Contribution from the Department of Chemistry,
Loyola College, Baltimore, Maryland 21210

Complexes of Vanadium(III) with Pentadentate Ligands

TIMOTHY J. McNEESE* and TIMOTHY E. MUELLER

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The preparation and characterization of chloro(*n*-butylbis(*N*-salicylidene-3-aminopropyl)aminato)vanadium(III) and chloro(*n*-butylbis(*N*-salicylidene-3-aminopropyl)phosphinato)vanadium(III) are described. The syntheses of a structurally related Schiff base containing a bridging pyridine group and of its vanadium(III) complex are also presented. On the basis of electronic spectra, octahedral structures are proposed and probable ligand conformations discussed. Chloro(*n*-butylbis(*N*-salicylidene-3-aminopropyl)aminato)vanadium(III) undergoes halide abstraction by thallium tetrafluoroborate in acetone to give an analogous acetone adduct and is oxidized by oxygen to the corresponding vanadyl complex.

Introduction

Pentadentate Schiff base ligands containing tertiary amines,[1] tertiary phosphines,[2] ether,[3] and thioether[4] functionalities, and their corresponding complexes with divalent first-row-metal ions, have been extensively studied due to their varied properties and ease of preparation.[5]

While few investigations have been performed with analogous complexes of trivalent metal ions, a related vanadium(III) system containing a tetradentate Schiff base ligand, Cl(salen)(py)V^{III} (salen = *N*,*N*′-ethylenebis(salicylideneaminato)), has been reported.[6] The interest in that compound originated because of its potential as a precursor to a V(III)–dioxygen adduct,[7] insofar as kinetic evidence was presented that suggests pyridine solutions of Cl(salen)(py)V^{III} oxidize to the vanadyl complex via an unstable V^{III}–O_2 intermediate.[6]

Since an examination of the kinetic data allows for formation of the dioxygen adduct from a five-coordinate intermediate, a systematic approach to the investigation of these systems requires the availability of suitable species. Consequently, the aim of this paper is to report the preparation and properties of a series of vanadium(III) complexes containing pentadentate Schiff base ligands.

Experimental Section

General Methods. All manipulations involving air-sensitive compounds were performed with Schlenk techniques under an argon atmosphere or in a Vacuum Atmospheres inert-atmosphere chamber under prepurified argon. All solvents were purified by distillation under nitrogen prior to use. Tetrahydrofuran was distilled from lithium aluminum hydride, *tert*-butyl alcohol was distilled from sodium, and hexane and toluene were distilled from sodium ketyl. IR spectra were obtained on a Perkin-Elmer 283 spectrometer. ^{1}H NMR spectra were recorded on a Varian EM-360 spectrometer or Varian XL-100 spectrometer. All NMR data are listed in ppm relative to internal Me_4Si. Visible and mass spectra were obtained with Beckman DU-8 and AEI MS9 spectrometers, respectively. Magnetic moments were measured at 35 °C by the Evans method[8] using CH_2Cl_2 as solvent. Diamagnetic corrections were computed by use of Pascal's constants.[9] A Mechrolab Model 301 vapor pressure osmometer was used for the molecular weight determination. Vanadium trichloride (Strem), 6-aminocaproic acid (Aldrich), dinicotinic acid (Aldrich), 1,8-bis(dimethylamino)naphthalene (Aldrich), and other reagents were used as received from commercial sources. Tris(2-cyanoethyl)phosphine was prepared by a literature method.[10] Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Bis(2-cyanoethyl)butylamine. The procedure used was similar to that described by Whitmore et al.[11] A 1-L flask equipped with a dropping funnel containing 70% aqueous butylamine (210 g, 2.0 mol) was charged with acrylonitrile (266 g, 5.0 mol). The amine was added dropwise with cooling over a 30-min interval. After refluxing for 4 h, the mixture was allowed to stand overnight. Addition of 50 g of potassium carbonate with shaking caused separation of the organic layer, which was distilled through a 30-cm Vigreux column under reduced pressure (15 mm). After a forerun of acrylonitrile and intermediate boiling material, the product was collected at 202–205 °C: yield 234 g (65%); ^{1}H NMR ($CDCl_3$) δ 0.97 (m, 3 H, CH_3), 1.45 (m, 4 H, $NCH_2CH_2CH_2$), 2.50 (m, 6 H, $N(CH_2-)_3$), 2.80 (m, 4 H, CH_2CN); IR (ν(CN), neat) 2241 cm^{-1}; mass spectrum *m*/*e* 179 (M^+).

Anal. Calcd for $C_{10}H_{17}N_3$: C, 67.01; H, 9.56. Found: C, 67.08; H, 9.73.

Bis(3-aminopropyl)butylamine. A 1-L flask equipped with a condenser and dropping funnel was charged with $LiAlH_4$ (15 g, 0.44 mol) and 400 mL of anhydrous ether. Neat bis(2-cyanoethyl)butylamine (37.0 g, 0.21 mol) was added to the stirred slurry at a rate sufficient to maintain a gentle reflux, and the suspension was refluxed for 4 h. After the mixture was cooled and hydrolyzed by sequential addition of 15 mL of water, 15 mL of 15% NaOH, and 45 mL of water, the white suspension was filtered and the residue washed with 3 × 50 mL of ether. The combined washings and filtrate were concentrated to ca. 100 mL and extracted with 2 × 100 mL of 3 N HCl. The aqueous extracts were made strongly basic by addition of NaOH pellets while cooling in an ice bath. The separated amine was extracted into ether, dried over potassium carbonate, and, after removal of ether with the aid of a rotovap, distilled. The fraction boiling at 127–130 °C (5 mm) was collected: yield 28.1 g (71%); ^{1}H NMR (neat) δ 0.90 (m, 3 H, CH_3), 1.10 (s, 4 H, NH_2), 1.40 (m, 8 H, internal CH_2), 2.50 (m, 10 H, CH_2 α to N); IR (ν(NH), neat) 3360 (m, br), 3280 (m, br) cm^{-1}; mass spectrum *m*/*e* 187 (M^+).

Anal. Calcd for $C_{10}H_{25}N_3$: C, 64.12; H, 13.45. Found: C, 64.48; H, 13.71.

***n*-Butylbis(*N*-salicylidene-3-aminopropyl)amine (1).** Absolute ethanol (50 mL), bis(3-aminopropyl)butylamine (16.4 g, 0.087 mol), and salicylaldehyde (21.3 g, 0.174 mol) were mixed to afford a yellow solution. After dilution with an additional 200 mL of ethanol, the solution was heated to boiling for 3 h, allowing the volume to decrease to ca. 75 mL. Benzene was added (200 mL), the solution again concentrated at the boiling point to a small volume, and the product dried to constant weight in vacuo. The residual yellow oil could not be induced to crystallize. However, TLC analysis indicated only one component (R_f 0.55, silica gel, 1/1 methanol/ethyl acetate eluent); spectral properties were consistent with those anticipated for **1** and revealed no detectable impurities. The product was dissolved volumetrically in THF, affording 250 mL of a 0.35 M solution, which was used for subsequent preparations: ^{1}H NMR ($CDCl_3$) δ 0.90 (m, 3 H, CH_3), 1.40 (m, 4 H, $NCH_2CH_2CH_2CH_3$), 1.90 (m, 6 H, $N(CH_2)_3$), 2.40 (q, 4 H, C=NCH_2CH_2), 3.52 (t, 4 H, C=

(1) (a) Calvin, M.; Barkelew, C. H. *J. Am. Chem. Soc.* **1946**, *68*, 2267. (b) Bailes, R. H.; Calvin, M. *J. Am. Chem. Soc.* **1947**, *69*, 1886. (c) Augustin, M.; Kerrines, H. J.; Kangenbeck, W. *J. Prakt. Chem.* **1964**, *26*, 13. (d) Sacconi, L.; Bertini, I. *J. Am. Chem. Soc.* **1966**, *88*, 5180. (e) Floriani, C.; Calderazzo, F. *J. Chem. Soc. A* **1969**, 946. (f) Coleman, W. M.; Taylor, L. T. *J. Am. Chem. Soc.* **1971**, *93*, 5446. (g) Coleman, W. M.; Taylor, L. T. *Inorg. Chem.* **1971**, *10*, 2195. (h) Spencer, C. T.; Taylor, L. T. *Inorg. Chem.* **1971**, *10*, 2407. (i) Wallis, W. N.; Cummings, S. C. *Inorg. Chem.* **1974**, *13*, 988. (j) Niswander, R. H.; Taylor, L. T. *J. Magn. Reson.* **1977**, *26*, 491.

(2) (a) Niswander, R. H.; St. Clair, A. K.; Edmondson, S. R.; Taylor, L. T. *Inorg. Chem.* **1975**, *14*, 478. (b) Niswander, R. H.; Taylor, L. T. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 339.

(3) Lane, L. W.; Taylor, L. T. *J. Coord. Chem.* **1973**, *2*, 295.

(4) (a) Coleman, W. M.; Taylor, L. T. *J. Am. Chem. Soc.* **1970**, *92*, 1449. (b) Bertine, I.; Sacconi, L.; Speroni, G. P. *Inorg. Chem.* **1972**, *11*, 1323. (c) Edmundson, S. R.; Coleman, W. M.; Taylor, L. T. *Inorg. Chem.* **1973**, *12*, 1191.

(5) (a) Lever, A. B. P.; Gray, H. B. *Acc. Chem. Res.* **1978**, *11*, 348. (b) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139.

(6) Swinehart, J. H. *J. Chem. Soc., Chem. Commun.* **1971**, 1443.

(7) Vanadium complexes capable of reversibly binding dioxygen in the blood of the marine animals *Ascidacea* are believed to account for oxygen transport in these primitive creatures: Goodbody, I. *Adv. Mar. Biol.* **1974**, *12*, 149.

(8) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(9) Earnshaw, A. "Introduction to Magnetochemistry"; Academic Press: New York, 1968.

(10) Rauhut, M. M.; Hechenbleikner, H. A.; Currier, H. A.; Schaefer, F. C.; Wystrach, V. P. *J. Am. Chem. Soc.* **1959**, *81*, 1103.

(11) Whitmore, F. C.; Mosher, H. S.; Adams, R. R.; Taylor, R. B.; Chapin, E. C.; Weisel, C.; Yanko, W. *J. Am. Chem. Soc.* **1944**, *66*, 725.

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NCH_2), 7.0 (m, 8 H, C_6H_4), 8.29 (s, 2 H, HC=N), 13.91 (s, 2 H, OH); IR (ν(OH), neat) 3200 (vbr), (ν(CN)) 1635 (s) cm^{-1}; mass spectrum m/e 395 (M^+).

Bis(2-cyanoethyl)butylphosphine. A procedure from that of Grayson et al.[12] was used. Tris(2-cyanoethyl)phosphine (20.0 g, 0.10 mol) was dissolved in 400 mL of isoamyl alcohol, the mixture combined with 23 g of *n*-butyl iodide in a 1-L flask equipped with a condenser, and the resulting homogeneous solution refluxed for 2 days. After the reflux period, two phases were present, one of which solidified on cooling. The solid was collected by filtration, washed with additional isoamyl alcohol, and dried in vacuo. The crude tris(2-cyanoethyl)butylphosphonium iodide (34.9 g) was used directly without further purification. The phosphonium salt was suspended in 150 mL of degassed absolute ethanol contained in a 1-L flask fitted with a condenser and dropping funnel and maintained under a nitrogen atmosphere. Sodium ethoxide (6.30 g, 0.093 mol) in 200 mL of ethanol was added dropwise to the refluxing suspension. After 2 h, the clear solution was cooled and evaporated to an oil, which was partitioned between 10 mL of water and 100 mL of benzene. The organic phase was withdrawn and dried over magnesium sulfate. After evaporation of benzene, the residual liquid was distilled through a 20-cm Vigreux column at 0.5 mm. Following a forerun of 3-ethoxypropionitrile (34–36 °C; identified by ^1H NMR), the product (12.7 g, 65%) was collected at 155–165 °C: ^1H NMR (neat) δ 0.95 (m, 3 H, CH_3), 1.50 (m, 6 H, overlapping butyl methylenes), 1.90 (m, 4H, P–CH_2CH_2CN), 2.50 (m, 4 H, CH_2CN); IR (ν(CN), neat) 2245 cm^{-1}; mass spectrum m/e 196 (M^+).

Bis(3-aminopropyl)butylphosphine. A procedure analogous to that for bis(3-aminopropyl)butylamine was used. The reaction and workup were performed under argon. The compound was isolated in comparable yield (bp 122–126 °C (1 mm)): ^1H NMR (neat) δ 0.90 (m, 3 H, CH_3), 1.16 (s, 4 H, NH_2), 1.45 (m, 14 H, overlapping internal methylenes), 2.60 (m, 4 H, CH_2NH_2); IR (ν(NH), neat) 3362 (m, br), 3240 (m, br) cm^{-1}; mass spectrum m/e 204 (M^+).

***n*-Butylbis(*N*-salicylidene-3-aminopropyl)phosphine (2).** A THF solution of the ligand was prepared in a manner analogous to that for **1** with the exception that an argon atmosphere was maintained throughout. The compound could not be crystallized; purity was assessed on the basis of TLC (R_f 0.33; silica gel, 1/1 methanol/ethyl acetate eluent) and spectroscopic parameters: ^1H NMR ($CDCl_3$) δ 0.60 (m, 3 H, CH_3), 1.20 (br m, 14 H, overlapping $CH_2CH_2CH_2P(CH_2CH_2)_2$), 2.70 (t, 4 H, C=$NCH_2$), 6.80 (m, 8 H, C_6H_4), 7.95 (s, 2 H, NCH), 15.48 (s, 2 H, OH); IV (ν(OH), neat) 3150 (br), (ν(CN)) 1630 (s) cm^{-1}; mass spectrum m/e 412 (M^+).

***N*-(Trifluoroacetyl)-6-aminocaproic Acid (3).** Two 10-g portions of 6-aminocaproic acid were cautiously added to 30 mL of stirred trifluoroacetic anhydride. After the solid had completely dissolved, 250 mL of water was added and the solution cooled to 5 °C overnight. The resulting crystalline solid was collected by filtration, washed with cold water, and dried in vacuo (22.7 g, 65%): mp 35.5–36 °C; ^1H NMR (acetone-d_6) δ 1.43 (m, 6 H, $-(CH_2)_3-$), 2.17 (t, 2 H, CH_2CO_2H), 3.27 (q, 2 H, $CONHCH_2$), 7.64 (s, 1 H, CONH), 9.14 (s, 1 H, CO_2H); IR (ν(CO), Nujol mull) 1710 (vs) cm^{-1}; mass spectrum m/e 227 (M^+).

Anal. Calcd for $C_8H_{12}F_3NO_3$: C, 42.29; H, 5.29. Found: C, 42.20; H, 5.11.

5-((Trifluoroacetyl)amino)pentylamine Hydrochloride (4). To **3** (22.7 g, 0.10 mol) in 200 mL dry benzene was added 7.80 mL of thionyl chloride (10% excess), and the solution was refluxed under an argon atmosphere for 5 h. Removal of the solvent and excess thionyl chloride in vacuo afforded a colorless solid, which was identified as the acid chloride of **3** by its ^1H NMR (disappearance of the acidic proton at δ 9.14) and IR (ν(CO) at 1715 and 1800 cm^{-1}) spectra.

The acid chloride and 11.0 g of activated sodium azide[13] were mixed in 200 mL of dry benzene, and the mixture was refluxed until gas evolution ceased. Evaporation of the solvent after filtration afforded 21.0 g of a colorless oil. An IR spectrum indicated a complete absense of ν(CO) at 1800 cm^{-1} and the appearance of an isocyanate band at 2265 cm^{-1}.

The oil was heated with three 100-mL portions of 1 N HCl for 15 min each. The combined aqueous extracts left a dark solid after evaporation. Crude **4** was purified by recrystallization from ethanol/ether, affording colorless crystals: yield 13.0 g (60%); ^1H NMR (Me_2SO-d_6) δ 1.44 (m, 6 H, $-(CH_2)_3-$), 2.71 (t, 2 H, $CH_2NH_3^+$), 3.17 (t, 2 H, $-CONHCH_2$), 8.10 (s, 3 H, NH_3^+), 9.40 (s, 1 H, CONH); IR (ν(NH), Nujol mull) 3450, 3300, (ν(CO)) 1725, 1690 cm^{-1}.

Anal. Calcd for $C_7H_{14}ClF_3N_2O$: C, 35.82; H, 5.97; N, 11.94. Found: C, 35.54; H, 6.05; N, 11.24.

***N*,*N*′-Bis(5-((trifluoroacetyl)amino)pentyl)dinicotinamide (5).** To 20 mL of water and 75 mL of ethyl acetate were added 1.20 g of magnesium oxide and **4** (7.30 g 0.031 mol). After the mixture was stirred vigorously for 1 h, the organic layer was withdrawn and replaced with an additional 75 mL of ethyl acetate. After five treatments, the combined extracts were dried over magnesium sulfate and evaporated to dryness, leaving 4.24 g (70% recovery) of the deprotonated amine as an oil: mass spectrum m/e 198 (M^+).

The amine (21.4 mmol) was dissolved in 50 mL of dry CH_2Cl_2 and treated with 1,8-bis(dimethylamino)naphthalene (4.80 g, 0.021 mol). Freshly prepared dinicotinoyl chloride[14] (2.27 g, 0.011 mol) in 20 mL of CH_2Cl_2 was added dropwise and the reaction mixture refluxed for 3 h. After evaporation of the solvent, the residue was washed with three 150-mL portions of water and dried in vacuo. The crude product (3.40 g, 58%) was purified by recrystallization from ethanol/hexane to give colorless crystals (mp 178–178.5 °C): ^1H NMR (Me_2SO-d_6) δ 1.48 (m, 12 H, $-(CH_2)_3-$), 3.25 (m, 8 H, overlapping $CONHCH_2$ and $-CH_2NHCOCF_3$), 8.58 (t, 1 H, py 4-H), 8.76 (s, 2 H, pyCONH–), 9.08 (d, 2 H, py2-H, 6-H), 9.35 (s, 2 H, CF_3CONH); IR (ν(NH), Nujol mull) 3320 (s), 3220 (w), (ν(CO)) 1710 (vs), 1650 (vs), 1630 (vs) cm^{-1}; mass spectrum m/e 527 (M^+).

Anal. Calcd for $C_{21}H_{27}F_6N_5O_4$: C, 47.82; H, 5.12; F, 21.63; N, 13.28. Found: C, 47.93; H, 5.44; F, 21.66; N, 13.23.

***N*,*N*′-Bis(5-ammoniopentyl)dinicotinamide Bis(tetraphenylborate) (6).** To 200 mL of 90% ethanol was added **5** (1.40 g, 0.027 mol), the pH adjusted to ca. 9–10 with 1 N NaOH, and the solution sealed from the air. As judged by TLC (silica gel—5 parts ethyl acetate, 5 parts pyridine, 1 part acetic acid, and 3 parts water as eluent), only two components were present after 8 h: completely deprotected **5** (R_f 0.39) and, presumably, the mono(trifluoroacetyl) derivative (R_f 0.71); no **5** was detectable (R_f 0.95). After a total of 46 h, only the product was observed. The pH was then adjusted to ca. 7 with 1 N HCl and the solution concentrated to dryness. Extraction of the residue with 100 mL of hot ethanol containing a little charcoal, filtration, and evaporation of the solvent afforded 1.22 g of a sticky solid. This material was dissolved in 20 mL of water, and the resulting solution was acidified to pH 3 with 1 N HCl and immediately treated with a filtered aqueous solution of excess $Na[B(C_6H_5)_4]$. The resulting precipitate was collected by filtration, washed thoroughly with water, and dried in vacuo over P_2O_5 to give **6**: yield 2.02 g (78%); ^1H NMR (Me_2SO-d_6) δ 1.50 (m, 12 H, $-(CH_2)_3-$), 2.78 (m, 4 H, $CH_2NH_3^+$), 3.32 (m, 4 H, $CONHCH_2$), 7.06 (ca. 42 H, C_6H_5 obscuring CONH), 7.54 (s, 6 H, NH_3^+), 8.56 (t, 1 H, py 4-H), 8.80 (d, 2 H, py 2-H, 6-H); IR (ν(NH), Nujol mull) 3360 (m), 3160 (m), (ν(CO)) 1645 (s) cm^{-1}.

Anal. Calcd for $C_{65}H_{71}B_2N_5O_2$: C, 80.00; H, 7.33; N, 7.17. Found: C, 79.70; H, 7.37; N, 6.67.

***N*,*N*′-Bis(*N*-salicylidene-5-aminopentyl)dinicotinamide (7).** To **6** (0.357 g, 0.366 mmol) in 20 mL of 95% ethanol was added 6.50 mL of a 0.113 M (0.733 mmol) solution of KOH in 95% ethanol. The precipitate of potassium tetraphenylborate was removed by filtration and washed with two 10-mL portions of ethanol. The combined filtrate and washings were treated with 80 μL (0.73 mmol) of salicylaldehyde, made up to 80 mL with benzene, and heated on a steam bath for 2 h with occasional addition of benzene to maintain a constant volume. Removal of the solvent with the aid of a rotovap left an orange oil. Purification by preparative TLC (silica gel, 10% methanol in ethyl acetate as eluent) and recrystallization from methanol afforded **7** as yellow needles: yield 78.6 mg (40%); ^1H NMR (Me_2SO-d_6) δ 1.56 (m, 12 H, $-(CH_2)_3-$), 3.33 (m, 4 H, $CNHCH_2$), 3.58 (m, 4 H, C=NCH_2), 7.10 (m, 8 H, salicylidene protons), 8.54 (s, 2 H, HNCO), 8.63 (t, 1 H, py 4-H), 8.83 (d, 2 H, py 2-H, 6-H), 9.10 (s, 2 H, HC=N), 13.66 (s, 2 H, OH); IR (ν(OH), Nujol mull) 3280 (br), (ν(CN)) 1625 (s), (ν(CO)) 1645 (sh) cm^{-1}; mass spectrum m/e 543 (M^+).

Anal. Calcd for $C_{31}H_{37}N_5O_4$: C, 68.50; H, 6.81; N, 12.80. Found: C, 68.52; H, 6.36; N, 12.55.

Chloro(*n*-butylbis(*N*-salicylidene-3-aminopropyl)aminato)vanadium(III) (8). A 100-mL flask equipped with a condenser, a dropping funnel containing potassium *tert*-butoxide (2.60 g, 0.014 mol) in a minimum of *tert*-butyl alcohol, and an argon inlet was charged with 20.0 mL of a solution 0.35 M in **1**. To the stirred solution was added VCl_3 (1.10 g, 7.0 mmol), dissolved in ca. 30 mL of hot THF, via a stainless-steel cannula. Upon addition, a light-colored precipitate formed immediately. The potassium butoxide solution was added dropwise and the mixture refluxed overnight, resulting in nearly complete dissolution of the precipitate and formation of a dark red-brown solution. Evaporation of the solvent, extraction of the residue with 50 mL of hot toluene, and addition of hexane to the filtered extract gave red-brown **8**, which was collected

(12) Grayson, M.; Keough, P. T.; Johnson, G. A. *J. Am. Chem. Soc.* **1959**, *81*, 4803.

(13) Smith, P. A. S. *Org. React. (N.Y.)* **1946**, *3*, 337.

(14) Kuthan, J.; Palecek, J. *Collect. Czech. Chem. Commun.* **1966**, *31*, 2618.

by filtration and dried in vacuo: yield 1.14 g (34%). Double recrystallization from hot toluene/hexane gave red prisms: IR (ν(CN), Nujol mull) 1618 cm^{-1}. The mass spectrum exhibited isotope envelopes centered at m/e 480 and 445, which agree nearly exactly with those calculated for M^+ and $(M - Cl)^+$; μ_{eff} = 2.50 μ_B.

Anal. Calcd for $C_{24}H_{31}ClN_3O_2V$: C, 60.10; H, 6.52; Cl, 7.39; N, 8.76; V, 10.61. Found: C, 60.20; H, 6.59; Cl, 7.30; N, 8.60; V, 10.53. Mol wt: calcd, 480; found, 464 (C_6H_6).

Chloro(*n*-butylbis(*N*-salicylidene-3-aminopropyl)phosphinato)vanadium(III) (9). The compound was prepared by a procedure exactly analogous to that for **8** and was isolated in comparable yield: IR (ν(CN), Nujol mull) 1610 cm^{-1}. The mass spectrum exhibited isotope envelopes centered at m/e 497 and 462, which agree nearly exactly with those calculated for M^+ and $(M - Cl)^+$; μ_{eff} = 2.55 μ_B.

Anal. Calcd for $C_{24}H_{31}ClN_2O_2PV$: C, 58.00; H, 6.30; Cl, 7.13; N, 5.64; P, 6.23. Found: C, 57.97; H, 6.22; Cl, 7.03; N, 5.36; P, 6.15.

Chloro(*N*,*N*'-bis(*N*-salicylidene-5-aminopentyl)dinicotinamidato)vanadium(III) (10). To **7** (53.1 mg, 0.098 mmol), dissolved in 2 mL of 4/1 THF/triethylamine, was added 1.90 mL of a THF solution 0.0497 M in VCl_3 (0.094 mmol) with a syringe. The brown slurry was stirred for 6 h, and the product was collected by filtration, washed with five 2-mL portions of acetone, and dried in vacuo. Dark brown **10** weighed 43.6 mg (71%): IR (ν(NH), Nujol mull) 3260 (br), (ν(CN)) 1610 (s), (ν(CO)) 1645 (sh) cm^{-1}. The mass spectrum featured isotope envelopes centered at m/e 629 and 594, which agree closely with those calculated for M^+ and $(M - Cl)^+$; μ_{eff} = 2.54 μ_B.

Anal. Calcd for $C_{31}H_{35}ClN_5O_4V$: C, 59.29; H, 5.62; Cl, 5.65; N, 11.15; V, 8.11. Found: C, 59.21; H, 5.55; Cl, 5.28; N, 10.76; V, 8.20.

(*n*-Butylbis(*N*-salicylidene-3-aminopropyl)aminato)(acetone)vanadium(III) Tetrafluoroborate (11). To **8** (0.400 g, 0.84 mmol) dissolved in 10 mL of acetone was added thallium tetrafluoroborate (240 mg, 0.84 mmol) dissolved in 20 mL of acetone, resulting in immediate formation of a flocculent precipitate. After refluxing for 1 h, the solution was filtered through a tared frit. Thorough washing with acetone and drying at 110 °C left 196.7 mg of white solid (200.2 mg calculated for 0.84 mmol of TlCl). The red-brown filtrate was concentrated to 10 mL, and then 20 mL of hexane was added; **11** separated as an oil. Repeated trituration with hexane afforded an orange solid, which was dried in vacuo: yield 414.6 mg (84%); IR (ν(CO), Nujol mull) 1705 (m), (ν(CN)) 1625 (s) cm^{-1}; μ_{eff} = 2.61 μ_B.

Anal. Calcd for $C_{27}H_{37}BF_4N_3O_3V$: C, 55.03; H, 6.33; F, 12.89; N, 7.13; V, 8.64. Found: C, 54.97; H, 6.28; F, 13.06; N, 6.92; V, 8.56.

Oxo(*n*-butylbis(*N*-salicylidene-3-aminopropyl)aminato)vanadium(IV) (12). A dichloromethane solution of **8** (99.2 mg, 0.21 mmol) was stirred in the air overnight. The resulting green solution was evaporated to dryness and the residue washed with water. After drying in vacuo over P_2O_5, **12** was obtained as a green solid: yield 82.9 mg (87%); IR (ν(CN), Nujol mull) 1615 (s), (ν(V=O)) 968 (m) cm^{-1}; mass spectrum m/e 460 (M^+), 444 $(M - O)^+$. This material had an IR spectrum identical with that of a sample prepared from vanadyl acetate and **1** by use of a standard technique.[15]

Anal. Calcd for $C_{24}H_{31}N_3O_3V$: C, 62.58; H, 6.78; N, 9.12. Found: C, 62,83; H, 6.50; N, 8.92.

(*N*,*N*'-Bis(*N*-salicylidene-5-aminopentyl)dinicotinamidato)nickel(II) (13). To **7** (51.0 mg, 0.094 mmol) dissolved in 3 mL of methanol was added 9.10 mL of a methanol solution 0.0103 M in nickel acetate. After the mixture was stirred for 3 h, the light green precipitate was collected by filtration, washed with two 1-mL portions of methanol, and dried in vacuo at 80 °C: yield 34.0 mg (61%) of **13**; IR (ν(CN), Nujol mull) 1615 (s), (ν(CO)) 1645 cm^{-1}; mass spectrum m/e 600 (M^+).

Anal. Calcd for $C_{31}H_{35}N_5NiO_4$: C, 62.02; H, 5.88; N, 11.66; Ni, 9.78. Found: C, 61.69; H, 5.90; N, 11.36; Ni, 9.70.

Results and Discussion

Preparation of Ligands. The requirement for ligands with highly solubilizing properties is easily met in the pentadentate Schiff base system by alkylation of either the bridging ligand or the salicylidene ring. Complexes derived from ligands containing the 4-*sec*-butylsalicylidene unit proved to be too soluble for easy isolation or crystallization. Consequently, we restricted our attention to *n*-butyl-substituted ligands. *n*-Butylbis(*N*-salicylidene-3-aminopropyl)amine (**1**) was prepared by cyanoethylation of *n*-butylamine,[11] reduction of the resulting bis(2-cyanoethyl)butylamine with lithium aluminum hydride to bis(3-aminopropyl)butylamine, and condensation with salicylaldehyde.

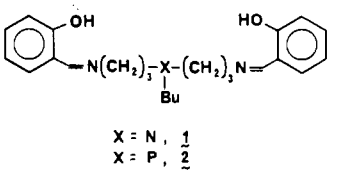
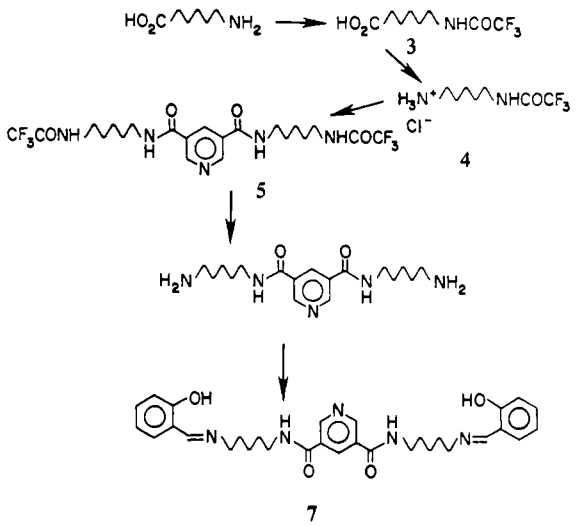


Figure 1. Structural representations for *n*-butyl-substituted ligands.

Scheme I. Synthesis of the Pyridyl Ligand, *N*,*N*'-Bis(*N*-salicylidene-5-aminopentyl)dinicotinamide (**7**)



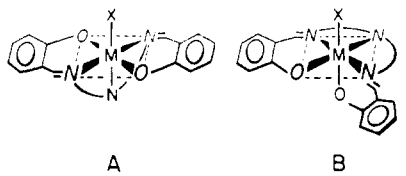
The corresponding phosphine compound, *n*-butylbis(*N*-salicylidene-3-aminopropyl)phosphine (**2**) was made by a similar procedure, both of which are detailed in the Experimental Section and represented in Figure 1. These methods are unexceptional and similar to those used by other workers for the synthesis of amine and *N*-methyl analogues.[1]

The structurally related pyridyl ligand, *N*,*N*'-bis(*N*-salicylidene-5-aminopentyl)dinicotinamide (**7**) was synthesized as outlined in Scheme I. The starting materials, 6-aminocaproic acid and 3,5-pyridinedicarboxylic acid, are available commercially in quantity. Trifluoroacetyl protection[16] of the amino acid proceeds smoothly and is necessary to prevent polymerization on condensation with the difunctional acid chloride used in a subsequent step. The protected acid, **3**, is transformed to the amine via the isocyanate by the Curtius reaction;[13] attempts using the Schmidt reaction[17] were unsuccessful. Hydrolysis of the intermediate isocyanate may be followed by IR spectroscopy and should be monitored, as prolonged reaction periods or too high an acid concentration result in loss of the protecting group. Condensation of the resulting amine with dinicotinoyl chloride[14] affords crystalline **5** in low to moderate yield. In terms of yield, this is the limiting step in the sequence. Factors influencing the yield have not been investigated, other than noting that addition of stoichiometric amounts of 1,8-bis(dimethylamino)naphthalene (which is recoverable) as a proton acceptor markedly favors formation of **5**. Deprotection of **5** is effected by prolonged standing at pH 9–10 in ethanol;[17] the reaction may be monitored by TLC. Further increase in pH to speed the reaction results in lower yields, presumably because of hydrolysis of the pyridyl amide. The deprotected material is obtained as an oil, which was difficult to purify. However, acidification and treatment with $Na[BPh_4]$ afford a crystalline bis(tetraphenylborate) salt (**6**). Addition of a stoichiometric amount of ethanolic KOH affords, after removal of insoluble potassium tetraphenylborate, the pure free amine. Condensation with salicylaldehyde gives the crystalline Schiff base **7** after chromatography. Alternate approaches to Schiff bases related to **7** using 3,5-diaminopyridine, which have been exploited

(15) Pfeiffer, P.; Hesse, T.; Pfitzner, H.; Scholl, W.; Thielert, H. *J. Prakt. Chem.* **1937**, *149*, 217.

(16) Greenstein, J. P.; Winitz, M. "Chemistry of the Amino Acids"; Wiley: New York, 1961; Vol. II, p 911.

(17) Weygand, F.; Csendes, E. *Agnew. Chem.* **1952**, *64*, 136.



A B

Figure 2. Structures A and B found for bromo(bis(*N*-salicylidene-3-aminopropyl)aminato)(1-methylimidazole)cobalt(III) and (μ-peroxo)-bis[(bis(*N*-salicylidene-3-aminopropyl)aminato)cobalt(III)], respectively.

elsewhere for preparation of oxime-based ligands,[18] are, in our experience, limited because of the difficulty of synthesis and air sensitivity of 3,5-diaminopyridines.

The inherent usefulness of **7** arises principally from geometric factors. Functionalization of the pyridine unit at the 3,5-positions does not significantly reduce the nucleophilicity of the pyridyl nitrogen atom, an observed effect for 2,5-substitution with Lewis acids other than a proton.[19] Further, inspection of space-filling models suggests the five-membered methylene chain is the minimum length required to allow intramolecular bonding of pyridine in a metal complex. Fewer methylene units force intermolecular bonding; more allow dissociation. This geometry, then, represents the optimum for formation of complexes of **7** bound in a pentadentate fashion, since the length of the connecting linkages and the chelate effect force formation of mononuclear metal complexes containing bound pyridine.

Since complexes of **7** are anticipated to adopt conformation A in Figure 2 (vide infra), **7** should be of use whenever a nondissociable aromatic amine is desired trans to a substituent.

Preparation of Vanadium(III) Complexes. The complexes were prepared by addition of the tetrahydrofuran adduct of VCl_3[20] to solutions of **1**, **2**, and **7** either with subsequent addition of potassium *tert*-butoxide or in the presence of triethylamine, affording **8**, **9**, and **10**, respectively. In the preparation of **10**, a light-colored precipitate forms, which redissolves on addition of base. The intermediate was not isolated but is, presumably, a VCl_3 adduct of the protonated ligand. Similar behavior has been noted by Calderazzo in the synthesis of dichloro(*N*,*N*′-ethylenebis(salicyldeneaminato))titanium(IV), which proceeds via a $TiCl_4$ adduct.[21] The products are all red-brown solids, susceptible to oxidation on exposure of their solutions to air.

Analytical and mass spectral data support the formulation of the compounds as ClVL (L = twice deprotonated **1**, **2**, or **7**). In each case a parent ion was observed, exhibiting an isotope pattern corresponding nearly exactly with that calculated. Further, a $(M - Cl)^+$ ion was a major feature in each spectrum. No higher mass fragments were observed, which, coupled with a molecular weight determination on **8**, is evidence for monomeric species. However, **10** is insoluble in nonpolar solvents and only slightly soluble in polar media—insufficiently so for a molecular weight measurement. These solubility properties suggest that a polymeric structure must be considered. To test this proposal, we prepared a nickel(II) complex of **7** (**13**) by the reaction of **7** with nickel acetate. This compound exhibits solubility characteristics essentially identical with those of **10**. The mass spectrum of **13** shows a parent ion and lacks features of higher mass. Although we cannot rule out structures of a polymeric nature, we feel the low solubility may well be attributable to an intrinsic property of the ligand. We note that **7** is insoluble in nonpolar solvents, as are similar oxime-based ligands unless alkylated at the amide nitrogen,[18] an avenue we have not explored with this system.

Solution magnetic moments all fall within the range 2.5–2.7 μ_B, consistent with those typically found for octahedral vanadium(III) complexes.[22] All the complexes have no appreciable O–H absorption in their IR spectra. All the complexes exhibit a small shift (ca. 20 cm^{-1}) to lower frequencies for ν(CN), as compared to the free ligands. The infrared data, therefore, confirm phenolic oxygen and azomethine nitrogen binding. Further, complexes derived from **7** show no appreciable shifts of amide carbonyl or amide N–H bonds from that of the free ligand, suggesting these groups do not serve as ligating functionalities.

Table I. Visible Spectra of Vanadium(III) Complexes

complex	ϵ^a (×10³)	λ_{max}, nm
8[b]	7.65	357
	3.08	403 (sh)
	1.63	452 (sh)
9[b]	6.74	345
	2.51	398 (sh)
	0.66	452 (sh)
10[c]	7.19	340
	2.04	409 (sh)
	0.58	464 (sh)
chloro(*N*,*N*′-ethylenebis-(salicyldeneaminato))(pyridine)-vanadium(III)[b]	5.45	357
	2.96	385 (sh)
	1.35	418 (sh)

[a] Extinction coefficients are in L mol^{-1} cm^{-1}. [b] Methylene chloride solution. [c] Dimethylformamide solution.

The visible spectra, whose features are presented in Table I, are very similar; each contains an intense charge-transfer band with d–d transitions at ca. 400 and 450 nm, consistent with pseudooctahedral V(III).[23] The resemblance of the spectra to that of chloro(*N*,*N*′-ethylenebis(salicylideneaminato))(pyridine)vanadium(III),[6] which undoubtedly has a trans octahedral structure,[24] is striking and suggests that the bridging ligand is coordinated in all cases.

Crystallographic data for Co(III) and Ni(II) complexes of the *N*-methyl analogue of **1**, as well as spectral data for Co(II) complexes of *N*-methyl and *P*-methyl analogues,[2a] also indicate coordination of the bridging ligands in these systems. For ligands of this nature, two arrangements have been noted. Structures A and B, illustrated in Figure 2, have been found for bromo(bis-(*N*-salicylidene-3-aminopropyl)aminato)(1-methylimidazole)cobalt(III)[25] and the peroxo-bridged dimer, (μ-peroxo)bis[(bis(*N*-salicylidene-3-aminopropyl)aminato)cobalt(III),[25] respectively. A conformation similar to A, although distorted toward a trigonal bipyramid, has been shown for (methylbis(*N*-salicylidene-3-aminopropyl)aminato)nickel(II).[26] Kistenmacher et al. have suggested that repulsion between the salicylidene rings of the dimer halves is responsible for conformation B found for the peroxo-bridged dimer and that A is anticipated for X not having this feature.[25] By these criteria, the V(III) complexes described herein are likely to exist in conformation A, with X trans to the bridging ligand. NMR spectra, which could confirm the point, had lines too broad to be useful.

Chloro(*n*-butylbis(*N*-salicylidene-3-aminopropyl)aminato)vanadium(III) (**8**) in acetone undergoes halide abstraction on treatment with thallium tetrafluoroborate (Ag^+ is not suitable because of rapid reduction by V(III)), affording a quantitative yield of TlCl and a red-brown solution. From **8**, (*n*-butylbis(*N*-salicylidene-3-aminopropyl)aminato)(acetone)vanadium(III) tetrafluoroborate (**11**) was isolated. The analytical, infrared, and magnetic susceptibility data are consistent with the formulation. A lowering of ν(CO) vs. that of free acetone (1705 vs. 1720 cm^{-1}) suggests a structure related to **8** by a simple displacement of

(18) Sharpless, K. B.; Jensen, H. P. *Inorg. Chem.* **1974**, *13*, 2617.
(19) Brown, H. C.; Horowitz, R. H. *J. Am. Chem. Soc.* **1955**, *77*, 1733.
(20) Kurras, E. *Naturwissenschaften* **1959**, *46*, 171.
(21) Calderazzo, F. *Pure Appl. Chem.* **1973**, *33*, 453.
(22) Clark, R. J. H. "The Chemistry of Titanium and Vanadium"; Elsevier: Amsterdam, 1968; p 182.
(23) Ballhausen, C. J. "Introduction to Ligand Field Theory"; McGraw-Hill: New York, 1962; p 228 and references therein.
(24) Visible spectra obtained with a KBr disk of Cl(salen)(py)V^{III} show no difference on comparison with solution spectra in methylene chloride or toluene. Further, the compound obeys Beer's law. Disproportionation to equilibrating components is, therefore, unlikely. Since the two-carbon backbone of salen forces planarity of the Schiff base donor atoms, the remaining ligands are necessarily trans. For a summary of structural data, see: Holm, R. H.; Everett, G. W.; Chakravorty, A. *Prog. Inorg. Chem.* **1965**, *7*, 83.
(25) Kistenmacher, T. J.; Marzilli, L. G.; Marzilli, P. A. *Inorg. Chem.* **1971**, *10*, 553.
(26) DiVaira, M.; Orioli, P. L.; Sacconi, L. *Inorg. Chem.* **1971**, *10*, 553.

chloride with O-coordinated acetone.

Oxidation of **8** by molecular oxygen to the corresponding vanadyl compound occurs in solution; oxo(*n*-butylbis(*N*-salicylidene-3-aminopropyl)aminato)vanadium(IV) (**12**), isolated by overnight oxygenation of a dichloromethane solution of **8**, was identical with that prepared from vanadyl acetate and **1** by use of a standard method.[15]

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Registry No. **1**, 97390-85-7; **2**, 97390-86-8; **3**, 407-91-0; **4**, 97390-87-9; **5**, 97390-88-0; **6**, 97390-90-4; **7**, 97390-91-5; **8**, 97403-32-2; **9**, 97403-33-3; **10**, 97403-34-4; **11**, 97390-93-7; **12**, 97390-94-8; **13**, 97390-95-9; (2-cyanoethyl)butylamine, 1789-37-3; butylamine, 109-73-9; acrylonitrile, 107-13-1; (3-aminopropyl)butylamine, 1555-68-6; salicylaldehyde, 90-02-8; (2-cyanoethyl)butylphosphine, 32272-08-5; tris(2-cyanoethyl)phosphine, 4023-53-4; *n*-butyl iodide, 542-69-8; bis(3-aminopropyl)butylphosphine, 6779-39-1; 6-aminocaproic acid, 60-32-2; trifluoroacetic anhydride, 407-25-0; dinicotinoyl chloride, 15074-61-0.

Contribution from the Departments of Chemistry, University of Oklahoma, Norman, Oklahoma 73019, and University of North Dakota, Grand Forks, North Dakota 58202

Reaction of Vaska's Complex with Thionyl Chloride

RICHARD A. VANDERPOOL and HARMON B. ABRAHAMSON*

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The title reaction has been studied by using ^{31}P NMR spectroscopy, and the products have been identified. If thionyl chloride is in excess throughout the reaction, only $IrCl_2(CO)(PPh_3)_2(SOCl)$ is formed. If Vaska's complex, $IrCl(CO)(PPh_3)_2$, is present in excess at some point, a substantial amount of decomposition is observed, some of it irreversible. The decomposition is due to attack of the reactive S(O)Cl ligand by Vaska's complex. One of the side products, $IrCl(CO)(PPh_3)_2(SO_2)$, displays a reversible exchange reaction in the presence of free Vaska's complex. Thermodynamic parameters for the exchange have been calculated from variable-temperature ^{31}P NMR data: $\Delta G^* = 40 \pm 8$ kJ mol^{-1}, $\Delta H^* = 74 \pm 5$ kJ mol^{-1}, $\Delta S^* = 113 \pm 20$ J K^{-1} mol^{-1}. These values are consistent with a dissociated intermediate in the exchange.

Few examples of complexes of sulfur monoxide (SO) are known.[1] This analogue of other two-atom ligands like O_2, NO, and CO is unstable in the free state[2] but is a possible intermediate in reactions of sulfur–oxygen compounds. We are currently engaged in the preparation of new complexes of sulfur monoxide, as the chemistry of these complexes can be important in the study of the formation of sulfur oxide pollutants and reagents for their removal.

Iridium complexes have been used as models for reactions important in transition-metal homogeneous catalysis,[3] including oxidative-addition reactions with small molecules.[4] Consequently, as part of a program to prepare new sulfur monoxide complexes, oxidative addition of thionyl chloride to iridium(I) complexes is of interest. The reaction of Vaska's complex,[5] $IrCl(CO)(PPh_3)_2$ (**1**), with thionyl chloride (Cl_2SO) is the first reaction of this series.

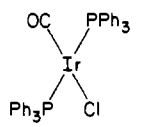
This reaction has been previously reported to yield $IrCl_2(CO)(PPh_3)_2(SOCl)$ (**2**). The addition of Vaska's complex to Cl_2SO in a 1:1 molar ratio reportedly[6] gives a 99% yield of **2**, based on elemental analysis and infrared spectra, but two carbonyl bands are observed. A second report of the synthesis[7] using excess Cl_2SO reaches the same conclusions, but with a simpler infrared spectrum. The confusion over spectra, and the report of dramatic color changes during the reaction,[6] has led us to reexamine this reaction with the aid of ^{31}P NMR spectroscopy. We find the system to be considerably more complex than previously reported and that under many conditions a mixture of products results.

Results and Discussion

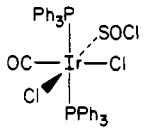
Reaction. Vaska's complex (**1**) reacts with excess thionyl chloride (Cl_2SO) (eq 1) at low temperature as previously described by Blake et al.[7] Pure $IrCl_2(CO)(PPh_3)_2(SOCl)$ (**2**) is isolated

$$IrCl(CO)(PPh_3)_2 + Cl_2SO \rightarrow IrCl_2(CO)(PPh_3)_2(SOCl) \quad (1)$$

as a yellow solid after recrystallization. The ^{31}P NMR spectrum



1



2

of this material in $CHCl_3$ solution shows four lines with the central doublet much more intense than the outer pair of lines (Figure 1G, Table I). Oxidative addition to $IrCl(CO)(PPh_3)_2$ (**1**) normally yields products with *trans*-phosphines, giving a singlet in the ^{31}P NMR spectrum.[8,9] The quartet observed for **2** is due to the phosphine ligands occupying different environments owing to the asymmetrical nature of the pyramidal S(O)Cl ligand; i.e., the phosphines are diastereotopic. This structure (**2**) is also consistent with infrared and ^1H NMR data collected by Blake et al.[7] The values of $^2J_{PP}$ (Table I) are consistent with *trans*-phosphines on iridium.[10a]

In contrast, when a solution of Cl_2SO is slowly added to a solution of **1** at room temperature or 263 K, the reaction proceeds

* To whom correspondence should be addressed at the University of North Dakota.

(1) (a) Schmid, G.; Ritter, G.; Debaerdemaeker, T. *Chem. Ber.* **1975**, *108*, 3008–3013. (b) Höfler, M.; Baitz, A. *Chem. Ber.* **1976**, *109*, 3147–3150. (c) Markó, L.; Markó-Monostory, B.; Madach, T.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 226–227. (d) Winter, A.; Zsolnai, L.; Huttner, G. *J. Organomet. Chem.* **1982**, *234*, 337–353. (e) Arulsamy, K. S.; Pandey, K. K.; Agarwala, U. C. *Inorg. Chim. Acta* **1981**, *54*, L51. (f) Hoots, J. E.; Lesch, D. A.; Rauchfuss, T. B. *Inorg. Chem.* **1984**, *23*, 3130–3136.
(2) Schenk, P. W.; Steudel, R. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 402–409.
(3) Collman, J. P.; Roper, W. R. *Adv. Organomet. Chem.* **1968**, *7*, 53–94.
(4) Vaska, L. *Acc. Chem. Res.* **1968**, *1*, 335–344.
(5) Vaska, L.; DiLuzio, J. W. *J. Am. Chem. Soc.* **1961**, *83*, 2784–2785.
(6) Schmid, G.; Ritter, G. *Z. Anorg. Allg. Chem.* **1975**, *415*, 97–103.
(7) Markham, S. J.; Chung, Y. L.; Branum, G. D.; Blake, D. M. *J. Organomet. Chem.* **1976**, *107*, 121–127.
(8) Collman, J. P.; Sears, C. T., Jr. *Inorg. Chem.* **1968**, *7*, 27–32.
(9) Al-Jibori, S.; Crocker, C.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1981**, 319–321.
(10) (a) Pregosin, P. S.; Kunz, R. W. "NMR Basic Principles and Progress"; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer Verlag: New York, 1979; Vol. 16. (b) Nixon, J. F.; Pidcock, A. *Annu. Rev. NMR Spectros.* **1969**, *2*, 345–422.

0020-1669/85/1324-2985$01.50/0