^{17}O NMR ($C_6H_4CH_3$): δ 1002 ($\Delta\nu_{1/2}$ = 600 Hz). IR: 1512 (s), 1440 (s), 1355 (w), 1301 (w), 1282 (s), 1209 (m), 1169 (w), 1154 (w), 1096 (w), 1076 (w), 1006 (w), 969 (w), 921 (w), 874 (s), 852 (w), 829 (m), 784 (w), 647 (w), 496 (w), 438 (w) cm^{-1}.

Preparation of $[Mo(Ntol)(S_2CNEt_2)_2]_2O$. A portion of PPh_3 (0.128 g; 0.49 mmol) was added to a stirred solution of $MoO(Ntol)(S_2CNEt_2)_2$ (0.500 g; 0.97 mmol) in CH_2Cl_2 (25 mL) at room temperature. After 12 h, the violet solution was taken to dryness, and the purple residue was triturated with Et_2O (3 × 25 mL), collected by filtration, and dried in vacuo. Analysis of the Et_2O washings by IR and ^{31}P NMR spectroscopy revealed the presence of Ph_3PO. Elemental analysis of the purple product indicates that the dimeric complex is obtained as the CH_2Cl_2 solvate. Anal. Calcd for $C_{35}H_{56}N_6OS_8Cl_2Mo_2$: C, 38.35; H, 5.15; N, 7.67. Found: C, 38.38; H, 5.30; N, 7.89. ^1H NMR (CD_2Cl_2): δ 7.22 (AB quartet, J_{AB} = 8 Hz, 4 H, $C_6\mathit{H}_4CH_3$), 3.80 (m, 8 H, $C\mathit{H}_2CH_3$), 2.30 (s, 3 H, $C_6H_4C\mathit{H}_3$), 1.36–1.20 (m, 12 H, $CH_2C\mathit{H}_3$). ^{17}O NMR ($C_6H_4CH_3$): δ 643 ($\Delta\nu_{1/2}$ = 1300 Hz). IR: 1495 (s), 1432 (s), 1354 (m), 1323 (m), 1302 (w), 1273 (s), 1212 (m), 1171 (w), 1149 (m), 1096 (w), 1077 (m), 1007 (m), 988 (w), 916 (w), 852 (m), 831 (m), 784 (w), 754 (w), 441 (w) cm^{-1}.

Reaction of $MoO(Ntol)(S_2CNEt_2)_2$ with Excess R_3P (R_3P = Ph_3P, $EtPh_2P$) in the Presence of O_2. A solution of $MoO(Ntol)(S_2CNEt_2)_2$ (1.05 g; 2.04 mmol) in toluene (60 mL) was stirred with Ph_3P (1.85 g; 7.08 mmol; 3.5 equiv) at room temperature under one atm of O_2. The dark purple characteristic of $[Mo(Ntol)(S_2CNEt_2)_2]_2O$ was evident until ca. 36 h later, at which time the solution was orange-brown. Solvent was evaporated and the residue was triturated with absolute ethanol (2 × 40 mL) and diethyl ether (40 mL), leaving an orange powder that was identified as $MoO(Ntol)(S_2CNEt_2)_2$ by comparison of its IR spectrum to that of an authentic sample. The combined washings were taken to dryness, yielding a white solid identified as Ph_3PO as determined by IR and ^{31}P NMR spectroscopy. A similar experiment performed with 3.4 equiv of $EtPh_2P$ required 20 h for completion; the reaction products were determined to be $MoO(Ntol)(S_2CNEt_2)_2$ and $EtPh_2PO$.

Similar results were obtained in a large-scale reaction using $MoO(Ntol)(S_2CNEt_2)_2$ (0.70 g; 1.36 mmol) and Ph_3P (12.48 g; 47.6 mmol; 35 equiv) in toluene (80 mL). In this case, the reaction mixture was heated to 50 °C for 10 h, after which heating was discontinued and the system was stirred until completion (an additional 72 h).

Reaction of $MoO(Ntol)(S_2CNEt_2)_2$ with 3 Equiv of Ph_3P and 3 Equiv of Me_2SO. To 50 mL of a toluene solution containing $MoO(Ntol)(S_2CNEt_2)$ (0.96 g; 1.87 mmol) and PPh_3 (1.47 g; 5.6 mmol) was added 5.6 mmol of dimethyl sulfoxide in toluene (10 mL). The violet solution was stirred under N_2 at 55 °C for 24 h, after which time the reaction mixture was burnt orange. The formation of dimethyl sulfide was confirmed by GC/MS analysis. Evaporation of solvent and trituration of the residue as described above allowed the separation and recovery of $MoO(Ntol)(S_2CNEt_2)_2$ and Ph_3PO.

Preparation of $Mo(Ntol)(DMAC)(S_2CNEt_2)_2$. A solution of $MoO(Ntol)(S_2CNEt_2)_2$ (1.39 g; 2.7 mmol) in toluene (60 mL) was stirred with $EtPh_2P$ (0.64 g; 3.0 mmol) under an N_2 atmosphere at 55 °C for 1 h. A solution of dimethyl acetylenedicarboxylate (1.92 g; 13.5 mmol) in toluene (20 mL) was then added, and the mixture was stirred at 55 °C for an additional 15 h. The dark yellow solution was filtered, and toluene was removed in vacuo. The residue was triturated with Et_2O (3 × 25 mL), affording a brown powder. The powder was dissolved in a minimum amount of toluene from which yellow-brown crystals were obtained upon incremental addition of hexane. These crystals were washed with 1–2 mL of acetone, yielding a bright yellow powder which was recrystallized from acetone, affording the product as bright yellow needles. The product thus obtained is the acetone hemisolvate; drying in vacuo yields the unsolvated product. Anal. Calcd for $C_{23}H_{33}N_3O_4S_4Mo$: C, 43.18; H, 5.20; N, 6.57. Found: C, 43.39; H, 5.33; N, 6.38. ^1H NMR ($CDCl_3$): δ 7.00 (AB quartet, J_{AB} = 8.3 Hz, 4 H, $C_6\mathit{H}_4CH_3$), 3.93–3.50 (m, 8 H, $C\mathit{H}_2CH_3$), 3.87 (s, 3 H, DMAC($C\mathit{H}_3$)), 3.86 (s, 3 H, DMAC($C\mathit{H}_3$)), 2.27 (s, 3 H, $C_6H_4C\mathit{H}_3$), 1.35–1.15 (m, 12 H, $CH_2C\mathit{H}_3$). IR: 1819 (m), 1802 (s), 1790 (s), 1512 (sh), 1500 (s), 1436 (s), 1357 (w), 1301 (w), 1276 (m), 1238 (w), 1211 (s), 1175 (w), 1152 (m), 1089 (w), 1079 (w), 1036 (w), 1019 (w), 1008 (w), 983 (w), 916 (w), 902 (w), 852 (w), 837 (w), 826 (w), 811 (w), 782 (w), 735 (m), 603 (w), 435 (w) cm^{-1}.

Preparation of ^{17}O-Enriched $MoO(Ntol)(S_2CNEt_2)_2$ and $[Mo(Ntol)(S_2CNEt_2)_2]_2O$. The starting material in these preparations was ^{17}O-enriched $MoO_2(S_2CNEt_2)_2$, which was synthesized by the method of J. W. McDonald as described in ref 29d. This species was reduced by Ph_3P to provide labeled $MoO(S_2CNEt_2)_2$, which was subsequently oxidized with *p*-tolyl azide as described above to yield ^{17}O-enriched $MoO(Ntol)(S_2CNEt_2)_2$. Treatment of this species with 0.5 equiv of Ph_3P as above afforded the ^{17}O-enriched dimer $[Mo(Ntol)(S_2CNEt_2)_2]_2O$.

Acknowledgment. We thank Sara C. Huckett for valuable assistance in the preliminary stages of this investigation. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Bureau of General Research at Kansas State University for support of this research. The WM-400 NMR spectrometer employed in this work was purchased with the aid of an NSF instrumentation award.

Registry No. $MoO(Ntol)(S_2CNEt_2)_2$, 75900-17-3; $Mo^V{}_2O(Ntol)_2(S_2CNEt_2)_4$, 97391-47-4; Mo(Ntol), 97391-48-5; $Mo(Ntol)(DMAC)(S_2CNEt_2)_2$, 9739-49-6; Ph_3P, 603-35-0; $EtPh_2P$, 607-01-2; Ph_3PO, 791-28-6; $EtPh_2PO$, 1733-57-9; $MoO(S_2CNEt_2)_2$, 25395-92-0; Me_2SO, 67-68-5; tolyl azide, 2101-86-2.

Notes

Contribution from the Department of Chemistry,
The Royal Military College of Science,
Shrivenham, Wiltshire, SN6 8LA, United Kingdom,
and The Materials Quality Assurance Directorate,
Woolwich, London, SE18 6TD, United Kingdom

Preparation, Characterization, and Properties of Platinum(0) Complexes with Tri-*n*-butyl Phosphite, Tri-*n*-butylarsine, and Tri-*n*-butylstibine

D. H. Goldsworthy,[1a] F. R. Hartley,*[1a] G. L. Marshall,[1b] and S. G. Murray*[1a]

Received June 8, 1984

Our current interest in the chemistry of long-alkyl-chain phosphine complexes of group 8–10 metals[2,34] prompted us to examine the chemistry of low-valent metal compounds with the less well studied ligands of phosphite, arsine, and stibine, especially their reactivity toward oxidative addition. In particular, by development of coordinative unsaturation at the metal center, some progress toward the synthesis of highly reactive metal complexes, capable of reacting with C–H bonds, might be achieved, with the greater electron-acceptor ability of phosphites compared with that of phosphines to promote oxidative addition. It was hoped that the greater flexibility within the P–O–R linkages compared with that of P–R[3] would also enable easier access to the metal center by an incoming substrate; this should also be the case for the larger donor atoms of arsenic and antimony. The *n*-butyl group would be expected to impart a greater degree of solubility to these complexes, compared to shorter alkyl chain derivatives, without hindering access to the metal as observed for larger *n*-alkyl groups.[2,4]

Experimental Section

All manipulations and reactions were carried out under an atmosphere of white spot nitrogen that had previously been passed through a column

---

(1) (a) The Royal Military College of Science. (b) The Materials Quality Assurance Directorate.

(2) (a) Franks, S.; Hartley, F. R. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2233. (b) Franks, S.; Hartley, F. R. *Inorg. Chim. Acta* **1981**, *47*, 235. (c) Franks, S.; Hartley, F. R.; Chipperfield, J. R. *Adv. Chem. Ser.* **1982**, *No. 196*, 273.

(3) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(4) (a) Goldsworthy, D. H.; Hartley, F. R.; Murray, S. G. *J. Mol. Catal.* **1983**, *19*, 257. (b) Goldsworthy, D. H.; Hartley, F. R.; Murray, S. G. *J. Mol. Catal.* **1983**, *19*, 269.

containing a BTS deoxygenation catalyst (BSAF) at 160 °C and dried over P_2O_5.

Tri-*n*-butyl phosphite was available commercially and distilled under nitrogen before use. Tri-*n*-butylarsine[5] and -stibine[6] were prepared by literature methods and distilled twice under nitrogen (bp 55 °C (0.4 mmHg) and 66 °C (0.44 mmHg), respectively). $[Pt(cod)_2]$ was prepared according to a literature procedure[7] (cod = cyclooctadiene). The solvents toluene and *n*-hexane were distilled from sodium, methanol and ethanol from magnesium methoxide and ethoxide, *n*-butyl alcohol from anhydrous potassium carbonate, and dichloromethane from anhydrous calcium chloride, under nitrogen. Pentafluorobenzene was available commercially and distilled under nitrogen prior to use.

Infrared spectra were recorded on a Perkin-Elmer Model 577 grating spectrophotometer. Samples were prepared as Nujol mulls or liquid films between CsI plates. ^1H NMR spectra were obtained on a Perkin-Elmer R32 90-MHz NMR spectrometer and referenced with respect to Me_4Si. $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR spectra were obtained on a JEOL FX90 NMR spectrometer operating at 36.2, 22.6, and 19.1 MHz, respectively, with use of degassed toluene-d_8 solutions sealed under nitrogen. The spectra were recorded at probe temperature, and chemical shifts are quoted relative to 80% H_3PO_4, Me_4Si, and H_2PtCl_6, respectively.

UV irradiations were carried out with a 200-W focusing-beam medium-pressure mercury lamp in quartz apparatus.

Tetrakis(tri-*n*-butyl phosphite)platinum(0). Method 1. To a stirred solution of $[Pt(cod)_2]$ (0.11 g, 0.26 mmol) in toluene (4 mL) at room temperature was added dropwise a solution of tri-*n*-butyl phosphite (0.26 g, 1.04 mmol) in toluene (2 mL). After the mixture was stirred for 30 min, the solvent was removed in vacuo and the pale yellow residue dried for 3 h at 10^{-2} mmHg. Recrystallization from hot methanol yielded white crystals, which were washed with ice-cold methanol (3 mL) and dried at 10^{-2} mmHg for 8 h.

Method 2. To a stirred suspension of $[Pt(PPh_3)_4]$ (0.5 g, 0.4 mmol) in *n*-butyl alcohol (10 mL) was added tri-*n*-butyl phosphite (0.5 mL, 1.9 mmol). The mixture became colorless and homogeneous within 2–3 min. Stirring was continued for 10 min at room temperature and 30 min at 60–70 °C. The solution was concentrated to ca. 5 mL and cooled at −20 °C overnight. White crystals of triphenylphosphine were removed, and the mother liquor was further concentrated to about half the volume and cooled. After removal of a further crop of triphenylphosphine the solution was evaporated to dryness and the residue extracted with ice-cold *n*-butyl alcohol, filtered, and evaporated to dryness. Recrystallization of the resulting waxy solid from hot methanol yielded white crystals of $[Pt(P(O\text{-}n\text{-}Bu)_3)_4]$, which were dried as in method 1. Anal. Calcd for $C_{48}H_{108}O_4P_4Pt$: C, 48.2; H, 9.1. Found: C, 48.4; H, 9.3.

Tetrakis(tri-*n*-butylarsine)platinum(0). To a stirred suspension of $[Pt(cod)_2]$ (0.11 g, 0.26 mmol) in *n*-hexane (2 mL) was added a solution of tri-*n*-butylarsine (0.26 g, 1.06 mmol) in *n*-hexane (3 mL). The mixture became homogeneous and bright yellow almost immediately, and stirring was continued for 1 h. Removal of solvent under vacuum yielded an orange oil, which was dried for 7 h at 10^{-4} mmHg at room temperature. Recrystallization of the residue from 0.5 mL of *n*-hexane at −63 °C gave light yellow crystalline blocks. The mother liquor was syringed off at this temperature and the product dried under high vacuum. Anal. Calcd for $C_{48}H_{108}As_4Pt$: C, 48.9; H, 9.2. Found: C, 49.0; H, 9.7.

Tetrakis(tri-*n*-butylstibine)platinum(0). A stirred suspension of $[Pt(cod)_2]$ (0.15 g, 0.38 mmol) in *n*-hexane (1.5 mL) was treated with a solution of tri-*n*-butylstibine (0.43 g, 1.5 mmol) in *n*-hexane (2 mL). The mixture became orange and homogeneous within 30 s. After the mixture was stirred at room temperature for 45 min, the solvent was removed in vacuo and the orange oily residue dried for 17 h at 10^{-4} mmHg at room temperature. The oil was dissolved in a mixture of toluene (0.5 mL) and methanol (3.5 mL) and cooled to −85 °C. A yellow-orange waxy solid precipitate after 4 h, and the mother liquor was syringed off. The product was dried under high vacuum. Anal. Calcd for $C_{48}H_{108}Sb_4Pt$: C, 42.1; H, 7.9. Found: C, 41.4; H, 7.1.

***cis*-Iodobis(tri-*n*-butyl phosphite)platinum(II).** A stirred suspension of $[PtI_2(cod)]$[8] (0.59 g, 1.06 mmol) in *n*-hexane (2 mL) was treated with a solution of tri-*n*-butyl phosphite (0.52 g, 2.08 mmol) in *n*-hexane (2 mL). The mixture was stirred for $2^1/_2$ h, the bright yellow solution evaporated to dryness, and the resulting yellow oil dried under vacuum. The product was purified by chromatography through a short alumina column (neutral, Brockmann activity I) by eluting with dry diethyl ether. The yield of clear yellow oil was 0.95 g (95%). Anal. Calcd for $C_{24}H_{54}I_2O_6P_2Pt$: C, 30.4; H, 5.7. Found: C, 30.6; H, 5.8.

(Carbonato)bis(tri-*n*-butyl phosphite)platinum(II). To a degassed solution of *cis*-$[PtI_2(P(O\text{-}n\text{-}Bu)_3)_2]$ (0.28 g, 0.3 mmol) in dichloromethane (5 mL) was added a freshly prepared sample of Ag_2CO_3 (1.6 g, 0.6 mmol). The mixture was freeze–thaw degassed three times and then stirred at room temperature in the dark for 3 h. The silver salts were filtered off, and the brown-tinged solution was evaporated to dryness. The pale brown residue was recrystallized from *n*-hexane, yielding long, fine off-white needles. $[Pt(CO_3)(P(O\text{-}n\text{-}Bu)_3)_2]$ is an extremely air-sensitive compound and will start to decompose immediately on exposure to air; therefore, great care must be taken to ensure that all oxygen is precluded from the reaction mixture. IR (cm^{-1}): 1691 (vs) (ν(C=O)), 1174 (s) (ν(C—O)), 811 (s) (π), 370 (vs) (ν(M—O)).

(Oxalato)bis(tri-*n*-butyl phosphite)platinum(II). A freshly prepared sample of $Ag_2C_2O_4$ (0.32 g, 1.06 mmol) was added to a degassed solution of *cis*-$[PtI_2(P(O\text{-}n\text{-}Bu)_3)_2]$ (0.5 g, 0.53 mmol) in dichloromethane (7 mL) and the mixture freeze–thaw degassed twice. *Caution*! $Ag_2C_2O_4$ explodes on heating over 100 °C. After the mixture was stirred in the dark for 3 h, the silver salts were filtered off and the colorless filtrate evaporated to dryness. The resulting oil was dissolved in ca. 4 mL of hot *n*-hexane and a few drops of ethanol added to ensure dissolution. When the mixture was cooled to −20 °C, a colorless oil was precipitated. The supernatant liquid was syringed off and the oil washed with 3 × 1 mL of cold *n*-hexane; yield 0.4 g (96%). Anal. Calcd for $C_{26}H_{54}O_{10}P_2Pt$: C, 39.9; H, 6.9. Found: C, 40.4; H, 7.2. IR (cm^{-1}): 1721 (vs) (ν(C=O)), 1678 (vs) (ν(C=O)), 1345 (vs) (ν(C—O)), 360 (m) (ν(M—O)), 282 (m) (π). ^{31}P NMR: $\delta(P) = 65.1$ (singlet), $^1J_{PtP} = 5635$ Hz.

Reactions of $[Pt(cod)_2]$ with 2 and 3 Equiv of Tri-*n*-butyl Phosphite. Solutions of tri-*n*-butyl phosphite (2 or 3 equiv) in either *n*-hexane or toluene were added dropwise with stirring over a period of 2–3 min to either a stirred suspension of $[Pt(cod)_2]$ (1 equiv) in *n*-hexane or a solution of $[Pt(cod)_2]$ in toluene. After the mixture was stirred for 2 h, the deep orange-red solution was evaporated to dryness, yielding a dark red oil. This residue was then dried at 10^{-4} mmHg at room temperature for 18 h. Owing to the instability of these compounds, no attempt was made at further purification or separation of the product mixtures, but the complexes were analyzed directly by NMR spectroscopy.

Reaction of Tris(tri-*n*-butyl phosphite)platinum(0) with Pentafluorobenzene. A solution of $[Pt(P(O\text{-}n\text{-}Bu)_3)_3]$ (0.12 g of a sample containing ca. 90% of the tris complex) in C_6HF_5 (1.2 mL) was freeze–thaw degassed twice and stirred at room temperature under nitrogen for 50 h. The initial deep orange-red solution gradually became light brown. The solvent was removed under vacuum and the orange-brown oily residue dried at 10^{-4} mmHg at room temperature for 10 h. IR (cm^{-1}): 2035 (s) (ν(M—H)), 1630 (w), 1603 (w), 1495 (s), 1450 (s), 1278 (w).

UV Irradiation of $[Pt(C_2O_4)(P(O\text{-}n\text{-}Bu)_3)_2]$. A solution of $[Pt(C_2O_4)(P(O\text{-}n\text{-}Bu)_3)_2]$ (0.39 g, 0.5 mmol) in toluene (12 mL), contained in a quartz Schlenk tube fitted with a water-cooled cold finger, was freeze–thaw degassed twice. The solution was then irradiated for 10 h with stirring, at a distance of 150 mm from a focused mercury lamp (light source). The solution became deep orange-red. On evaporation to dryness, a dark brown oil was obtained, which was dried under vacuum.

Results and Discussion

1. Preparation of Complexes $[PtL_4]$, L = $P(O\text{-}n\text{-}Bu)_3$, $As\text{-}n\text{-}Bu_3$, $Sb\text{-}n\text{-}Bu_3$. When $[Pt(cod)_2]$ and tri-*n*-butyl phosphite, tri-*n*-butylarsine, or tri-*n*-butylstibine are reacted together in the molar ratio 1:4 in either *n*-hexane or toluene solution, subsequent workup of the reaction leads to the isolation of $[PtL_4]$, L = $P(O\text{-}n\text{-}Bu)_3$, $As\text{-}n\text{-}Bu_3$, or $Sb\text{-}n\text{-}Bu_3$.

$[Pt(P(O\text{-}n\text{-}Bu)_3)_4]$, unlike[9] $[Pt(P(O\text{-}n\text{-}Bu)_3)_5]^{2+}$, does not undergo transesterification in alcoholic solvents. The complex may be recovered unchanged from methanolic solution, even after refluxing for 4 h. This compound may also be prepared from the reaction of $[Pt(PPh_3)_4]$ with a slight excess of tri-*n*-butyl phosphite, as previously reported,[10] but by modification of the preparation by use of *n*-butyl alcohol as the solvent instead of ethanol it has now been possible to isolate a pure sample.

$[Pt(P(O\text{-}n\text{-}Bu)_3)_4]$ is a white, air-stable solid and is soluble in most common organic solvents. It is inert toward organic molecules such as C_6HF_5, 1,3,5-$C_3H_3F_3$, C_6H_5CN, and *p*-$IC_6H_4CH_3$ even on refluxing for long periods. It does, however, react with difficulty with CH_3I, but it was found that a mixture of at least three, at present inseparable, unidentified platinum(II) compounds

---

(5) Dyke, W. J. C.; Jones, W. J. *J. Chem. Soc.* **1930**, 2426.
(6) Dyke, W. J. C.; Davies, W. C.; Jones, W. J. *J. Chem. Soc.* **1930**, 463.
(7) Spencer, J. L. *Inorg. Synth.* **1979**, *19*, 213.
(8) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411.
(9) Meakin, P.; Jesson, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 5751.
(10) Pregosin, P. S.; Sze, S. N. *Helv. Chim. Acta* **1977**, *60*, 1371.

Table I. ^{31}P, ^{195}Pt, and ^{13}C NMR Parameters for the $[PtL_4]$ Complexes

	^{31}P		^{195}Pt		$^{13}C^a$			
L	$\delta(P)$	$^1J_{PtP}$/Hz	$\delta(Pt)$	$^1J_{PtP}$/Hz	C_α/ppm	C_β/ppm	C_γ/ppm	C_δ/ppm
$P(O\text{-}n\text{-}Bu)_3$	127.7	5393	−5739 (quin)^b	5401^b	62.2	32.4	18.8	13.1
$As\text{-}n\text{-}Bu_3$			−5181		24.3	28.2	26.2	12.9
$Sb\text{-}n\text{-}Bu_3$			−5355		25.5	28.3	25.5	12.8

^{a}Labeling of C atoms: $Q–C_\alpha–C_\beta–C_\gamma–C_\delta H_3$, Q = As, Sb, PO. ^{b}The ^{195}Pt NMR spectrum of $[Pt(P(O\text{-}n\text{-}Bu)_3)_4]$ is available in the supplementary material.

were formed, as detected from the ^{31}P NMR spectrum. It has been shown that the compounds $[ML_4]$ (L = $P(OMe)_3$, $P(OPh)_3$; M = Pd, Pt) will oxidatively add small fluorocarbon molecules,[11,12] but these reactions appear to take place only under vigorous conditions.

$[Pt(As\text{-}n\text{-}Bu_3)_4]$ has been isolated as a yellow crystalline compound that is both air-sensitive and unstable in solution. The ^{195}Pt NMR spectrum shows (after 2 months in a sealed tube under nitrogen) the presence of at least five new platinum-containing species at −4813, −5004, −5103, −5181, and −5662 ppm. However, in contrast to this, $[Pt(Sb\text{-}n\text{-}Bu_3)_4]$ is remarkably stable. This complex showed a broad ^{195}Pt signal at −5355 ppm and very little decomposition even when exposed to air. After 2 months the ^{195}Pt NMR spectrum showed only one additional small peak, due to a decomposition product, at −5241 ppm. The literature reveals that there is only one other report of a $[PtL_4]$ complex for L = stibine.[13] Previous attempts to prepare these species have generally led to the isolation of mixed-phosphine–stibine platinum(0) complexes.[14] The method used here seems to provide a very convenient route to the synthesis of the $[ML_4]$ type.

All the complexes reported here display remarkable solubility in a wide range of solvents varying in polarity from *n*-hexane to methanol. This has made purification of the complexes difficult, and it is essential that all starting materials must be extremely pure in order to minimize the formation of side products.

2. Spectroscopic Data on the Complexes $[PtL_4]$, L = $P(O\text{-}n\text{-}Bu)_3$, $As\text{-}n\text{-}Bu_3$, $Sb\text{-}n\text{-}Bu_3$. Infrared and ^1H NMR spectroscopy of these complexes revealed only the presence of coordinated ligand, the spectra being essentially the same as that of the starting material. A more appropriate study has been undertaken with the use of ^{31}P and ^{195}Pt NMR spectroscopy, the data of which are presented in Table I.

For L = $P(O\text{-}n\text{-}Bu)_3$, the ^{31}P NMR spectrum gives a singlet at 127.7 ppm flanked by ^{195}Pt satellites, $^1J_{PtP}$ = 5393 Hz. These values are very close to those previously reported for the spectrum of an impure sample of this compound in dichloromethane (127.2 ppm, 5388 Hz).[10] Unlike the phosphine complexes, those of phosphites recorded here do not exhibit ligand-exchange phenomena at room temperature and sharp signals with ^{195}Pt coupling are observed. This is in accord with earlier work that shows that $[Pt(P(OEt)_3)_4]$ is not extensively dissociated in solution.[14] The ^{195}Pt NMR spectrum shows a 1:4:6:4:1 quintet of signals extending across 21 000 Hz and centered at −5739 ppm, due to coupling to four equivalent phosphorus nuclei. This chemical shift compares favorably to that reported for $[Pt(P(OMe)_3)_4]$ at −5832 ppm relative to H_2PtCl_6.[15]

For L = $As\text{-}n\text{-}Bu_3$ and $Sb\text{-}n\text{-}Bu_3$ the ^{195}Pt NMR spectra both show broad singlets at −5181 and −5355 ppm, respectively, at room temperature. The broad resonances ($\Delta\nu_{1/2} \approx 150$ Hz) are attributable to the large quadrupolar moments of arsenic and antimony rather than any ligand-exchange process, which would be expected to produce a much wider signal. The compounds $[M(SbPh_3)_4]$, M = Pd, Ni,[14] do not exhibit exchange spectra at room temperature, and this has been attributed to the smaller steric size of SbR_3 over PR_3. This would also be the case for $As\text{-}n\text{-}Bu_3$ and $P(O\text{-}n\text{-}Bu)_3$ compared to PR_3.

Table II. ^{31}P and ^{195}Pt NMR Parameters of the Products of the Reaction between $[Pt(cod)_2]$ and 3 Equiv of $P(O\text{-}n\text{-}Bu)_3$^{a}

	^{31}P		^{195}Pt	
component	$\delta(P)$	$^1J_{PtP}$/Hz	$\delta(Pt)^b$	$^1J_{PtP}$/Hz
A	127.7	5393	−5739 (quin)	5401
B	192.6	6398	−4984 (quar)	6393

^{a} ^{31}P and ^{195}Pt NMR spectra are recorded in the supplementary material. ^{b}Abbreviations: quin = quintet; quar = quartet.

Table III. ^{31}P NMR Parameters from Figure 1

peak	δ	$^1J_{PtP}$/Hz	$\Delta\delta^a$
A ($[PtL_4]$)	127.7	5393	−11.3
B ($[PtL_3]$)	192.6	6398	+53.6
C	161.3	5476	+22.3
D	160.3	5453	+21.3
E	159.0	5417	+20.0

^{a} $\Delta\delta$ = coordination chemical shift = $\delta(P)$(complex) − $\delta(P)$(free ligand).

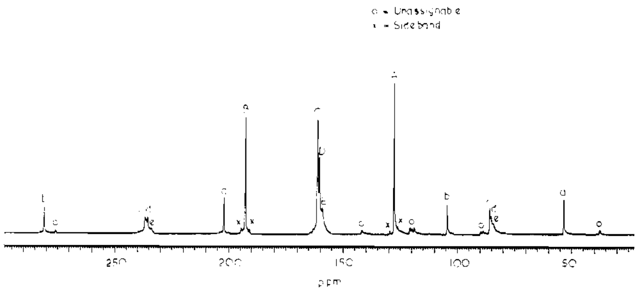


Figure 1. ^{31}P NMR spectrum of the products of the reaction between $[Pt(cod)_2]$ and 2 equiv of $P(O\text{-}n\text{-}Bu)_3$.

The ^{195}Pt NMR chemical shifts for these complexes all appear in the range expected for platinum(0) species,[16] the values decreasing in the order L = $As\text{-}n\text{-}Bu_3$ > $Sb\text{-}n\text{-}Bu_3$ > $P(O\text{-}n\text{-}Bu)_3$. It has been observed that $\delta(Pt)$ often shows an upfield shift on descending a group;[16] however, this is not observed here. It is interesting to note that the order also follows a decreasing steric requirement of the ligand L, which agrees well with previous observations.[16] The assignment of the carbon atoms of the ligand in the ^{13}C NMR spectra of these compounds (Table I) has been based on the data available for $P\text{-}n\text{-}Bu_3$ complexes.[17] The C_α carbons of the $As\text{-}n\text{-}Bu_3$ and $Sb\text{-}n\text{-}Bu_3$ ligands show only a small unresolved $^2J_{PtC}$ coupling, a probable consequence of the quadrupolar nuclei.

3. Reaction of $[Pt(cod)_2]$ with 3 Equiv of Tri-*n*-Butyl Phosphite. Under strictly anhydrous and anaerobic conditions in either *n*-hexane or toluene this reaction leads to a mixture of the two components A and B (Table II), whose relative amounts vary from 1.5:1 to 9:1, depending on such factors as the rate of mixing, the rate of addition and the concentrations of the reactants, and the time of reaction. Species A is $[Pt(P(O\text{-}n\text{-}Bu)_3)_4]$. The other

---

(11) Browning, J.; Empsall, H. D.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 381.

(12) Empsall, H. D.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1972**, 96.

(13) Scherer, O. J.; Konrad, R.; Kruger, C.; Tsay, Y.-H. *Chem. Ber.* **1982**, *115*, 414.

(14) Garrou, P. E.; Hartwell, G. E. *Inorg. Chem.* **1976**, *15*, 730.

(15) Goggin, P. L.; Goodfellow, R. J.; Haddock, S. R.; Taylor, B. F.; Marshall, I. R. H. *J. Chem. Soc., Dalton Trans.* **1976**, 459.

(16) Pregosin, P. S. *Coord. Chem. Rev.* **1982**, *44*, 247.

(17) Gerlach, D. H.; Kane, A. R.; Parshall, G. W.; Jesson, J. P.; Muetterties, E. L. *J. Am. Chem. Soc.* **1971**, *93*, 3543.

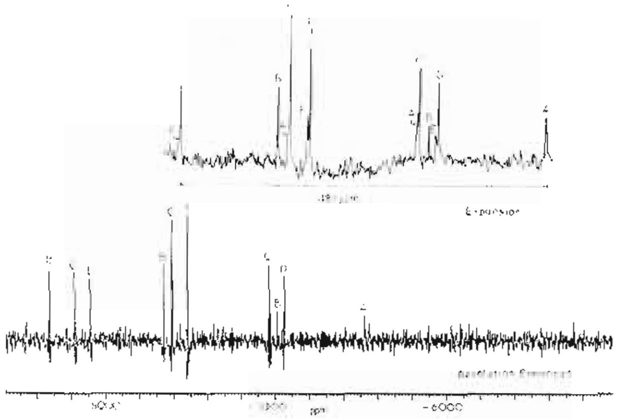
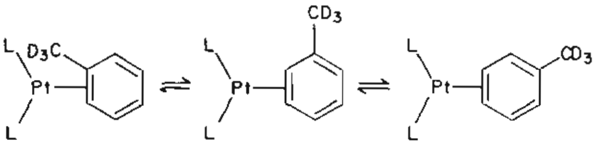


Figure 2. ^{195}Pt NMR spectrum of the products of the reaction between [Pt(cod)$_2$] and 2 equiv of P(O-*n*-Bu)$_3$.

species, B, is believed to be [Pt(P(O-*n*-Bu)$_3$)$_3$] in view of the large downfield shift in the ^{31}P NMR (consistent with the change from tetra- to tricoordination) and the large increase in ${}^{1}J_{\mathrm{PtP}}$. The latter derives from a greater degree of s-orbital character associated with the coordinatively unsaturated [PtL$_3$] species. The ratio ${}^{1}J_{\mathrm{PtP}}$[PtL$_4$]:${}^{1}J_{\mathrm{PtP}}$[PtL$_3$] = 0.84, comparable to that found in phosphine complexes in the range 0.86–0.89.[13,17-21] Finally, the ^{195}Pt NMR spectrum reveals a 1:3:3:1 quartet of signals centered at −4984 ppm at room temperature, showing that the platinum center is coupled to three equivalent phosphorus atoms. The ^{195}Pt chemical shift of [Pt(P(O-*n*-Bu)$_3$)$_3$] is moved some 755 ppm downfield from that of the tetrakis complex. [Pt(P(O-*n*-Bu)$_3$)$_3$] is unstable in solution even when sealed under nitrogen and decomposes to give [Pt(P(O-*n*-Bu)$_3$)$_4$] and other as yet unidentified platinum(0) species within a few months.

4. Reaction of [Pt(cod)$_2$] with 2 Equiv of Tri-*n*-butyl Phosphite. In either *n*-hexane or toluene the ^{31}P and ^{195}Pt NMR spectra of this reaction mixture showed the presence of several components (Figures 1 and 2 and Tables III and IV), whose relative concentrations depend on the detailed experimental conditions (including the concentrations and the relative order and rate of mixing of the solutions). Components A and B can be identified as [PtL$_3$] and [PtL$_4$]. ^{13}C NMR indicates the absence of both 1,5-cyclooctadiene and any Pt–C bonding arising from metalation of the phosphite. The values of the coupling constants together with the large positive ^{31}P chemical shifts[10,18] and the ^{195}Pt chemical shifts for species C, D, and E suggest that these compounds contain platinum(0). The similarity of all the ^{31}P and ^{195}Pt NMR parameters for these species ($\Delta\delta({}^{31}\mathrm{P})$ = 2.3 and $\Delta\delta({}^{195}\mathrm{Pt})$ = 45 ppm, $\Delta{}^{1}J_{\mathrm{PtP}}$ = 59 Hz)[22] indicates that they are structurally very similar. The ^{195}Pt NMR spectrum (Figure 2) consists of a 1:2:1 triplet pattern for all three species; i.e. the platinum center is coupled to two equivalent phosphorus atoms. Since there is no ^{195}Pt–^{195}Pt coupling and microanalysis together with ^{1}H and ^{13}C NMR spectroscopy reveals that only phosphite ligands are present, these compounds must be of the type "PtL$_2$S", where S = solvent. The "PtL$_2$" units are unlikely to exist as discrete molecules owing to the small phosphite cone angle size.[3,23,24] Further, the simplicity of the ^{31}P and ^{195}Pt NMR spectra precludes the formation of clusters of the type [PtL$_2$]$_n$ in toluene solution, of which only one example is known,[25] although they may well exist in the initial reaction mixture as a precursor to the species observed in solution. Statistical mixing of the platinum isotopes ^{194}Pt (I = 0), ^{195}Pt (I = ${}^{1}/_{2}$), and ^{196}Pt (I = 0) in a cluster would render the phosphite groups nonequivalent and give a complex pattern of signals in both the ^{195}Pt and ^{31}P NMR spectra. We therefore propose structures for these species shown in eq 1. Such interactions between the photochemically induced production of "Pt(PEt$_3$)$_2$" and benzene have been postulated,[26] and indeed the compound [Pt(η^2-C$_6$(CF$_3$)$_6$)(PPh$_3$)$_2$] has been isolated and the structure confirmed by X-ray analysis, the aromatic ring showing alternate single and double bonds.[27] It would be expected that the energy barrier for interconversion of these isomers would be low, leading to a broad spectrum at room temperature. This is not observed here, and a "static" spectrum is present.



(1)

This is consistent with our present data on the phosphite complexes of platinum(0), none of which have shown any sign of ligand-exchange processes occurring in solution at room temperature. The stabilization of these species is most likely a function of the small steric size of the phosphite coupled with its strong π-accepting and weak σ-donating properties.

In order to confirm the proposed structures of these complexes, an alternative route to their preparation was sought. It has been previously shown that [Pt(CO$_3$)(PPh$_3$)$_2$] will lose CO$_2$ on refluxing in ethanol, forming a "Pt(PPh$_3$)$_2$" intermediate.[28] We have prepared the compound [Pt(CO$_3$)(P(O-*n*-Bu)$_3$)$_2$] by the action of Ag$_2$CO$_3$ on *cis*-[PtI$_2$(P(O-*n*-Bu)$_3$)$_2$]. Owing to the extreme air-sensitivity of this material, it could only be characterized by comparison of its infrared spectrum (reported in the supplementary material) with those of other similar carbonato species.[29] In air it very rapidly forms a brown oil, which may contain the peroxycarbonate, [Pt(OCO$_3$)(P(O-*n*-Bu)$_3$)$_2$], as shown by the appearance of two new intense bands at 1623 (ν(C=O)) and 835 cm^{-1} (ν(O—O)).

An alternative approach was to study the photochemical behavior of the corresponding oxalate species. The complexes [Pt(C$_2$O$_4$)L$_2$], L = PPh$_3$[30] and PEt$_3$,[26] undergo photochemical reduction via the loss of 2 mol of CO$_2$ to produce the intermediate "PtL$_2$" species. The corresponding phosphite compound, [Pt(C$_2$O$_4$)(P(O-*n*-Bu)$_3$)$_2$], is an air-stable, colorless oil (the infrared spectrum is recorded in the supplementary material) that can be prepared by the action of Ag$_2$C$_2$O$_4$ on *cis*-[PtI$_2$(P(O-*n*-Bu)$_3$)$_2$]. Irradiation of the oxalate complex in toluene over a 10-h period produced an intense deep red solution in which only [PtL$_3$] and [PtL$_4$] could be positively identified.

5. Reaction of [Pt(P(O-*n*-Bu)$_3$)$_3$] with C$_6$HF$_5$. This reaction was attempted since [Pt(PEt$_3$)$_3$] has been shown to oxidatively add organic molecules,[17] in particular the C–H bond of pentafluorobenzene to form *trans*-[PtH(C$_6$F$_5$)(PEt$_3$)$_2$];[31] [Pt(P-*n*-Bu$_3$)$_3$] will also undergo the same reaction.[32] After the present work was complete, it was reported that [Pt(P(OR)$_3$)$_4$] complexes, where R = Me and Et, are susceptible to oxidation.[33]

---

(18) Pregosin, P. S.; Kunz, R. W. "^{31}P and ^{13}C NMR of Transition Metal Complexes"; Springer-Verlag: West Berlin, 1979.

(19) Sen, A.; Halpern, J. *Inorg. Chem.* **1980**, *19*, 1073.

(20) Mann, B. E.; Musco, A. *J. Chem. Soc., Dalton Trans.* **1980**, 776.

(21) Tolman, C. A.; Seidel, W. C.; Gerlach, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 2669.

(22) The total chemical shift range for δ(P) is ~200,[18] and that for δ(Pt) is ~13 000.[16]

(23) Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. *J. Am. Chem. Soc.* **1976**, *98*, 5850.

(24) P(O-*n*-Bu)$_3$ would be expected to have a cone angle similar to that of P(OEt)$_3$, which is 109°.[3]

(25) Yoshida, T.; Yamagata, T.; Tulip, T. H.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 2063.

(26) Paonessa, R. S.; Trogler, W. C. *Organometallics* **1982**, *1*, 768.

(27) Browning, J.; Green, M.; Penfold, B. R.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1973**, 31.

(28) Blake, D. M.; Mersecchi, R. *J. Chem. Soc. D* **1971**, 1045.

(29) Hayward, P. J.; Blake, D. M.; Wilkinson, G.; Nyman, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 5873.

(30) Blake, D. M.; Nyman, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 5359.

(31) Fornies, J.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1066.

(32) Goldsworthy, D. H.; Hartley, F. R.; Marshall, G. L.; Murray, S. G., unpublished results.

Table IV. ^{195}Pt NMR Parameters from Figure 2

peak	δ	$^1J_{PtP}$/Hz	peak	δ	$^1J_{PtP}$/Hz
A ([PtL_4])	−5741	5393	D triplet	−5222	5456
B ([PtL_3])	−4984	6398	E triplet	−5217	5413
C triplet	−5177	5471			

A solution of [Pt(cod)$_2$] and 2 equiv of P(O-*n*-Bu)$_3$ was treated with pentafluorobenzene. Three major products were observed in the proton-decoupled ^{31}P NMR spectrum, two of which were identified as [PtL_3] and [PtL_4]. The third component exhibited a ^{31}P NMR chemical shift at 123.7 ppm with ^{195}Pt satellites; $^1J_{PtP} = 4536$ Hz. The infrared spectrum of the crude materials (recorded in the supplementary material) showed a strong band at 2040 cm^{-1}, attributable to ν(M—H), together with other peaks assignable to a coordinated C_6F_5 group. We therefore propose that the compound *trans*-[PtH(C_6F_5)(P(O-*n*-Bu)$_3$)$_2$] is present. It has not been possible to obtain a satisfactory ^{195}Pt NMR spectrum of this compound owing to the weakness of the signals produced. This is not surprising since the ^{195}Pt center will be coupled to ^{1}H, ^{19}F, and ^{31}P nuclei. Similarly, we were not able to detect the hydride signal in the ^{1}H NMR spectrum. However, when the ^{31}P NMR spectrum is selectively decoupled by irradiating the phosphorus signal at the resonance frequency of the $-OCH_2-$ protons, the signal at $\delta = 123.7$ is split into a doublet with a $^2J_{PH}$ value of 6 Hz.

It has not been possible to isolate a pure sample of the hydride for analysis. Recrystallization from methanol will precipitate most of the [PtL_4] formed in the reaction according to eq 2 and 3. The hydride however appears to be too unstable for isolation. Indeed, heating a crude sample at 80 °C under vacuum at 10^{-2} mmHg for 4 h causes the loss of C_6HF_5 (indicated by the IR spectrum). The hydride may be regenerated from the resulting platinum-containing compound by treatment with C_6HF_5.

$$[PtL_3] + C_6HF_5 \rightleftharpoons [PtH(C_6F_5)L_2] + L \qquad (2)$$

$$[PtL_3] + L \rightarrow [PtL_4] \qquad (3)$$

If the ^{31}P NMR spectrum is run in the presence of excess C_6HF_5, no signal due to [PtL_3] is detected, due to eq 2 being shifted to the right.

Acknowledgment. We thank Johnson-Matthey Ltd. for the loan of platinum salts, the European Office of the U.S. Army for financial support under the auspices of Grant DAJA-81-C-0594, and R. Hall for his skillful production of specialist glassware.

Registry No. [Pt(cod)$_2$], 12130-66-4; [Pt(P(O-*n*-Bu)$_3$)$_4$], 63372-11-2; [Pt(PPh$_3$)$_4$], 14221-02-4; [Pt(As(*n*-Bu)$_3$)$_4$], 97277-51-5; [Pt(Sb(*n*-Bu)$_3$)$_4$], 97277-52-6; *cis*-[PtI$_2$(P(O-*n*-Bu)$_3$)$_2$], 97277-53-7; [PtI$_2$(cod)], 12266-72-7; [Pt(CO$_3$)(P(O-*n*-Bu)$_3$)$_2$], 97277-54-8; [Pt(C_2O_4)(P(O-*n*-Bu)$_3$)$_2$], 97277-55-9; [Pt(P(O-*n*-Bu)$_3$)$_3$], 97277-56-0; *trans*-[PtH(C_6F_5)(P(O-*n*-Bu)$_3$)$_2$], 97277-57-1; C_6HF_5, 363-72-4.

Supplementary Material Available: ^{195}Pt NMR spectrum of [Pt(P(O-*n*-Bu)$_3$)$_4$] (Figure 1), ^{31}P NMR spectrum of a freshly prepared mixture of [Pt(P(O-*n*-Bu)$_3$)$_n$], $n = 3$ and 4 (Figure 2), ^{31}P NMR spectrum of the mixture of [Pt(P(O-*n*-Bu)$_3$)$_3$] and [Pt(P(O-*n*-Bu)$_3$)$_4$] after 5 months (Figure 3), ^{195}Pt NMR spectrum of the mixture of [Pt(P(O-*n*-Bu)$_3$)$_3$] and [Pt(P(O-*n*-Bu)$_3$)$_4$] after 5 months (Figure 4), infrared spectrum of [Pt(CO$_3$)(P(O-*n*-Bu)$_3$)$_2$] (Figure 5), infrared spectrum of [Pt(C_2O_4)(P(O-*n*-Bu)$_3$)$_2$] (Figure 6), and infrared spectrum of *trans*-[PtH(C_6H_5)(P(O-*n*-Bu)$_3$)$_2$] (Figure 7) (7 pages). Ordering information is given on any current masthead page.

---

(33) Solar, J. M.; Rogers, R. D.; Mason, W. R. *Inorg. Chem.* **1984**, *23*, 373.
(34) 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.)

Contribution from the Institutes for Physical Chemistry and
Biophysical Chemistry, University of Frankfurt,
6000 Frankfurt am Main, Federal Republic of Germany

Catalytic Effect of Nitrate Ions on Cobalt(III) Substitution Reactions. Solvent-Exchange Data from Oxygen-17 NMR Measurements

S. Aygen,[1a] H. Hanssum,[1b] and R. van Eldik*[1a]

Received September 6, 1984

A rather remarkable nitrate ion catalysis of various substitution and isomerization reactions involving Co(III) and Cr(III) complexes in aqueous solution has been reported by several groups in recent years.[2–8] This is a rather discouraging observation since nitrate media are often selected and preferred for ionic strength adjustments mainly because many metal complexes are significantly more soluble in nitrate than for instance in perchlorate medium. Plane and Taube[9] reported that the rate of water exchange for $Cr(H_2O)_6^{3+}$ varied directly with the anion concentration at high salt concentrations, and nitrate ion was found to be the most effective catalyst in this sense. Later work[10] showed that the rate constant for solvent exchange at infinite dilution was similar for both nitrate and perchlorate media. Similar catalytic effects of nitrate ions were reported for the trans to cis isomerization of $Cr(C_3H_2O_4)_2(H_2O)_2^-$,[2] the anation of *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ by oxalate,[3,4] and the substitution of $Cr(C_2O_4)_2(NH_2CH_2COO)^{2-}$ by oxalate.[5] However, this is not a general tendency since no specific catalytic effect was observed for the anation of *cis*-$Cr(C_2O_4)(en)(H_2O)_2^+$ by oxalate.[11]

Very similar effects were recently reported for the anation of *cis*-$Co(en)_2(H_2O)_2^{3+}$, α-*cis*-$Co(edda)(H_2O)_2^+$ (edda = ethylenediaminediacetate), and $Co(NH_3)_4(H_2O)_2^{3+}$ by oxalic acid.[6–8] The nitrate medium resulted in abnormally high ion-pair formation constants[12,13] when compared to those found in perchlorate medium. It was suggested[6,7] that nitrate ions catalyze solvent exchange on the metal center via a pull-off interaction to produce a five-coordinate intermediate. The dissociative nature of this process was underlined by volume of activation data.[14–16] Other authors prefer to interpret such catalytic effects of nitrate ions as an enhancement of the ion-pair formation process.[8,17,18]

The present study was undertaken to determine the medium sensitivity of solvent exchange for *cis*-$Co(en)_2(H_2O)_2^{3+}$ in acidic medium. Earlier studies[19,20] determined the solvent-exchange rate constant in perchlorate medium with use of an ^{18}O-labeling technique, which involved precipitation of the exchanged complex, heating to remove the coordinated water, and conversion of the latter to CO_2 for a mass spectrometric analysis. Today a neater and less time-consuming method is available with which such solvent-exchange processes can be followed in situ, viz. ^{17}O NMR.

---

(1) (a) Institute for Physical Chemistry. (b) Institute for Biophysical Chemistry.
(2) Frank, M. J.; Huchital, D. H. *Inorg. Chem.* **1972**, *11*, 776.
(3) Kallen, T. W. *Inorg. Chem.* **1976**, *15*, 440.
(4) Kallen, T. W.; Senko, E. J. *Inorg. Chem.* **1983**, *22*, 2924.
(5) Kallen, T. W.; Hamm, R. E. *Inorg. Chem.* **1979**, *18*, 2151.
(6) van Eldik, R.; Harris, G. M. *Inorg. Chem.* **1979**, *18*, 1997.
(7) van Eldik, R. *Inorg. Chim. Acta* **1980**, *44*, L197.
(8) Davies, M. B.; Lethbridge, J. W. *J. Inorg. Nucl. Chem.* **1981**, *43*, 1579.
(9) Plane, R. A.; Taube, H. *J. Phys. Chem.* **1952**, *56*, 33.
(10) Hunt, J. P.; Plane, R. A. *J. Am. Chem. Soc.* **1954**, *76*, 5960.
(11) Kallen, T. W.; Stevens, W. C.; Hammond, D. G. *Inorg. Chem.* **1979**, *18*, 1358.
(12) Brown, P. M.; Harris, G. M. *Inorg. Chem.* **1968**, *7*, 1872.
(13) Weyh, J. A.; Maynard, R. B.; Baker, T. J. *Inorg. Chem.* **1976**, *15*, 2298.
(14) Stranks, D. R.; Vanderhoek, N. *Inorg. Chem.* **1976**, *15*, 2639.
(15) Tong, S. B.; Krouse, H. R.; Swaddle, T. W. *Inorg. Chem.* **1976**, *15*, 2643.
(16) van Eldik, R. *Inorg. Chim. Acta* **1981**, *49*, 5.
(17) Davies, M. B. *J. Inorg. Nucl. Chem.* **1981**, *43*, 1277.
(18) Bark, L. S.; Davies, M. B.; Powell, M. C. *Inorg. Chim. Acta* **1981**, *50*, 195.
(19) Jackson, J. A.; Lemens, J. F.; Taube, H. *J. Chem. Phys.* **1960**, *32*, 553.
(20) Kruse, W.; Taube, H. *J. Am. Chem. Soc.* **1961**, *83*, 1280.

0020-1669/85/1324-2853$01.50/0 © 1985 American Chemical Society