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.

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# Metal Vapor Syntheses of Fe[P(OMe)$_3$]$_5$ and Fe[P(OCH$_2$)$_3$CEt]$_5$ and Spectroscopic Studies of d$^8$ ML$_5$$^{n+}$ Complexes

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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 $Fe[P(OCH_2)_3CEt]_5$, 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 $Ni(BF_4)_2 \cdot 6H_2O$ 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-cm$^3$ portions of pentane and then three 5-cm$^3$ 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 (~15 Hz wide) at $\delta$ 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 FeCl$_2$.** 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

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and pumped to dryness. The fine black powder remaining was washed with two 50-ml portions of *n*-pentane and filtered to yield a clear yellow solution which, when pumped to dryness, produced a dark yellow-brown powder. Sublimation of this powder at 80 °C and 0.5 Torr onto a water-cooled finger gave clear yellow crystals of the desired product in 38% yield (lit.[3] yield 40%). The mass spectrum consisted of a strong parent ion followed by stepwise loss of $OCH_3$ and $P(OMe)_3$ to $Fe[P(OMe)_3]_2$. The base peak corresponded to $P(OMe)_3$.

**$Fe[P(OCH_2)_3CCH_2CH_3]_5$.** This complex was prepared by two methods.

**(a) Reaction of $Fe(COD)_2$[6] with $P(OCH_2)_3CEt$.** Iron (0.92 g) and 17 ml of 1,5-cyclooctadiene (COD) were cocondensed over a period of 70 min in a static reactor at liquid nitrogen temperature previously charged with 15.8 g of $P(OCH_2)_3CEt$ and a magnetic stirring bar. Crucible heating was discontinued and 50 ml of THF condensed in. The pump was closed off and the reactor allowed to warm slowly with magnetic stirring. $N_2$ was admitted to the reactor, which was capped and taken into a drybox. Treatment with activated charcoal, filtering through a short alumina column, and stripping to constant weight gave 9.7 g yellow crystals. The $^{31}P$ NMR spectrum showed that the product contained about 30% $Fe[P(OCH_2)_3CEt]_5$ and 70% free $P(OCH_2)_3CEt$, indicating a yield of about 20%. The $^1H$ spectrum showed that the sample was free of COD.

**(b) Na Amalgam Reduction of $FeCl_2$.** Method (c) in the previous preparation was duplicated with $P(OCH_2)_3CEt$ except that 30 g of ligand in 30 ml of THF was used. After separation from the amalgam, the thick black suspension was diluted by half its volume with THF and rotated at 30000 rpm for 30 min in a Beckman Model L-2 ultracentrifuge equipped with a Model 40 rotor with a fixed angle of 26° and an average radius of 5.9 cm. After carefully decanting the dark yellow solution from the black sediment, it was passed through a 0.45 μ Millipore filter and used (with the addition of ~15% by volume acetone-$d_6$ as a deuterium lock) for the $^{31}P$ NMR spectrum. The same filtered solution, after dilution with additional THF, was used to obtain the visible spectrum. The yield of the complex was estimated to be about 2%.[8]

## Discussion

Though we first prepared $Fe[P(OMe)_3]_5$ by direct cocondensation of Fe vapor and $P(OMe)_3$, condensing Fe into a solution of $P(OMe)_3$ or wet chemical reduction of $FeCl_2$ gives cleaner products. Attempts to prepare $Fe[P(OMe)_3]_5$ by displacement of COD from $Fe(COD)_2$[6] gave, to our surprise, $(1,3\text{-COD})Fe[P(OMe)_3]_3$,[9] from which the 1,3-COD cannot be easily removed.[10] Direct cocondensation of $P(OCH_2)_3CEt$ is not practical because of its low vapor pressure. The $Fe[P(OCH_2)_3CEt]_5$ complex could however be prepared from $Fe(COD)_2$. The different behavior of $P(OCH_2)_3CEt$ is probably due at least in part to its strongly electron-withdrawing character. Treatment of $Fe(COD)_2$ with CO gives some $Fe(CO)_5$.[9]

The synthesis of $Fe[P(OMe)_3]_5$ and $Fe[P(OCH_2)_3CEt]_5$ permits for the first time the study of the nature of the correlation between overall charge and the $^{31}P$ chemical shift in a series of complexes whose members ($FeL_5$, $CoL_5^+$, $NiL_5^{2+}$) are both isostructural and isoelectronic. Because these diamagnetic yellow trigonal-bipyramidal $d^8$ complexes[11-13] are expected to exhibit at least the lowest energy d–d transition,[13] it also becomes possible to obtain an indication of the trend in ligand field strength as a function of charge.

As shown in Table I and in Figure 1, the $^{31}P$ chemical shift progresses linearly to higher applied field with increasing charge for the two series $FeL_5$, $CoL_5^+$, $NiL_5^{2+}$ where L = $P(OMe)_3$ or $P(OCH_2)_3CR$. This trend suggests that the paramagnetic shielding term, $\sigma_{\text{para}}$, may dominate the diamagnetic contribution in the Ramsey equation.[14]

In the approach of Letcher and Van Wazer,[15] the paramagnetically dominated chemical shift (relative to a particular standard) is given by

$$\sigma_{\text{para}} = \frac{-2}{3}\left[\frac{e^2h^2}{m^2c^2}\right]\left[\left\langle\frac{1}{r^3}\right\rangle_{\text{p}}\zeta_1 + \left\langle\frac{1}{r^3}\right\rangle_{\text{d}}\zeta_2\right]\frac{1}{\Delta E} \qquad (1)$$

Table I. NMR and UV-Visible Spectral Parameters of $d^8$ $ML_5^{n+}$ Complexes[a]

| Complex | L | $\delta(^{31}P)$[b] | $\delta(^1H)$[c] | $\lambda$ ($\epsilon$)[d] |
|---|---|---|---|---|
| $FeL_5$ | $P(OMe)_3$ | −179.2 | 3.50 | 359.5 ($9.7 \times 10^2$) |
| | $P(OCH_2)_3CEt$ | −161.5 | 3.49 | 336.5 ($5 \times 10^3$)[e] |
| $[CoL_5]BF_4$ | $P(OMe)_3$ | −148.3 | 3.64 | 379.5 ($8.4 \times 10^2$) |
| | $P(OCH_2)_3CMe$ | −136.2 | 4.10 | 352.0 ($1.0 \times 10^3$) |
| $[NiL_5](BF_4)_2$ | $P(OMe)_3$ | −109.4 | 3.85 | 401.0 ($1.5 \times 10^3$) |
| | $P(OCH_2)_3CEt$ | −106.5 | 4.50 | 367.5 ($1.8 \times 10^3$) |

[a] The previously published $^{31}P$ and UV–visible spectral measurements on the $CoL_5^+$ and $NiL_5^{2+}$ ions[13] were remade and found to be comparable. The present data are more precise, however. [b] Spectra were taken on a Bruker HX-90 spectrometer in the FT mode using acetone-$d_6$ as a lock and solvent except where noted. All of the resonances in the proton-decoupled FT mode are downfield of the external standard (85% $H_3PO_4$) and are accurate to ±0.1 ppm. The absorptions were sharp except for the $[CoL_5]BF_4$ compound for which the peak was somewhat broadened. [c] Except where noted, the solvent used was acetonitrile-$d_3$ with TMS as the internal standard. The chemical shifts reported for $P(OCH_2)_3CR$ are for the $OCH_2$ protons. All of the compounds showed broadened singlets with ill-defined but symmetrical shoulders except $Co[P(OMe)_3]_5BF_4$ which displayed two peaks at 3.55 and 3.73 ppm with a less intense but very broad absorption between them. The $OCH_2$ proton peak in the case of $Fe[P(OCH_2)_3CEt]_5$ was broad, overlapping the resonance due to these protons in the free ligand present. [d] Except where noted, the solvent used was $CH_2Cl_2$. [e] Estimated by the method described to calculate an approximate yield (see ref 8) using THF as the solvent.

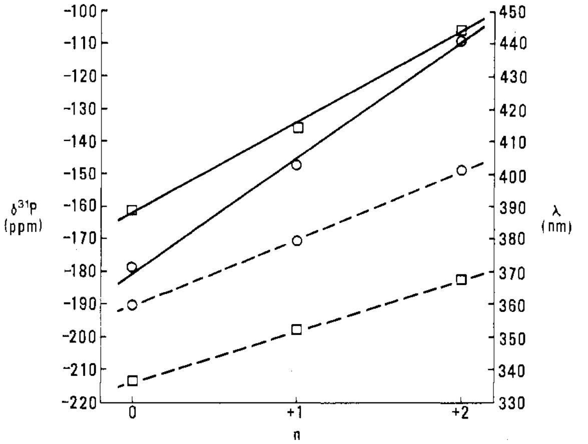

**Figure 1.** Graph showing linear correlation of charge *n* on $ML_5^{n+}$ complexes with $^{31}P$ chemical shift (full lines) and lowest d–d electronic transition (dashed lines). The ligand L is $P(OMe)_3$ (○) or $P(OCH_2)_3CR$ (□).

where $\zeta_1$ and $\zeta_2$ are dependent on the occupation of the phosphorus 3p and 3d orbitals, respectively. If it is assumed (as is done elsewhere for similar compounds[15]) that $\langle 1/r^3\rangle\cdot(1/\Delta E)$ is constant in the complexes studied here, $\zeta_1 + \zeta_2$ must decrease with increasing metal charge. This is not unreasonable considering that a rising positive charge is expected to shift 3p electron density toward the metal as well as reduce π back-bonding from the metal to the phosphorus 3d orbitals.

The linearity of the chemical shift with charge displayed by the complexes in Figure 1 could arise from the dominant dependence of $\sigma_{\text{para}}$ on $r$ or on $\zeta_1 + \zeta_2$ in eq 1 (assuming $\langle 1/r^3\rangle(1/\Delta E)$ is constant[15]). Only one of these two effects can dominate within the framework of present theory since a combination of two such linear influences would lead to a quadratic dependence of $\delta$ on charge according to eq 1.

Some support for the dominance of $\zeta_1 + \zeta_2$ stems from the monotonic decrease in energy of the lowest UV–visible band with rising charge (Table I and Figure 2). From arguments presented earlier regarding the electronic spectra of the $CoL_5^+$ and $NiL_5^{2+}$ complexes,[13] the band of lowest energy is reasonably assigned to the e′ → a′ d–d transition. The drop in energy of this absorption in the series $FeL_5^0$, $CoL_5^+$, $NiL_5^{2+}$ can be taken to reflect the expected decline in ligand field contribution from metal-to-ligand $\pi$ bonding. These results are consistent with the idea that the $\pi$ acidity of these phosphite esters dominates the ligand field parameter *Dq* in these systems, since, in the absence of such an effect, *Dq* is expected to rise with metallic charge. The shorter wave-length of the d–d absorption for a given $P(OCH_2)_3CEt$ complex compared with that of its $P(OMe)_3$ analogue is also in agreement with the poorer Lewis basicity of the caged ligand,[13,16,17] the lower negative charge calculated for its phosphorus,[18] and hence its higher $\pi$ acidity.[18]

It is interesting to note that the expected shift of $\delta(^1H)$ to lower applied field with increasing charge is also approximately linear in the series where L = $P(OMe)_3$.

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**Registry No.** $Fe(P(OMe)_3)_5$, 55102-04-0; $Fe(P(OCH_2)_3CEt)_5$, 61128-96-9; $[Co(P(OMe)_3)_5]BF_4$, 22323-14-4; $[Co(P(OCH_2)_3CMe)_5]BF_4$, 61128-97-0; $[Ni(P(OMe)_3)_5](BF_4)_2$, 53701-91-0; $[Ni(P(OCH_2)_3CEt)_5](BF_4)_2$, 53701-93-2; $^{31}P$, 7723-14-0.

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(18) A similar shift to shorter wavelengths was noted earlier in one of our laboratories for d–d transitions in the analogous $CoL_6^{3+}$ complexes for which the calculated *Dq* values were indeed larger for the caged ligand species.[13]

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# Study of Borane Production from Pyrolyzed Diborane by Molecular Beam Velocity Analysis Spectrometry

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Diborane must rank high on the list of most heavily studied compounds.[2,3] This is not surprising considering the early interest in boron compounds as fuels. New studies have appeared in the literature as interest rekindles in boron chemistry due to the possible utilization of higher boranes and carboranes as solid propellant ballistic moderators. New methods of synthesis involving both equilibrium as well as the exciting nonequilibrium techniques involving laser photochemistry are being attempted to improve specificity and efficiency of reaction paths for these compounds which undergo complex reaction mechanisms.[4,5]

Over 25 years of controversy have been associated with the mechanism for the thermodecomposition of diborane, the simplest of the stable boranes.[6-12] All mechanisms with the exception of that proposed by Fehlner and later withdrawn[8-10] were based upon the initial production of $BH_3$. However, direct unambiguous proof for the formation of $BH_3$ during $B_2H_6$ pyrolysis still does not exist. Sinke et al. based their evidence for the formation of $BH_3$ upon the changes occurring in the low-mass (10–13) ion fragmentation pattern relative to the high-mass ion group (21–27) as determined under pyrolyzing and nonpyrolyzing conditions.[11] Fehlner and Fridman based their evidence upon the increase in the mass 14 ion signal ($BH_3^+$) under pyrolyzing conditions relative to that at room temperature[10] while Wilson and McGee[12] argued that changes in the ionization efficiency curves for the mass 12 and 13 ions was evidence for $BH_3$. Evidence such as this, while reasonable, is not unambiguous. A required assumption is that the fragmentation pattern of $B_2H_6$ does not change with temperature. To obviate this assumption we have restudied the pyrolysis of $B_2H_6$ by a fundamental method that we call modulated molecular beam velocity analysis spectrometry. This method allows differentiation of neutrals before they undergo ionization and possible fragmentation when traversing the mass spectrometer ionizer.

## Experimental Section

The diborane, obtained from Callery Chemical Co., was stated to be at least 99 mol % pure at the time of shipment. Shipment at ambient temperatures and storage in a freezer between runs probably resulted in some decomposition. Careful multiple trap-to-trap distillations were made utilizing a glass vacuum manifold with traps immersed in acetone–Dry Ice, methylcyclohexane–liquid nitrogen, and liquid nitrogen. The purity of the diborane was checked with a quadrupole mass spectrometer, which is an integral part of the molecular beam apparatus. No impurities were detected under our operating conditions. The mass spectrum agreed very well with those published previously.[13]

A schematic of the molecular beam system is shown in Figure 1. The gas source was the glass vacuum manifold used for purifying the diborane. The diborane pressure and flow rate were monitored with Hasting Thermopile and Linear Mass Flow gauges in copper tubing connecting the glass manifold with the molecular beam apparatus. The pyrolysis oven was a 1-cm quartz tube packed with quartz capillaries. The oven was heated resistively by a tungsten wire wrapping. Oven temperature was measured with a thermocouple placed in the gas flow of the oven. The beam exited the oven through a 1 mm wide by 6.4 mm high slit into a high-vacuum drift space. The tuning fork modulated the beam at 504 Hz and supplied a direct reference signal for the Lock-In amplifier. The velocity selector was a duplication of that described by Grosser and was operated in the forward low-resolution (19.2%) mode for signal enhancement pur-