp)X]^+$ (X = anionic ligand) or $[Pt(ttp)Y]^{2+}$ (Y = neutral ligand) cationic complexes have been synthesized. Their preparations are summarized in Scheme I.

The $^{31}P\{^1H\}$ NMR spectrum of Pt(ttp)Cl_2 consists of a doublet and triplet with the corresponding ^{195}Pt satellites (^{195}Pt in 33.8% natural abundance, $I = {}^1/_2$), indicating that all three phosphorus nuclei are bonded to the platinum atom. The molar conductivity in nitromethane is 71.5 $cm^2\ \Omega^{-1}\ mol^{-1}$ (10^{-3} M), which is typical of a 1:1 electrolyte.[15] Thus, we can formulate Pt(ttp)Cl_2 as [Pt(ttp)Cl]Cl with an ionic chloride, which has been replaced easily by BF_4^-, NO_3^-, and AsF_6^-.

Treatment of [Pt(ttp)Cl]Cl with hydrazine hydrate yields the hydride [Pt(ttp)H]Cl. The completeness of the reaction was checked periodically by $^{31}P\{^1H\}$ NMR, as the starting material and the product give distinguishable patterns in the ^{31}P NMR spectra. The molar conductivity of [Pt(ttp)H]Cl in nitromethane is 74.3 $cm^2\ \Omega^{-1}\ mol^{-1}$, which confirms its ionic formulation. The spectroscopic data shown in Tables I and II for [Pt(ttp)H]Cl and [Pt(ttp)H]AsF_6 are almost identical, as expected. The hydride resonance for [Pt(ttp)H]AsF_6 at 90 MHz is first order (i.e., a doublet of triplets for the central portion and the upfield ^{195}Pt satellite). The downfield satellite is obscured by the methylene proton resonances from the ligand ttp.

Two strong (C≡N) thiocyanate bands are present in the infrared spectrum of [Pt(ttp)NCS]NCS. The lower frequency

Table II. ^{31}P NMR Data for Platinum(II) Complexes of ttp

complex[a]	chem shift		coupling const,[b] Hz		
	δ_{PPh_2}	δ_{PPh}	$^1J_{Pt-PPh_2}$	$^1J_{Pt-PPh}$	$^2J_{PPh_2-PPh}$
$[Pt(ttp)Cl]AsF_6$	−3.7	−20.8	2211	3109	27
$[Pt(ttp)Cl]Cl$	−3.9	−20.7	2229	3134	27
$[Pt(ttp)NCS]AsF_6$	−6.7	−26.6	2152	3049	27
$[Pt(ttp)NO_2]AsF_6$	−11.3	−33.0	2350	2453	29
$[Pt(ttp)P(OMe)_3][AsF_6]_2$[c]	−8.1	−29.6	2129	1980	34
$[Pt(ttp)PEt_3][AsF_6]_2$[d]	−5.7	−22.0	2252	1895	37
$[Pt(ttp)CH_2CN]AsF_6$	−3.5	−27.1	2422	1890	32
$[Pt(ttp)H]Cl$	0.5	−17.2	2531	1690	29
$[Pt(ttp)H]AsF_6$	0.6	−17.2	2530	1688	30
$[Pt(ttp)CH_3]AsF_6$	2.1	−23.5	2608	1624	32
$[Pt(ttp)COOCH_3]AsF_6$	−13.1	−29.8	2500	1582	34
$[Pt(ttp)CH_2CH{=}CH_2]AsF_6$	0.4	−25.3	2722	1541	34
$[Pt(ttp)Ph]Cl$	−3.4	−25.7	2623	1540	31

[a] The spectra of these complexes were run in $CD_3NO_2 + CH_3NO_2$ except for $[Pt(ttp)Ph]Cl$ which was run in $CH_2Cl_2 + CD_3NO_2$. [b] The NMR data were collected with a 16K computer; thus, an 8K transform with a sweep width of 8K gives a resolution of ±1 Hz for the coupling constants. [c] $\delta_{P(OMe)_3} = 86.1$, $J_{Pt-P(OMe)_3} = 4189$ Hz, $J_{PPh_2-P(OMe)_3} = 31$ Hz, $J_{PPh-P(OMe)_3} = 487$ Hz. [d] $\delta_{PEt_3} = 1.8$, $J_{Pt-PEt_3} = 2161$ Hz, $J_{PPh_2-PEt_3} = 18$ Hz, $J_{PPh-PEt_3} = 278$ Hz.

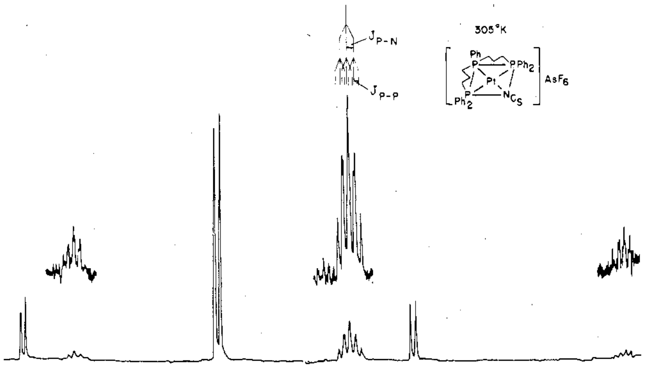


Figure 1. Proton-decoupled, phosphorus-31 NMR spectrum of $[Pt(ttp)NCS]AsF_6$ at 305 K in nitromethane. Inserts are expansions of the central and satellite peaks for the phosphorus nucleus trans to the thiocyanate group.

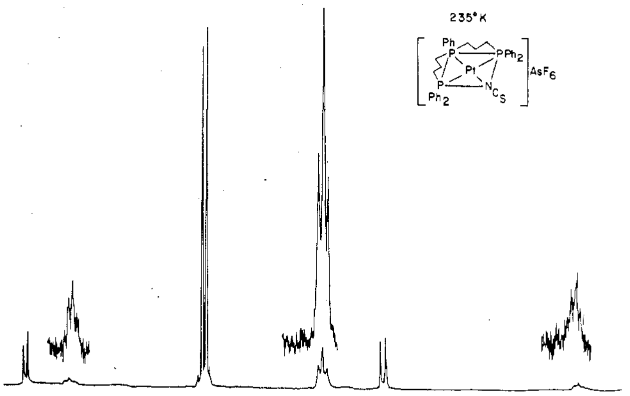


Figure 2. Proton-decoupled, phosphorus-31 NMR spectrum of $[Pt(ttp)NCS]AsF_6$ at 235 K in nitromethane. Inserts correspond as in Figure 1.

absorption occurs at 2051 cm^{-1} and is assigned to an ionic thiocyanate group; the higher frequency band at 2098 cm^{-1} is due to an N-bonded thiocyanate group.[16] The molar conductivity (86.4 cm^2 Ω^{-1} mol^{-1}) in 10^{-3} M nitromethane solution confirms the ionic formulation $[Pt(ttp)NCS]NCS$. The triplet in the $^{31}P\{^1H\}$ NMR spectrum of $[Pt(ttp)NCS]NCS$, which is due to the central phosphorus nucleus of the ttp ligand, is broad, suggesting that the ^{14}N nucleus from the NCS^- ligand is coupled to the phosphorus nucleus trans to it and exerts a quadrupolar effect. The spectroscopic data on $[Pt(ttp)NCS]AsF_6$ lends further support to this assignment. Its infrared spectrum shows only one (C≡N) band at 2098 cm^{-1} and the $^{31}P\{^1H\}$ spectrum at 305 K (Figure 1) clearly shows the coupling between ^{14}N and the central phosphorus nucleus with $^2J_{^{31}P-^{14}N} = 34$ Hz. When the temperature is decreased to 235 K, the multiplet from the central phosphorus nucleus collapses to a broad triplet (Figure 2). Elimination of $^{14}N-^{31}P$ coupling at lower temperature is caused by the more rapid ^{14}N quadrupolar relaxation which induces an increasing rate of interconversion between the nuclear spin states (i.e., $m_I = 1, 0, -1$), thus effectively decoupling ^{14}N from ^{31}P.[17] Although Carty et al. first reported the $^{14}N-^{31}P$ coupling constant in the ^{31}P NMR solution spectra of *cis*-$Pt(CNS)_2[P(OPh)_3]_2$,[18] the results here represent the first example that demonstrates both the $^{14}N-^{31}P$ coupling and the quadrupolar effect together in an isolated complex.

The NO_2^- ligand also can be an ambidentate ligand. However, the infrared spectrum of $[Pt(ttp)NO_2]AsF_6$ has absorption bands at 1401, 1325, and 815 cm^{-1} which are characteristic of nitro complexes.[19] Although the formation of the nitrito (ONO) complex may be sterically favorable with the bulky ttp ligand, the electronic effect seems to dominate in this case; X-ray crystallography has confirmed the $Pt-NO_2$ linkage.[20]

Treatment of a solution of $[Pt(ttp)Cl]Cl$ with gaseous SO_2 resulted in the isolation of a colorless crystalline compound whose infrared spectrum shows two new strong absorptions at 1269 and 1120 cm^{-1}, which are assigned to the antisymmetric and symmetric S–O stretching vibrations of a bonded SO_2 molecule. Since the SO_2 molecule can bond several different ways in a metal complex (e.g., sulfur bonded to a metal center in a coplanar[21] or bent fashion,[22] both sulfur and one oxygen bonded to a metal center,[23] sulfur bonded to a coordinated halide ion,[24] and sulfur bridged between two transition metal atoms[25]), an X-ray structure determination was performed by Dr. R. M. Kirchner. The structure of the compound shows that the SO_2 molecule is bonded to the ionic chloride through the sulfur atom[26] to form the SO_2Cl^- anion, which is analogous to the recently characterized SO_2I^- anion.[27] Thus, this complex is a rare example of an SO_2–metal compound in which the SO_2 molecule is not associated with either the metal center or its coordinated ligands.

The isolation of $[Pt(ttp)COOMe]AsF_6$ occurred during an attempt to prepare the carbonyl complex $[Pt(ttp)CO](AsF_6)_2$. The isolated solid does not show a ν_{CO} peak in the 1900–2100-cm^{-1} region; however, it does have a strong band in the infrared spectrum at 1625 cm^{-1}, which is in the range expected for an alkoxycarbonyl group.[28] This compound probably is formed via $[Pt(ttp)CO]^{2+}$ in which the strongly polarized C≡O undergoes nucleophilic attack by the methoxide ion. A

Table III. ^{31}P NMR Data for Platinum(0) Complexes (Solvent C_6H_6 + C_6D_6)

	chem shift			coupling const, Hz					
compd	δ_{PPh_2}	δ_{PPh}	δ_{PPh_3}	$^1J_{Pt-PPh_2}$	$^1J_{Pt-PPh}$	$^1J_{Pt-PPh_3}$	$^2J_{PPh_2-PPh}$	$^2J_{PPh_2-PPh_3}$	$^2J_{PPh-PPh_3}$
Pt(ttp)CO	−15.4	−28.4		3359	3179		31		
Pt(ttp)(PPh_3)	−12.3	−29.5	14.7	3664	3994	3356	42	53	42

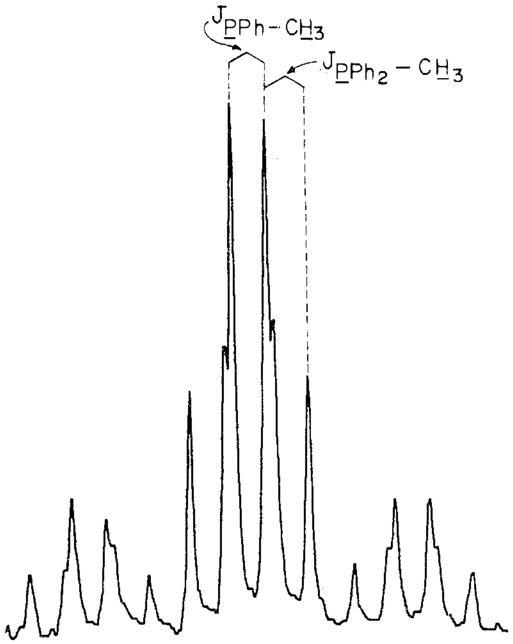


Figure 3. Proton NMR spectrum of the Pt–CH_3 region of [Pt(ttp)CH_3]AsF_6 in CD_3NO_2.

similar type of reaction has been observed even with the monopositive ion [PtCl(CO)(PPh_3)$_2$]$^+$ to form PtCl(COOMe)(PPh_3) and PtCl(COOEt)(PPh_3)$_2$ with methanol and ethanol, respectively.[29]

The platinum(0) complexes, Pt(ttp)(PPh_3) and Pt(ttp)CO, were synthesized primarily to serve as reagents for making σ Pt–C bonds via oxidative addition. The CO stretching frequency of Pt(ttp)CO occurs at 1920 cm^{-1} (Nujol mull), which is close to the values reported for the monophosphine analogues.[30] The ^{31}P NMR parameters of Pt(ttp)CO and Pt(ttp)(PPh_3) are given in Table III.

The Pt–C complexes [Pt(ttp)X]$^+$ (X = CH_3, CH_2CN, σ-allyl) have been isolated from reactions of the above Pt(0) compounds with the appropriate halocarbon molecule. The methyl compound [Pt(ttp)CH_3]FSO_3 was prepared by using methyl fluorosulfonate by a procedure that had been reported for [Pt(PPh_3)$_3CH_3$]FSO_3;[31] the FSO_3^- anion was then replaced by AsF_6^-. The proton NMR spectrum of [Pt(ttp)CH_3]AsF_6 in the Pt–CH_3 region is shown in Figure 3 and the data are summarized as follows: $\delta_{CH_3} = 0.10$, $^3J_{PPh_2-CH_3} = 7.5$ Hz, $^3J_{PPh-CH_3} = 6.2$ Hz, and $^2J_{Pt-CH_3} = 57.2$ Hz. These spectra data are very similar to the corresponding values observed for [Pt(PPh_3)$_3CH_3$]FSO_3. The [Pt(ttp)CH_2CN]AsF_6 complex has a strong infrared band at 2210 cm^{-1}, indicating the presence of a cyanomethyl group.[32] The ^{31}P{^{1}H} NMR data (Table II) are consistent with a Pt–C σ bond. For the [Pt(ttp)allyl]AsF_6 complex the infrared absorption at 1605 cm^{-1} ($\nu_{C=C}$) and the ^{1}H and ^{31}P{^{1}H} NMR data (Table II) all indicate a σ bonded allyl group. This has been confirmed recently by an X-ray structure determination (Pt–C bond distance = 2.15 (1) Å, while all the other Pt–C distances from the allyl group are >3.08 (2) Å).[33]

Treatment of Pt(ttp)CO or Pt(ttp)PPh_3 with several other possible oxidative-addition agents have, in general, produced halide complexes rather than the desired Pt–C compound. For example, treatment of Pt(ttp)(PPh_3) with 2-bromopropane yields the [Pt(ttp)Br]Br complex, rather than the desired [Pt(ttp)(CH(CH_3)$_2$)]Br complex. Similarly, Pt(ttp)(PPh_3) reacts readily with CCl_3CN, but the isolated compound is [Pt(ttp)Cl]Cl. The phenylating agent $Ph_2I^+Cl^-$[34] reacts readily with Pt(ttp)CO, but it does not give the Pt(II) σ-phenyl complex. Instead, the product is the iodo complex [Pt(ttp)I]Cl. Treatment of PhC≡CCH_2Br or $(CH_3)_2NCOCl$ with Pt(ttp)CO produces mixtures of the halide and the corresponding Pt–C species.

Although an excess of trimethyl phosphite was used in the reaction with [Pt(ttp)Cl]Cl, only a four-coordinate [Pt(ttp)P(OMe)$_3$][AsF_6]$_2$ complex was isolated. The two strong bands at 1045 and 800 cm^{-1} in the infrared spectrum of [Pt(ttp)P(OMe)$_3$][AsF_6]$_2$ can be assigned to the asymmetric and symmetric P–O–C stretching frequencies, respectively. Both the platinum–phosphorus coupling constant ($^1J_{Pt-P(OMe)_3} = 4189$ Hz) and the phosphorus–phosphorus ($^2J_{PPh-P(OMe)_3} = 487$ Hz) coupling to the trans phosphorus atom are significantly larger for this P(OCH_3)$_3$ complex than for similar phosphine complexes.

^{31}P NMR Studies on the Cis and Trans Influences of Ligands. The variation in J_{Pt-P} for P trans to a ligand L may be represented primarily as a change in the 6s character of the hybrid orbital of platinum used in bonding to that phosphorus atom. Thus, ligands which exhibit a high trans influence increase the platinum 6s character of the Pt–L bond at the expense of the trans Pt–P bond that is in competition for the same s ± d hybrid orbital. Consequently, a larger value of J_{Pt-P} corresponds to a smaller trans influence by the competing ligand L and vice versa.

The ^{31}P NMR spectral data for [Pt(ttp)X]$^+$ (X = anionic ligand) and [Pt(ttp)Y]$^{2+}$ (Y = neutral ligand) are listed in Table II. The values of $^1J_{Pt-PPh}$ in the complexes decrease in the order Cl^- > NCS > NO_2^- > P(OMe)$_3$ > PEt_3 > CH_2CN^- > H^- > CH_3^- > $COOCH_3^-$ > $CH_2CH{=}CH_2^-$ ~ Ph^-. In general, this order is in agreement with several series of trans-influence ligands that have been obtained by other methods.[6] The trend given by the σ-donor ligands is easiest to interpret. In terms of electrostatics and the resultant effect on the trans Pt–P bond, one would expect the stronger σ-donor ligands to produce a smaller value of $^1J_{Pt-PPh}$, i.e., to cause a larger NMR trans influence. At first glance, it is perplexing that phenyl exerts a larger trans influence than methyl. Usually we assume that a methyl group is a better electron donor group than a phenyl group. However, these results for phenyl and methyl are consistent with the relative trans influences observed recently by Appleton and Bennett[35] for PtXR(dppe) complexes (dppe = $Ph_2PCH_2CH_2PPh_2$); these results are also consistent with the relative J_{Pt-P} values for *cis*-PtClR(PEt_3)$_2$ (R = CH_3,C_6H_5)[36] and with earlier ^{1}H and ^{19}F NMR data on various platinum(II) complexes.[37-39]

The following cis influence series is produced by the $^1J_{Pt-PPh_2}$ values in Table II: P(OMe)$_3$ > NCS^- > Cl^- > PEt_3 > NO_2^- > CH_2CN^- > $COOCH_3^-$ > H^- > Ph^- > $CH_2CH{=}CH_2^-$. As the fourth ligand is varied, changes in the cis coupling constants, $^1J_{Pt-PPh_2}$, are small compared to the changes in the trans coupling constants, $^1J_{Pt-PPh}$. However, note that those σ-donor ligands that produce a large trans influence (e.g., $CH_2CH{=}CH_2^-$) give a small cis influence and vice versa. A similar trend

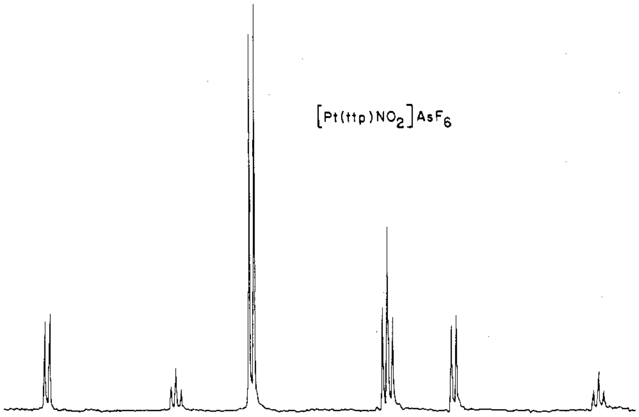


Figure 4. Proton-decoupled, phosphorus-31 NMR spectrum of $[Pt(ttp)NO_2]AsF_6$ in nitromethane solution.

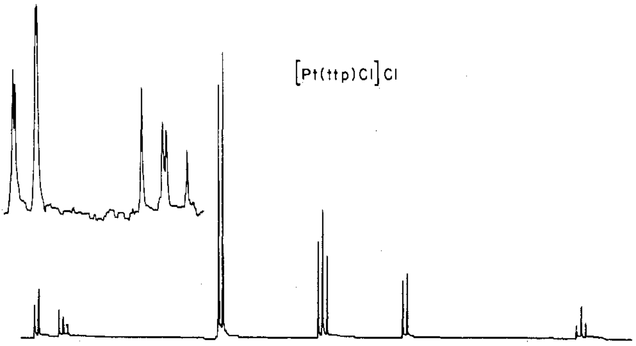


Figure 5. Proton-decoupled, phosphorus-31 NMR spectrum of $[Pt(ttp)Cl]Cl$ in nitromethane solution. The insert is an expansion of the downfield satellite pattern.

has been found for the phosphorus ligands in *cis*-$\{PtCl_2(Bu_3P)L\}$,[40] where the trans influence order was obtained from other studies. This observation is contrary to Zumdahl and Drago's[3] predictions that were based on molecular orbital calculations, i.e., that a ligand with a large trans influence would also produce a cis influence of comparable magnitude.

Theoretically, all of the $\{Pt(ttp)X\}^+$ complexes (X = anionic ligand) should give $^{31}P\{^1H\}$ spectra with an A_2B pattern for the central resonance (due to molecules containing Pt isotopes with $I = 0$; 66.2% natural abundance). In the limit of small values of J_{AB}/ν_{A-B}, the A_2B spectrum is a first-order doublet and triplet pattern with the separation of the lines in the multiplet equal to the coupling constant J_{AB}. Such a pattern is observed for the central portion of the $^{31}P\{^1H\}$ spectra of the $\{Pt(ttp)X\}^+$ complexes. However, the satellites (due to molecules containing ^{195}Pt, 33.8% abundant, $I = {}^1/_2$) are an A_2B portion of the A_2BX spin system. By using the X approximation, the A_2B portion consists of two a_2b subspectra, one having $m_X = {}^1/_2$ and the other $m_X = -{}^1/_2$. Each a_2b subspectrum is a normal A_2B spectrum except that ν_A and ν_B are replaced by "effective" chemical shifts $\nu_A{}^*$ and $\nu_B{}^*$ which are determined as follows:[41]

$$\text{(a) } m_X = \tfrac{1}{2},\ \nu_A{}^* = \nu_A + (1/2)J_{AX}$$

$$\nu_B{}^* = \nu_B + (1/2)J_{BX}$$

$$\delta_{AB}{}^* = \delta_{AB} + (1/2)(J_{AX} - J_{BX})$$

$$\text{(b) } m_X = -\tfrac{1}{2},\ \nu_A{}^* = \nu_A - (1/2)J_{AX}$$

$$\nu_B{}^* = \nu_B - (1/2)J_{BX}$$

$$\delta_{AB}{}^* = \delta_{AB} - (1/2)(J_{AX} - J_{BX})$$

Since J_{AX} and J_{BX} vary as the fourth ligand is changed, the ratio of $J_{AB}/\delta_{AB}{}^*$ may be changed so as to give an A_2B second-order spectrum. For example, both the central and two satellite resonances of $\{Pt(ttp)NO_2\}AsF_6$ (Figure 4) are first order, whereas the downfield ^{195}Pt satellite of $\{Pt(ttp)Cl\}Cl$ (Figure 5) and the upfield satellite of $\{Pt(ttp)COOCH_3\}AsF_6$ (Figure 6) are second order. From the last two spectra, it can be concluded that both $^1J_{Pt-PPh_2}$ and $^1J_{Pt-PPh}$ have the same sign (positive or negative). In the absence of the X portion of the spectra, the relative sign of J_{AB} is undetermined. By use of double-resonance technique, the sign of $^1J_{Pt-P}$ has been determined[42] to be positive in *trans*-$PtHCl(PEt_3)_2$, assuming that $^1J_{Pt-H}$ is positive. Most investigators now assume that $^1J_{Pt-P}$ is positive in the platinum(II) complexes in order to determine the sign of other coupling constants (e.g., $^2J_{Pt-H}$, $^3J_{P-H}$ in methyplatinum(II) complexes).[43,44] Recently, Kennedy et al. extended this logic to determine the sign of $^1J_{Rh-P}$ in some rhodium(I) and rhodium(III) compounds.[45]

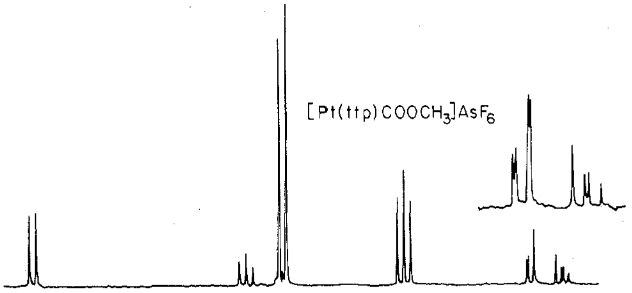


Figure 6. Proton-decoupled, phosphorus-31 NMR spectrum of $[Pt(ttp)COOCH_3]AsF_6$ in nitromethane. The insert corresponds to an expansion of the upfield satellite pattern.

Owing to the large difference in the chemical shift of trimethyl phosphite, the ^{31}P NMR spectrum of $\{Pt(ttp)P(OMe)_3\}\{AsF_6\}_2$ is first order and easily analyzed. However, $\{Pt(ttp)(PEt_3)\}\{AsF_6\}_2$ gives a mixed ABM_2 and ABM_2X spin pattern in the $^{31}P\{^1H\}$ NMR spectrum; the spectrum was first analyzed by a standard procedure and then confirmed by a computer simulation.

Acknowledgment. We thank T. J. Mazanec for assistance in collecting some of the $^{31}P\{^1H\}$ NMR spectra. We are grateful to the National Science Foundation for an instrument grant that aided the purchase of the Bruker HX-90 NMR spectrometer.

Registry No. $[Pt(ttp)Cl]AsF_6$, 71597-20-1; $[Pt(ttp)Cl]Cl$, 71597-21-2; $[Pt(ttp)NCS]AsF_6$, 71597-23-4; $[Pt(ttp)NO_2]AsF_6$, 71597-25-6; $[Pt(ttp)P(OMe)_3][AsF_6]_2$, 71597-27-8; $[Pt(ttp)PEt_3][AsF_6]_2$, 71597-29-0; $[Pt(ttp)CH_2CN]AsF_6$, 71597-31-4; $[Pt(ttp)H]Cl$, 71597-32-5; $[Pt(ttp)H]AsF_6$, 71597-34-7; $[Pt(ttp)CH_3]AsF_6$, 71597-36-9; $[Pt(ttp)COOCH_3]AsF_6$, 71597-38-1; $[Pt(ttp)CH_2CH{=}CH_2]AsF_6$, 71597-40-5; $[Pt(ttp)Ph]Cl$, 71597-41-6; $[Pt(ttp)Cl]Cl{\cdot}SO_2$, 71597-42-7; $[Pt(ttp)NCS]NCS$, 71597-43-8; $[Pt(ttp)CH_2CH{=}CH_2]Cl$, 71597-44-9; $[Pt(ttp)Br]Br$, 71597-45-0; $Pt(COD)Cl_2$, 12080-32-9; $Pt(ttp)PPh_3$, 71597-46-1; $Pt(ttp)CO$, 71597-47-2; $Pt(COD)(Ph)Cl$, 51177-65-2.

References and Notes

(1) Paper abstracted from the Ph.D. Dissertation of K. D. Tau, The Ohio State University, March 1978.

(2) (a) A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. A*, 1707 (1966); (b) L. M. Venanzi, *Chem. Br.*, **4**, 162 (1968).

(3) S. S. Zumdahl and R. S. Drago, *J. Am. Chem. Soc.*, **90**, 6669 (1968).

(4) (a) R. McWeeny, R. Mason, and A. D. C. Towl, *Discuss. Faraday Soc.*, **47**, 20 (1969); (b) R. Mason and A. D. C. Towl, *J. Chem. Soc. A*, 1601 (1970).

(5) (a) P. B. Hitchcock, M. McPartlin, and R. Mason, *Chem. Commun.*, 1367 (1969); (b) I. Macleod, Lj. Manojlović-Muir, D. Millington, K. W. Muir, D. W. A. Sharp, and R. Walker, *J. Organomet. Chem.*, **97**, C7 (1975); (c) P. B. Hitchcock, B. Jacobson, and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 2043 (1977).

(6) A good review of the earlier chemical and spectroscopic studies on the trans influence is given by T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).

(7) G. G. Mather, A. Pidcock, and G. J. N. Rapsey, *J. Chem. Soc., Dalton Trans.*, 2095 (1973).

(8) Lj. Manojlović-Muir, K. W. Muir, and T. Solomon, *J. Organomet. Chem.*, **142**, 265 (1977).

(9) R. M. Kirchner, R. G. Little, K. D. Tau, and D. W. Meek, *J. Organomet. Chem.*, **149**, C15 (1978).

(10) P. B. Hitchcock, B. Jacobson, and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 2038 (1977).

(11) H. C. Clark and L. E. Manzer, *J. Organomet. Chem.*, **59**, 411 (1973).

(12) T. E. Nappier, Jr., D. W. Meek, R. M. Kirchner, and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 4194 (1973).

(13) K. D. Tau, Ph.D. Dissertation, The Ohio State University, March 1978.

(14) We thank Dr. A. Pidcock, University of Sussex, for a sample of this compound.

(15) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).

(16) D. W. Meek, P. E. Nicpon, and V. I. Meek, *J. Am. Chem. Soc.*, **92**, 5351 (1970).

(17) H. Beall and C. H. Bushweller, *Chem. Rev.*, **73**, 465 (1973).

(18) A. J. Carty and S. E. Jacobson, *J. Chem. Soc., Chem. Commun.*, 175 (1975).

(19) J. L. Burmeister, *Coord. Chem. Rev.*, **3**, 225 (1968).

(20) M. J. Heeg, G. Christoph, and D. W. Meek, unpublished data, 1978.

(21) (a) L. H. Vogt, Jr., J. L. Katz, and S. E. Wiberley, *Inorg. Chem.*, **4**, 1157 (1965); (b) C. Barbeau and R. J. Dubey, *Can. J. Chem.*, **51**, 3684 (1973); (c) P. Dapporto, S. Midollini, A. Orlandine, and L. Sacconi, *Inorg. Chem.*, **15**, 2768 (1976).

(22) (a) S. J. Laplaca and J. A. Ibers, *Inorg. Chem.*, **5**, 405 (1966); (b) K. W. Muir and J. A. Ibers, *ibid.*, **8**, 1921 (1969).

(23) D. C. Moody and R. R. Ryan, *Inorg. Chem.*, **16**, 2473 (1977).

(24) M. R. Snow and J. A. Ibers, *Inorg. Chem.*, **12**, 224 (1973).

(25) (a) M. R. Churchill, B. G. DeBoer, and K. L. Kalra, *Inorg. Chem.*, **12**, 1646 (1973), and references therein; (b) M. R. Churchill and K. L. Kalra, *ibid.*, **12**, 1650 (1973).

(26) R. M. Kirchner, personal communication, 1977; American Crystallographic Association Abstracts.

(27) P. G. Eller and G. J. Kubas, *Inorg. Chem.*, **17**, 894 (1978).

(28) R. J. Angelici, *Acc. Chem. Res.*, **5**, 335 (1972).

(29) H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Am. Chem. Soc.*, **91**, 1346 (1969).

(30) P. Chini and G. Longoni, *J. Chem. Soc. A*, 1542 (1970).

(31) J. L. Peterson, T. E. Nappier, Jr., and D. W. Meek, *J. Am. Chem. Soc.*, **95**, 8195 (1973).

(32) K. Suzuki, H. Yamamoto, and S. Kanie, *J. Organomet. Chem.*, **73**, 131 (1974).

(33) M. J. Heeg and D. W. Meek, unpublished data, 1978.

(34) N. Farrell and D. Sutton, *Can. J. Chem.*, **55**, 360 (1977).

(35) T. G. Appleton and M. A. Bennett, *Inorg. Chem.*, **17**, 738 (1978).

(36) F. H. Allen and A. Pidcock, *J. Chem. Soc. A*, 2700 (1968).

(37) T. G. Appleton, H. C. Clark, and L. E. Manzer, *J. Organomet. Chem.*, **65**, 275 (1974).

(38) T. G. Appleton, M. H. Chisholm, H. C. Clark, and L. E. Manzer, *Can. J. Chem.*, **51**, 2243 (1973).

(39) K. R. Dixon, K. C. Moss, and M. A. R. Smith, *J. Chem. Soc., Dalton Trans.*, 990 (1975).

(40) F. H. Allen and S. N. Sze, *J. Chem. Soc. A*, 2054 (1971).

(41) R. J. Abraham, "The Analysis of High Resolution NMR Spectra", Elsevier, New York, 1971.

(42) W. McFarlane, *J. Chem. Soc., Chem. Commun.*, 772 (1967).

(43) M. A. Bennett, R. Bramley, and I. B. Tomkins, *J. Chem. Soc., Dalton Trans.*, 166 (1973).

(44) R. J. Goodfellow, M. J. Hardy, and B. F. Taylor, *J. Chem. Soc., Dalton Trans.*, 2450 (1973).

(45) E. M. Hyde, J. D. Kennedy, B. L. Shaw, and W. McFarlane, *J. Chem. Soc., Dalton Trans.*, 1571 (1977).