enhances the observed tendency for crystals of the complexes to occlude solvent molecules. The symmetrical coordination of the cbpS ligand to the metals (oxygen atoms on opposite sides of the metal and imine nitrogens also opposite) is the most common bonding arrangement for ligands of the cbpX type in both five- and six-coordinated complexes[6,7,36] though an exception is known.[36] Comparison with the known cbpN complexes[6,7] suggests strongly that the five-coordinated complexes [Co(cbpS)] and [Ni(cbpS)], formed by removal of the adducted mpy or py, would have a square-pyramidal structure, distorted markedly in the direction of a trigonal bipyramid. The axis of this hypothetical trigonal bipyramid would pass through the imine nitrogens. Moreover, it now seems likely from the discussion above that the salS analogues of the cbpS complexes generally have similar structures, including a metal–sulfur bond.

Acknowledgment. Support received for instrumentation under NSF Grant Gp-41679 is gratefully acknowledged.

Registry No. Co(cbpS), 61218-50-6; Ni(cbpS), 61218-51-7; Co(cbpS)mpy, 61218-52-8; Ni(cbpS)mpy, 61218-53-9; Ni(cbpS)py, 61218-54-0.

Supplementary Material Available: Listings of structure factor amplitudes (42 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) University of Wollongong. (b) University of Virginia.
(2) M. Di Vaira, P. L. Orioli, and L. Sacconi, *Inorg. Chem.*, **10**, 553 (1971).
(3) M. Seleborg, S. L. Holt, and B. Post, *Inorg. Chem.*, **10**, 1501 (1971).
(4) R. H. Niswander, A. K. St Clair, S. R. Edmondson, and L. T. Taylor, *Inorg. Chem.*, **14**, 478 (1975).
(5) L. W. Lane and L. T. Taylor, *J. Coord. Chem.*, **2**, 295 (1973).
(6) P. C. Healy, G. M. Mockler, D. P. Freyberg, and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 691 (1975).
(7) D. P. Freyberg, G. M. Mockler, and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 447 (1976).
(8) E. M. Boge, D. P. Freyberg, E. Kokot, G. M. Mockler, and E. Sinn, submitted for publication.
(9) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(10) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.
(11) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(12) D. T. Cromer and J. A. Ibers, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.
(13) Supplementary material.
(14) P. C. Chia, D. P. Freyberg, G. M. Mockler, and E. Sinn, *Inorg. Chem.*, **16**, 254 (1977).
(15) L. G. Warner, T. Otterson, and K. Seff, *Inorg. Chem.*, **13**, 2529 (1974).
(16) P. E. Riley and K. Seff, *Inorg. Chem.*, **11**, 2993 (1972).
(17) W. T. Robinson, S. Holt, Jr., and G. B. Carpenter, *Inorg. Chem.*, **6**, 605 (1967).
(18) M. Nardelli, G. Gasparri, G. Battistini, and P. Domiago, *Acta Crystallogr.*, **20**, 349 (1966).
(19) P. Porta, A. Sgamellotti, and N. Vinciguerra, *Inorg. Chem.*, **10**, 541 (1971).
(20) A. Lopez-Castro and M. T. Truter, *J. Chem. Soc.*, 3478 (1963).
(21) H. Luth and M. R. Truter, *J. Chem. Soc. A*, 1879 (1968).
(22) P. H. Davis, L. K. White, and R. L. Belford, *Inorg. Chem.*, **14**, 1753 (1975).
(23) J. F. McConnell and V. Kastalsky, *Acta Crystallogr.*, **22**, 853 (1967).
(24) P. W. G. Newman, C. L. Raston, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1332 (1973).
(25) M. R. Truter and K. W. Rutherford, *J. Chem. Soc.*, 1748 (1962).
(26) M. D. Glick, D. P. Gavel, L. L. Daddario, and D. B. Rorabacher, *Inorg. Chem.*, **15**, 1190 (1976).
(27) N. R. Kunchur and M. R. Truter, *J. Chem. Soc.*, 3478 (1958).
(28) L. Cavalca, G. F. Gasparri, G. D. Andretti, and P. Domiano, *Acta Crystallogr.*, **22**, 90 (1967).
(29) K. A. Fraser and M. M. Harding, *Acta Crystallogr.*, **22**, 75 (1967).
(30) M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *J. Chem. Soc., Dalton Trans.*, 67 (1976).
(31) T. Li and S. J. Lippard, *Inorg. Chem.*, **13**, 1791 (1976).
(32) E. Sinn, *Inorg. Chem.*, **15**, 369 (1976).
(33) C. Stein, S. Bouma, J. Carlson, C. Cornelius, J. Maeda, C. Weschler, E. Dentsch, and K. O. Hodgson, *Inorg. Chem.*, **15**, 1183 (1976).
(34) R. C. Elder, L. R. Florian, R. E. Lake, and A. M. Yacynych, *Inorg. Chem.*, **12**, 2690 (1973).
(35) M. M. Kadooka, L. G. Warner, and K. Seff, *Inorg. Chem.*, **15**, 812 (1976).
(36) D. P. Freyberg, G. M. Mockler, and E. Sinn, unpublished work.

Notes

Contribution from the Departments of Chemistry, Ahmadu Bello University, Zaria, Nigeria, and the University of Ife, Ile-Ife, Nigeria

Kinetics and Mechanism of the Reduction of Thiocyanatopentaamminecobalt(III) by Titanium(III)

Adeleye Adegite* and J. F. Ojo

There has been considerable upsurge in the literature on kinetic and mechanistic studies involving aquotitanium(III) as the reducing ion.[1-7] The most recent reports have been on the reduction of cobalt(III)–ammine complexes by this ion. Mechanistic classification into the inner- or the outer-sphere type for these latter reactions[4-7] has been predominantly based on the complexity of the rate dependence on hydrogen ion concentration. The rate expressions obtained can only be rationalized by invoking a series of reaction steps involving the formation of binuclear precursor complexes as preceding the electron-transfer step. The reduction of azidopentaamminecobalt(III) by Birk,[6] the reduction of fluoropentaamminecobalt(III) by Thompson and Sykes,[7] and the reduction of a series of carboxylatopentaamminecobalt(III) complexes by Martin and Gould[4] provide such examples. Moreover, Sykes and Thompson suggested the relative "hardness" or "softness" of a potential bridging ligand as an important consideration in the choice of mechanism by the "hard acid" titanous ion and, hence, explains why the sulfato, acetato, fluoro, and μ-superoxo complexes are reduced by the inner-sphere mechanism while the chloro, bromo, and iodo complexes react by the outer-sphere mechanism.[7] In this work, our rate studies are on the reduction of $Co(NH_3)_5SCN^{2+}$ by Ti^{3+}. The potential bridging ligand is very close to Cl^- in terms of the hard acid–hard base concept. Our results also provide additional data to Birk's work[6] on the reactivity pattern of the thiocyanato-, azido-, and isothiocyanatopentaamminecobalt(III) complexes with a common reducing ion.

Experimental Section

[Co(NH$_3$)$_5$SCN]Cl$_2$·1.5H$_2$O was prepared and characterized by means of the UV–visible spectra as reported in the literature.[8] Titanium(III) solutions were prepared by dissolving anhydrous TiCl$_3$ in 0.1 M HCl. LiClO$_4$ was prepared by neutralizing Li$_2$CO$_3$ (AR grade) with HClO$_4$ (AR grade). LiCl and HCl (AR grade) were used without further purification. Concentrations of titanium(III) solution were determined by indirect iodometry; viz., a known excess of deaerated Ce(IV) solution was added to an aliquot of the titanium(III) solution, and the excess Ce(IV) was determined by adding KI and titrating the liberated iodine against standardized Na$_2$S$_2$O$_3$ solution.

The course of the reaction was followed by monitoring the decrease in the absorbance of the cobalt(III) complex at λ 288 nm, a wavelength, where, for the concentrations of reactants and products, the cobalt complex is the dominant absorbing species. The reaction was followed using a Durrum–Gibson stopped-flow spectrophotometer. In all runs, titanium(III) concentrations were in large excess over cobalt(III), rate profiles were analyzed with a pseudo-first-order rate

Table I. Rate Constants for the $Ti^{3+}-Co(NH_3)_5SCN^{2+}$ Reaction ($I = 1.0$ M (LiCl), $T = 25.0$ °C, $[Co(NH_3)_5SCN^{2+}] = (0.7-1.7) \times 10^{-5}$ M)[a]

[H⁺], M	10³[Ti(III)], M	10⁻²k_{obsd}, M⁻¹ s⁻¹	10⁻²k_{calcd}, M⁻¹ s⁻¹
0.008	4.55	4.38	3.77
0.01	4.55	3.73	3.55
0.012	4.55	3.59	3.37
0.014	4.55	3.12	3.19
0.016	4.53	2.90	3.04
0.02	4.55	2.96	2.78
0.0225	4.55	2.56	2.31
0.025	4.55	2.30	2.50
0.03	4.55	2.04	2.28
0.05	4.55	1.56	1.67
0.10	1.25	0.94	1.01
0.10	2.51	0.88	1.01
0.10	3.75	0.97	1.01
0.10	7.50	0.90[a]	1.01
0.10	15.0	1.06[b]	1.01
0.10	5.20	0.97	1.01
0.10	5.20	1.06	1.01
0.20	7.50	0.52	0.56
0.35	9.50	0.35	0.34
0.50	7.50	0.26	0.24
0.75	7.50	0.17	0.16
0.90	7.50	0.13	0.14

[a] [Cl⁻] = 0.02 M and ionic strength was made to 1.0 M with $LiClO_4$. [b] [Cl⁻] = 0.12 M and ionic strength was made to 1.0 M with $LiClO_4$.

equation, and plots of log $(D_t - D_\infty)$ vs. t (D = absorbance) were linear for more than 5 half-lives even where solutions contained ClO_4^-. Ionic strength was maintained constant at $I = 1.0$ M with HCl and LiCl and with $LiClO_4$ where necessary.

Results

The linearity of the pseudo-first-order plots and the constancy within experimental error of the second-order rate constant (k_{obsd}, Table I) confirm that the apparent rate equation for this system at a constant acid is

$$\frac{-d}{dt}[Co(NH_3)_5SCN^{2+}] = k_{obsd}[Co(III)][Ti(III)] \qquad (1)$$

The dependence of k_{obsd} on [H⁺] was also investigated, and our results, Table I, show that k_{obsd} decreases as [H⁺] increases. A plot of k_{obsd} against [H⁺]⁻¹ was nonlinear (Figure 1), but $1/k_{obsd}$ vs. [H⁺] was linear (Figure 2), with a finite intercept, showing that eq 2 best describes the form of the dependence

$$1/k_{obsd} = a + b[H^+] \qquad (2)$$

of k_{obsd} on [H⁺]. From least-mean-square computation of the slope and intercept of the linear plot, the values $a = (2.02 \pm 0.32) \times 10^{-3}$ M s and $b = (78.7 \pm 1.5) \times 10^{-3}$ were obtained. Values of k_{obsd} computed with these parameters for different hydrogen ion concentrations are shown in the last column of Table I.

Discussion

The form of acid dependence obtained in this work is similar to that obtained by Sykes and Thompson[7] for the reduction of the fluoropentaammine complex and that obtained for the azidopentaammine complex by Birk.[6] Such a complex acid-dependence term is suggestive of a series of pre-electron-transfer equilibrium steps involving the formation of a binuclear precursor complex. The paths given by (3) and (4)
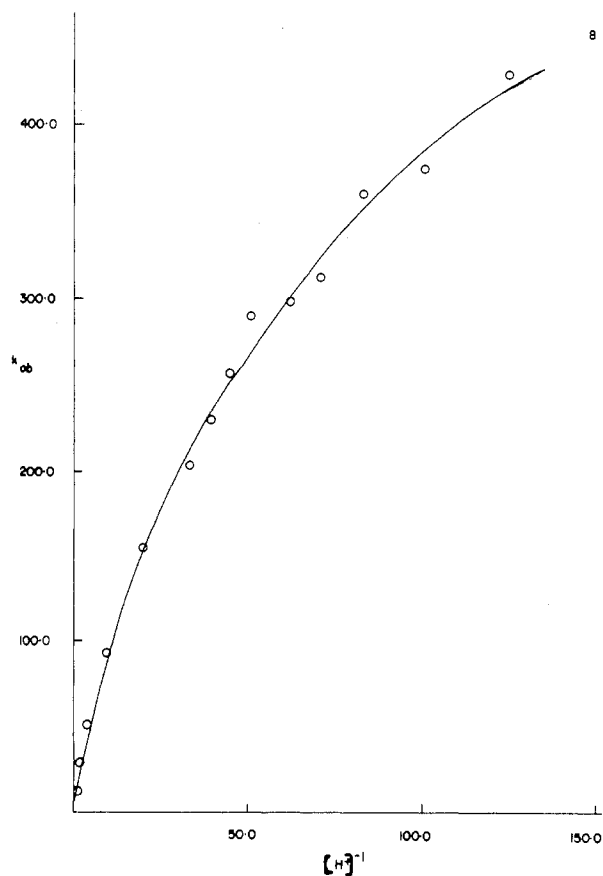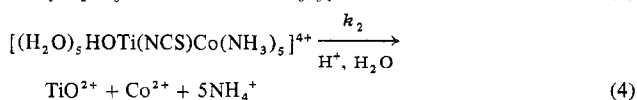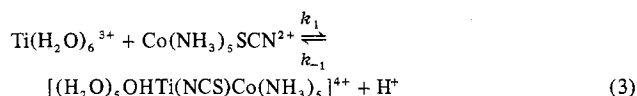
$$Ti(H_2O)_6{}^{3+} + Co(NH_3)_5SCN^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$

$$[(H_2O)_5OHTi(NCS)Co(NH_3)_5]^{4+} + H^+ \qquad (3)$$

$$[(H_2O)_5HOTi(NCS)Co(NH_3)_5]^{4+} \xrightarrow[H^+, H_2O]{k_2}$$

$$TiO^{2+} + Co^{2+} + 5NH_4^+ \qquad (4)$$

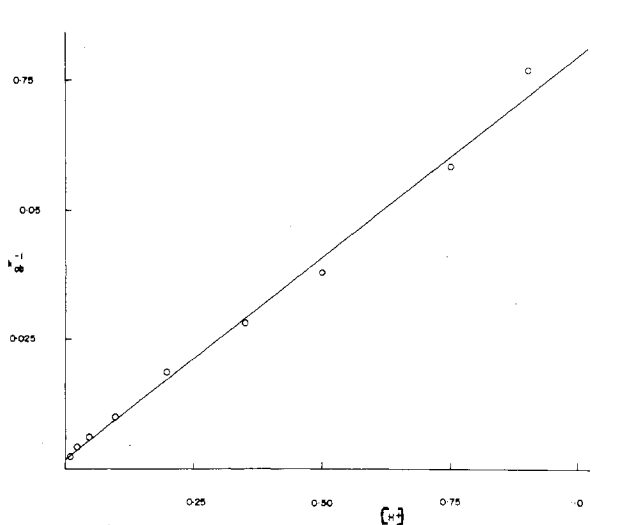**Figure 1.** Acid dependence of rate constants for the $Ti^{3+}-Co(NH_3)_5SCN^{2+}$ reaction: plot of k_{obsd} vs. [H⁺]⁻¹.

Figure 2. Acid dependence of rate constants for the $Ti^{3+}-Co(NH_3)_5SCN^{2+}$ reaction: plot of k_{obsd}^{-1} vs. [H⁺].

illustrate such a series of steps among other possibilities.[9]

Applying the steady-state approximation to the concentration of the intermediate and assuming $K_a[H^+]^{-1} \ll 1$ (K_a is the acid dissociation constant of Ti^{3+})[13] for the greater part of the acid range employed, it can be deduced from (2)-(4) that $k_{-1}/k_2k_1 = b$ and $1/k_1 = a$, and therefore from our rate data $k_1 = 495.0 \pm 9.4$ M⁻¹ s⁻¹ and $k_2/k_1 = 0.026$ M. These values compare favorably with 562.0 (erroneously put as 56.2 in their report[7]) and 0.112 obtained by Thompson and Sykes for the fluoropentaammine reaction and are consistent with 47.0 and 0.045 obtained for the azido complex by Birk.[6]

The reactivity order obtained for the thiocyanato, isothiocyanato, and azido complexes is as expected, $k_{SCN} > k_{N_3} > k_{NCS}$. Explanations for this reactivity order have been amply provided in previous reports.[10,11] That the Co-$(NH_3)_5SCN^{2+}$–Ti^{III} reaction proceeds by the inner-sphere mechanism is also supported by the small ratio $k_{SCN}/k_{N_3} = 10.5$, i.e., $k_{1(SCN)}/k_{1(N_3)}$ (k_{N_3} is k_1 in mechanism I of Birk's paper[6]). Our earlier studies with some outer-sphere reducing ions ($Ru(NH_3)_6^{2+}$, $Ru(en)_3^{2+}$, and $Cr(bpy)_3^{2+}$)[12] have shown that the ratio k_{SCN}/k_{N_3} is much larger for the outer-sphere reductants than for aquo ions, whose reactions with these ammine complexes are known to proceed by the inner-sphere mechanism. The fact that the thiocyanato complex reacts by the inner-sphere mechanism while the chloro complex reacts by the outer-sphere mechanism in their reduction by Ti^{3+} suggests that the stability of the prescursor complex is higher with the former complex than with the latter, and this may be indicative of the relative "hardness" of the potential bridging ligands in the two complexes. It is interesting to note that Ti^{3+} behaves similarly to V^{2+}, in that both reduce $Co(NH_3)_5SCN^{2+}$ by the inner-sphere mechanism and react with $Co(NH_3)_5Cl^{2+}$ by the outer-sphere mechanism but behaves unlike Cr^{2+} and Eu^{2+} which react with both complexes by the inner-sphere mechanism.

Registry No. $Ti(H_2O)_6^{3+}$, 17524-20-8; $[Co(NH_3)_5SCN]^{2+}$, 14970-18-4.

References and Notes

(1) J. P. Birk and T. P. Logan, *Inorg. Chem.*, **12**, 580, 2464 (1973).
(2) J. D. Ellis and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 537, 2553 (1973).
(3) A. Adegite and S. Edeogu, *J. Chem. Soc., Dalton Trans.*, 1203 (1975).
(4) A. H. Martin and E. S. Gould, *Inorg. Chem.*, **14**, 873 (1975).
(5) M. Orhanovic and J. E. Earley, *Inorg. Chem.*, **14**, 1478 (1975).
(6) J. P. Birk, *Inorg. Chem.*, **14**, 1728 (1975).
(7) G. A. K. Thompson and A. G. Sykes, *Inorg. Chem.*, **15**, 638 (1976).
(8) D. A. Buckingham, I. I. Creases, and A. M. Sargeson, *Inorg. Chem.*, **9**, 655 (1970).
(9) J. P. Birk, *J. Chem. Educ.*, **47**, 805 (1970).
(10) D. P. Fay and H. Sutin, *Inorg. Chem.*, **9**, 1291 (1970).
(11) A. Adegite and T. Kuku, *J. Chem. Soc., Dalton Trans.*, 158 (1976).
(12) A Adegite, F. Dosumu, and J. F. Ojo, *J. Chem. Soc., Dalton Trans.*, in press.
(13) M. R. Paris and C. L. Gregoire, *Anal. Chim. Acta*, **42** 439 (1968); H. Krentzien and F. Brio, *Chem. Abstr.*, **73**, 78 656 (1970).

Contribution No. 2426 from the Central Research and Development Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898, and from Gilman Hall, Department of Chemistry, Iowa State University, Ames, Iowa 50011

Metal Vapor Syntheses of Fe[P(OMe)₃]₅ and Fe[P(OCH₂)₃CEt]₅ and Spectroscopic Studies of d⁸ ML₅ⁿ⁺ Complexes

C. A. Tolman, L. W. Yarbrough, II, and J. G. Verkade*

Some years ago we noted that the ^{31}P chemical shifts for several pairs of isoelectronic and isostructural complexes of phosphites moved to higher applied field with increasing charge.[1] Thus, for example, $\delta(^{31}P)$ progresses from −147 in $Co[P(OMe)_3]_5^+$ to −110 ppm in $Ni[P(OMe)_3]_5^{2+}$.[2] In order to determine whether this progression is monotonic, we made $Fe[P(OMe)_3]_5$ for comparison. We have also prepared the ML_5^{n+} analogues with $L = P(OCH_2)_3CEt$. Here we describe various methods for the preparation of $Fe[P(OMe)_3]_5$[3] and

* To whom correspondence should be addressed at Iowa State University.

$Fe[P(OCH_2)_3CEt]_5$, including metal atom evaporation, and show that both the shift of $\delta(^{31}P)$ to higher field and the shift of the lowest energy d–d electronic band to lower energy in the series FeL_5^0, CoL_5^+, NiL_5^{2+} ($L = P(OMe)_3$ or $P(OCH_2)_3CR$) are linear with charge.

Experimental Section

The $[NiL_5](BF_4)_2$ complexes were prepared in acetone and isolated according to a published procedure for $Ni[P(OMe)_3]_5(BF_4)_2$[4] except that $Ni(BF_4)_2·6H_2O$ was used instead of the hydrated perchlorate salt. The $[CoL_5]BF_4$ complexes were also made following this procedure except that the $Co(BF_4)_2$ solution was added to neat excess $P(OMe)_3$ or excess $P(OCH_2)_3CMe$ as a saturated acetone solution. Trimethyl phosphite was distilled at atmospheric pressure. The fraction boiling at 112–113 °C was retained and stored over Molecular Sieves. Caged phosphites are toxic and should be handled with caution.[5]

$Fe[P(OMe)_3]_5$. This complex was prepared by three methods.

(a) Direct Cocondensation of Fe Vapor with P(OMe)₃. A static reactor with a resistively heated crucible, similar to that described by Timms,[6] was used to cocondense Fe vapor and $P(OMe)_3$ at liquid nitrogen temperature. In a typical run 0.58 g of Fe and 10 ml of $P(OMe)_3$ were cocondensed over a period of 1 h. Crucible heating and liquid nitrogen cooling were discontinued and the reactor was allowed to warm to room temperature for 1.5 h. Excess $P(OMe)_3$ was removed with a vacuum pump and liquid nitrogen trap. N_2 was admitted to the reactor, which was capped and taken into a N_2 drybox for workup. The black oily crude product was extracted with four 5-cm³ portions of pentane and then three 5-cm³ portions of methanol; powdered Fe (25 mg) was fished out of the latter with a magnet. Stripping the pentane and methanol solutions to constant weight gave 1.36 g of brown oil and 1.16 g of black tar, respectively. Further attempts to purify these materials were not successful. They were shown to be mixtures by their ^{31}P and ^1H NMR spectra. The tar (in C_6D_6) showed strong multiplets ($\sim$15 Hz wide) at δ 3.68 assigned to the Me protons in $Fe[P(OMe)_3]_5$. Initially we had difficulty obtaining good NMR spectra until we removed finely divided Fe particles by filtration through Millipore filters. High-pressure liquid chromatography (Du Pont LC830 009-902 using a 1-m, 2.1-mm i.d. Corasil II column at ambient temperature, 500 psig, 2% p-dioxane/98% isooctane–100% p-dioxane, concave gradient solution at 10%/min, UV detector) of the crude product from a similar preparation showed five components. The mass spectrum of the major component established that it is $Fe[P(OMe)_3]_5$.

(b) Condensation of Fe Vapor into a Cooled Solution of P(OMe)₃. A rotating-flask assembly based on the brief description of Timms and Green[7] was constructed with a Buchi Rotavapor unit and an alumina-coated, resistance-heated tungsten wire basket (made from 8–9 cm of 18-gauge wire). In a typical run, a solution of 20 ml of $P(OMe)_3$ in 150 ml of methylcyclohexane was placed in the 1-l. flask and several small pieces of iron weighing about 0.5 g were inserted into the basket. With the flask cooled in a pentane slush bath, the system was evacuated to 10^{-5} Torr and the flask rotated at about 60 rpm. Heating the wire basket by passing a current of 18 A at 12–13 V caused a rapid rise in the pressure after a few seconds of evaporation. Upon cessation of heating for less than 1 min, the vapor pressure in the system was again reduced to about 10^{-5} Torr, allowing the evaporation to continue. Four to eight repetitions of this cycle were found to be sufficient to evaporate about 0.5 g of iron.

After the black suspension produced by the evaporation was allowed to warm to room temperature, the flask was transferred to a drybox, the liquid filtered, and the filtrate evaporated to a dark yellow-brown oil. Extraction of the oil with 80 ml of pentane and evaporation of the solvent produced 0.28 g of a pale yellow oily powder which was sublimed under vacuum at 80 °C. The ^{31}P NMR spectrum in acetone showed the yellow sublimate to be contaminated with $(MeO)_3PO$. Addition of a known amount of $(MeO)_3PO$ and comparison of the changes in relative peak areas of the ^{31}P NMR spectra revealed that 0.21 g of the desired product had been formed which represented a 4% yield based on evaporated iron.

(c) Wet Chemical Synthesis by Na Amalgam Reduction of FeCl₂. A pure sample of $Fe[P(OMe)_3]_5$ was made by reducing $FeCl_2$ with sodium amalgam in the presence of a solution of excess ligand.[3] To 50 ml of dry THF was added 50 ml of $P(OMe)_3$, 2.63 g (20.0 mmol) of anhydrous $FeCl_2$, and an amalgam consisting of 1.38 g of Na (60.0 mmol) and 50 ml of Hg. After 3 h of vigorous stirring at room temperature, the black suspension was decanted from the amalgam