A PROTON NMR INVESTIGATION OF dπdπ BONDING IN LOW-VALENT COBALT AND NICKEL COMPLEXES WITH ALKYLDIPHENYLPHOSPHINES

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A PROTON NMR INVESTIGATION OF dπdπ BONDING IN LOW-VALENT COBALT AND NICKEL COMPLEXES WITH ALKYLDIPHENYLPHOSPHINES

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The proton nmr spectra for a series of paramagnetic, pseudo-tetrahedral complexes, $L_{4-n}M(n)Br_n$, with L = methyldiphenylphosphine, M = cobalt, with $n = 0,1,2$, and M = nickel, with $n = 1,2$, have been recorded. The shifts arise primarily from π spin density in the phenyl rings. From the observation that the calculated relative covalencies increase slightly upon reducing the divalent species, M(II)→M(I), and increase significantly upon further reduction of the cobalt complex, M(I)→M(O), we conclude that in the zero valent complex dπ-dπ bonding is present and constitutes the dominant spin transfer mechanism, while for the divalent species, dπ-dπ bonding is unimportant, with the spin transfer occurring mainly by σ-π non-orthogonality. In the monovalent complexes spin transfer probably occurs via both dπ-dπ and σ bonding, although the former mechnaism is less important than in the zero-valent complex.

INTRODUCTION

The extent of participation of the vacant 3d orbitals on phosphorus in bonding has been a subject of considerable controversy.[1-4] A particularly interesting subarea of this controversy has been the question of the importance or even existence of dπ-dπ bonding between phosphorus and transition metal ions.[2-4] Experimental data can be interpreted[2-5] to support either the presence or absence of this type of back-bonding, since many of the physical observables cannot be interpreted unambiguously. Initially, it may seem that one of the most direct methods for detecting such dπ-dπ covalency would be to observe the delocalization of a significant amount of spin density[6] into the ligand π orbitals in a paramagnetic complex where the unpaired electrons reside in π type metal d orbitals. The observed contact shift[6] could then be related to the metal-ligand covalency if proper account[7] is taken of the spin multiplicity of the metal ion and the occupation probability of unpaired electrons in the appropriate metal d orbitals. However, closer inspection reveals that such data

are also ambiguous, due to the fact that in ligands such as triarylphosphines or alkyldiarylphosphines, the phenyl π orbitals are not orthogonal[8] to the phosphorus lone pair orbital, so that a simple σ interaction with spin-containing metal d orbitals can place spin density into the ligand π orbitals.[9] Thus for any one complex, it is not possible to differentiate between a spin transfer mechanism arising from dπ-dπ back bonding and one resulting from σ bonding and the ligand σ-π non-orthogonality.

The proton nmr spectra of the *bis*-ligand complexes of divalent cobalt and nickel with triphenylphosphine and alkyldiphenylphosphine have been reported[10-12] and though the phenyl contact shifts in each case are indicative of spin density in the ligand π MO's, the exact mechanism of the spin transfer remains in doubt.[13] It occurred to us, however, that the relative importance of the spin transmission via dπ-dπ bonding and the σ-π non-orthogonality mechanism could be assessed by investigating the ligand contact shifts as a function of the oxidation state of the metal ion, keeping the coordination geometry fixed.

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Model for Metal-Ligand Bonding

For a phosphine ligand, the energy of the phosphorus lone pair σ orbital is expected to be well

below that of the metal 3d orbitals; on the other hand, the phosphorus 3d orbitals, which interact with the phenyl π MO's, are expected to be energetically much less stable[2, 3] than the metal 3d orbitals in all but highly reduced metal ions. The relative ligand and metal energy levels, (not to scale), are depicted in Figure 1. Upon reducing a
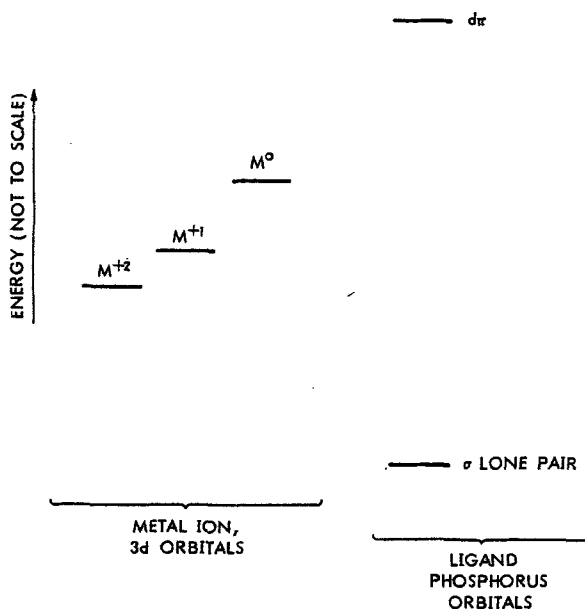

FIGURE 1

given metal ion, the ligand orbital energies remain unchanged, while the metal d orbital energies are raised sharply.[14] Therefore, since the extent of mixing (covalency) of a given ligand orbital with the metal 3d orbital is approximately inversely proportional to their energy separation,[15] lowering the oxidation state will have the effect of *decreasing* the σ covalency,[16] while simultaneously *increasing* the $d\pi$–$d\pi$ covalency.[17] If the relative π covalency, obtained from the phenyl contact shifts, with a metal ion in a given oxidation state M^{+n}, decreases significantly upon reducing to the $M^{+(n-1)}$ state, the spin transfer in both oxidation states can be assumed to occur primarily via σ bonding[16] and σ–π non-orthogonality; if the relative π covalency increases significantly upon reducing the metal ion, then the spin transfer in at least the more reduced state can be concluded to occur predominantly via $d\pi$–$d\pi$ bonding.[2-4, 17] Should the calculated relative π covalency not decrease or increase significantly upon going from $M^{+n} \rightarrow M^{+(n-1)}$, this can be taken as an indication that some $d\pi$–$d\pi$ bonding

in the $M^{+(n-1)}$ state is present, though both spin transfer mechanisms are probably operative.

The compounds chosen for this investigation are the pseudo-tetrahedral complexes $L_{4-n}MBr_n$, where L = methyldiphenylphosphine, $MeP\phi_2$, and M = cobalt and nickel. The divalent complexes, n = 2, for a number of phosphine ligands are well characterized and some of their proton nmr spectra have been reported.[18, 19] The preparation of the mono-valent, n = 1, complexes has also been reported recently.[20-23] The present preparation of the zero-valent cobalt complex, n = 0, therefore, affords a series of paramagnetic complexes with cobalt in the configurations $d^7(S = 3/2)$, $d^8(S = 1)$, $d^9(S = 1/2)$, and with nickel in the configurations $d^8(S = 1)$ and $d^9(S = 1/2)$. The electronic ground states for each of these configurations in a pseudo-tetrahedral environment is expected to lead[24, 25] to the very short electron spin relaxation time necessary to obtain well resolved proton nmr spectra.

Previous work with triphenylphosphine complexes has shown that the extent of spin transfer, and hence the covalency, for a fixed oxidation state is relatively insensitive to the nature of the halide or the number of phosphine ligands in the complex. For example, L_2MX_2 and LMX_3^- complexes with M = Co(II) and Ni(II) vary by less than 5%. Thus any significant changes in π covalency, or lack thereof, upon altering the oxidation state can be taken as an index of the direction of the change in covalency[26] arising primarily from the oxidation or reduction of the metal ion.

EXPERIMENTAL

Sample Preparation and NMR Spectra

All manipulations and sample preparation were carried out in a Vacuum Atmospheres Corporation Dri-Lab to prevent oxidation of the complexes. Samples were prepared in nmr tubes by dissolving the complex in the appropriate solvent, d_2-methylene chloride (Merck, Sharp and Dohme), d_6-benzene (Norrel Chem Co.) or d_8-toluene (Diaprep, Inc.), and taping the caps with Teflon tape. The tape prevented any detectable oxidation during the time required to obtain all nmr data. Sample concentrations ranged from 0.07 to 0.2 M depending on the solubility. For the more concentrated samples, no significant concentration dependence of either the shifts or line widths was noted.

The proton nmr spectra were recorded on a Varian HR-100 spectrometer modified to operate with

variable modulating frequency. TMS was used as the internal reference and the shifts were calibrated by the conventional audio sideband technique. The sample temperature was controlled by a Varian V-4343 control unit which was precalibrated with methanol. The temperature dependences of the mono-valent complexes were obtained in the temperature interval $+42$ to $-50°$, and the zero-valent complex in the range 5 to $55°$. The proton nmr spectra of the mono-valent complexes were also recorded in the presence of a 15–20% excess of uncoordinated ligand.

The isotropic shifts are given in ppm, referenced against the planar, diamagnetic isomer of $(MeP\phi_2)_2NiBr_2$; line widths are given in Hz at 100 MHz. The solution susceptibilities were determined by the method of Evans,[27] using a Varian A-60 spectrometer. The solid susceptibilities were determined on a Gouy balance.

Preparation of Complexes

(MePϕ_2)$_2$NiBr$_2$ The preparation and characterization of this compound has been described previously.[19]

(MePϕ_2)$_3$NiBr This complex was prepared by constant potential electrolysis of $(MeP\phi_2)_2NiBr_2$ at a platinum foil cathode in a 10% v/v mixture of benzene-acetonitrile. The electrolysis was carried out in a nitrogen atmosphere at -0.85 volts *vs* a silver/0.100 M silver nitrate in acetonitrile reference electrode. At this potential only the reduction of nickel(II) to nickel(I) was observed as determined by polarographic and voltametric measurements.[23] A detailed description of the electrochemical procedure is given below. The catholyte was prepared by dissolving $(MeP\phi_2)_2NiBr_2$ (1.24 g, 2.0 mmoles) and MePϕ_2 (0.804 g, 4.0 mmoles) in 200 ml of the benzene-acetonitrile solvent which was also 0.10 M in tetraethylammonium perchlorate. The dark red solution was placed in the cell and electrolyzed potentiostatically at -0.85 volts at a platinum foil cathode. A platinum electrode in the supporting electrolyte served as the anode. The anolyte was isolated from the catholyte by a medium porosity fritted glass disk. After 2 hours the current had decreased to 2% of its initial value and the catholyte was yellow-green in color. The catholyte was removed from the cell and the volume reduced to 50 ml at 2 mm Hg and room temperature. The yellow-green product was filtered off, washed well with acetonitrile and dried for 24 hours at 10^{-5} mm Hg and room temperature (yield 0.94 g,

63.5%). The air-sensitive solid melted at $163–5°$ with decomposition. *Analysis*: Found: C,63.7; H,5.3; P,12.4%. Calculated for $(MeP\phi_2)_3NiBr$: C,63.45; H,5.34; P,12.58%. μ solid: 1.70 B.M.

(MePϕ_2)$_3$NiI This complex was prepared in the same manner as the analogous bromide. The electrolysis was performed at -0.80 volts and afforded a yellow-orange compound melting at $180–3°$ with decomposition. *Analysis*: Found: C,59.5; H,5.0; P,12.4; I,16.4%. Calculated for $(MeP\phi_2)_3NiI$: C,59.57; H,5.00; P,11.82; I,16.14%. μ solid: 1.4 B.M.

(MePϕ_2)$_2$CoBr$_2$ The method of Chatt and Shaw[28] was used. A solution of $CoBr_2.6H_2O$ (3.27 g, 10.0 mmoles) in absolute ethanol (45ml) was reacted with MePϕ_2(4.0 g, 20.0 mmoles) at room temperature under nitrogen. After several minutes of stirring, a green-blue precipitate formed. The product was removed by filtration and washed several times with ethanol under nitrogen. The complex was dried for 24 hours at room temperature and 10^{-5} mm Hg. *Analysis*: Found: C,50.3; H,4.2; Br,26.0%. Calculated for $(MeP\phi_2)_2CoBr_2$: C,50.43; H,4.23; Br,25.81%. μ solid: 4.39 B.M.

(MePϕ_2)$_3$CoBr A variation of the method of Aresta *et al.*[20] was employed. Under a nitrogen atmosphere a solution of $CoBr_2.6H_2O$ (0.68 g, mmole) and MePϕ_2 (1.40 g, 7.0 mmoles) in absolute ethanol (70 ml) was treated with zinc powder (0.50 g, 7.6 mmoles). After 3 hours with vigorous stirring a mixture of unreacted zinc and a green solid was filtered from the reaction mixture. The mixture was treated with warm toluene, to which a small amount of MePϕ_2 had been added. The green complex readily dissolved and could be easily separated from the unreacted zinc. Addition of dry hexane to the toluene solution afforded the pure product. After drying for 24 hours at 10^{-5} mm Hg, the complex was obtained as a green powder (yield 0.71 g, 46%). *Analysis*: Found: C,63.4; H,5.4; Br,10.8%. Calculated for $(MeP\phi_2)_3CoBr$: C,63.34; H,5.32; Br,10.81%. μ solid: 3.03 B.M.

(MePϕ_2)$_4$Co A suspension of $(MeP\phi_2)_2CoCl_2$ (5.4 g, 10.2 mmoles) and MePϕ_2 (4.08 g 20.4 mmoles) in dry ether (50 ml) was treated under argon with 0.23% sodium amalgam prepared from freshly cut sodium (0.80 g, 34.8 mmoles) and 350 g mercury. After vigorous shaking for one-half hour, the dark brown reaction mixture was extracted with dry ether (1.5 1). The ether solution was filtered and

then concentrated to 150 m.l Addition of *n*-hexane yielded a brown-black crystalline solid which was dried at room temperature and 10^{-3} mm Hg for 24 hours. The crude product was recrystallized under argon at $-20°$, (yield 4.3 g, 49%). *Analysis*: Found: C,70.4; H,6.0; P,15.5; Co,6.4; Cl,0.0%. Calculated for $(MeP\phi_2)_4Co$: C,72.64; H.6.10; P,14.41; Co, 6.85%. μ solution: 1.71 B.M.

Reaction of this complex with CH_3COOD produced a gas which by mass spectral analysis exhibited a H_2:HD:D_2 distribution of 2:11:88. The predominance of D_2 suggests reduction of the acid by the zero-valent cobalt, since a hydrido complex should exhibit a H_2:HD:D_2 distribution of 25:50:25. The related, five coordinate hydrido complex, which has been prepared,[29] exhibits a characteristic Co-H IR band at 1958 cm^{-1}, and is diamagnetic neither of which properties characterize our zero-valent species. The infrared spectrum (Nujol) exhibits only bands attributable to the ligand, with no evidence for a hydride band in the the 1900–2000 cm^{-1} region. The possible presence of the halide is excluded by the analysis. The proton nmr spectrum of the complex in d_6–benzene displayed, in addition to the four prominent peaks arising from the paramagnetic complex, a weak set of multiplets in the methyl region which indicate a small trace of *n*-hexane which was incompletely removed in the drying.

RESULTS AND DISCUSSION

The observed proton nmr at 25°, referenced against the diamagnetic isomer of $(MeP\phi)_2NiBr_2$ com-

plex,[19] are given in Table 1; the linewidths in Hz at 100 MHz are also included in parentheses. The four expected peaks are resolved for each complex, and are assigned on the basis of intensities 3:2:2:1 for CH_3:*o*-H:*m*-H:*p*-H, with the ambiguity between the *o*-H and *m*-H resonances resolved by the much greater linewidth for the former peak. The phenyl resonances closely resemble the pattern previously reported for the triarylphosphine complexes, [10, 11] where assignments were established by methyl substitution.

The pseudo-tetrahedral configuration for the divalent[10,18,19] and monovalent[20, 22, 23] complexes of both metals have already been established. For the new d^9 cobalt(O) complex, which is isoelectronic with copper(II), either a square-planar or tetrahedral configuration is possible. However, detailed theoretical considerations,[25] supported by extensive experimental data,[30] have shown that the electron spin relaxation time, T_{1e}, in the square planar configuration is expected to be quite long, $>10^{-8}$ sec, giving rise to well resolved *esr spectra* at ambient temperatures. For the tetrahedral configuration, T_{1e} is expected to be very much shorter,[25] $<10^{-11}$ sec, giving rise to well resolved *nmr spectra*. These conditions are clearly illustrated by Cu(II), where the planar species all yield room temperature esr spectra but no nmr[31] spectra, while the pseudo-tetrahedral species yield relatively narrow nmr lines.[32] The narrow nmr lines associated with the tetrahedral environment emerge as a planar complex is increasingly distorted[32] towards a pseudo-tetrahedral configuration by steric interactions. The very narrow nmr resonances for the Co(O) complex strongly support the tetrahedral

TABLE 1
Observed isotropic shifts for $(MeP\phi_2)_{4-n}MX_n{}^a$

Complex	d^m	Isotropic shifts			
		o-H	*m*-H	*p*-H	CH_3
$(MeP\phi_2)_2CoBr_2{}^b$	d^7	+14.07(~220)	−8.78(24)	+14.78(24)	−112.0(~250)
$(MeP\phi_2)_3CoBr^c$	d^8	+6.76(~300)	−4.16(24)	+8.01(22)	−63.4(~430)
$(MeP\phi_2)_4Co^d$	d^9	+4.43(~100)	−1.74(28)	+3.63(26)	−19.8(~170)
$(MeP\phi_2)_2NiBr_2{}^{b,e}$	d^8	+10.60	−13.98	+15.94	−124.0
$(MeP\phi_2)_3NiBr^c$	d^9	+4.43(~150)	−3.28(29)	+5.71(26)	−31.9(~350)
$(MeP\phi_2)_3NiI^c$	d^9	+4.54(~140)	−3.37(20)	+5.79(27)	−32.0(~300)

[a] Shifts in ppm at 100MHz, at 25°, referenced against diamagnetic planar $(MeP\phi_2)_2NiBr_2$ complex, (Ref. 19); linewidths in parentheses in Hz at 100 MHz.
[b] In d_2-methylene chloride.
[c] In d_8-toluene.
[d] In d_6-benzene.
[e] Data taken from Ref. 19.

configuration. In particular, the Co(O) o-H line-width is significantly smaller than for the isoelectronic d^9 Ni(I) complex, where a small C$_{3v}$ distortion is present.

The phenyl ring protons exhibit shifts indicative of π spin density, and the clear alternation of shift directions indicates that the shifts are primarily contact in origin. Table 2 gives the relative shifts

TABLE 2

Relative isotropic shifts for (MePϕ_2)$_{4-n}$MX$_n$[a]

Complex	o-H	m-H	p-H	CH$_3$
(MePϕ_2)$_2$CoBr$_2$	+0.97	−0.60	+1.00	−7.73
(MePϕ_2)$_3$CoBr	+0.84	−0.52	+1.00	−7.90
(MePϕ_2)$_4$Co	+1.22	−0.48	+1.00	−5.46
(MePϕ_2)$_2$NiBr$_2$	+0.67	−0.88	+1.00	−7.78
(MePϕ_2)$_3$NiBr	+0.78	−0.57	+1.00	−5.59
(MePϕ_2)$_3$NiI	+0.78	−0.58	+1.00	−5.53

[a] The p-H shift is normalized to unity.

for each complex, with the p-H shift normalized to unity. The close similarity of the relative shifts for the four non-equivalent ligand positions argues strongly against significant dipolar contributions. The dipolar shift for m-H and p-H has been shown[10, 12] to be of comparable magnitude and the same sign in both C$_{2v}$ and C$_{3v}$ symmetry, while the contact shifts also have comparable magnitude but opposite signs for these positions; thus any sizable dipolar contribution in any one complex or a highly

variable dipolar contribution among the different complexes would be expected to cause widely differing shift patterns among the complexes. For Co(II), the dipolar shifts, though present, have been shown[10] to be small, contributing less than 10% at p-H; for Ni(II), the dipolar contributions are even less than in Co(II). Co(I) is isoelectronic with Ni(II) and the similar shift patterns also suggest dipolar shifts much less than 10% for p-H. The Ni(I) shift pattern is almost identical to that for the Co(I), so again dipolar shifts must be negligible. For Co(O), the postulated tetrahedral symmetry eliminates any magnetic anisotropy. We, therefore, conclude that, at least for the p-H position, dipolar shifts are negligible, so that the relative p-H shifts in the various complexes are an index of the relative amounts of spin delocalized into the ligand π system by either of the two possible mechanisms.

The hyperfine coupling constant, A, is obtained from equation (1), which assumes that the Curie law is valid, where all parameters are defined as usual,[6]

$$\frac{\Delta H}{H} = -A\frac{g\beta S(S+1)}{(\gamma/2\pi)3kT} \quad (1)$$

and A is in frequency units. The values for A are listed in Table 3. The validity of the 1/T dependence of the shifts has already been demonstrated[10, 19] for related Co(II) and Ni(II) complexes. For the Co(I) and Ni(I) species, the temperature data are plotted in Figure 2, and indicate that the shifts follow the 1/T law within experimental error. Of particular interest is the fact that in the presence of excess ligand, the Co(I) complex exhibits separate

TABLE 3

Hyperfine coupling constants, spin densities and relative covalencies for (MePϕ_2)$_{4-n}$MBr$_n$

Complex	d^m	μ[a]	(A) × 10^{-5}[b]	ρ × 10^3	2S	Relative Covalency[c]
(MePϕ_2)$_2$CoBr$_2$	d^7	4.39	0.96	4.6	3	1.00
(MePϕ_2)$_3$CoBr	d^8	3.03	1.06	3.4	2	1.10
(MePϕ_2)$_4$Co	d^9	1.71	1.39	2.2	1	1.45
(MePϕ_2)$_2$NiBr$_2$	d^8	3.35[d]	1.91	6.1	2	1.98
(MePϕ_2)$_3$NiBr	d^9	1.7	2.21	3.5	1	2.25

[a] Magnetic moment, in B.M. at 25°.
[b] Hyperfine coupling constant, in Hz.
[c] Relative covalency, obtained as in Ref. 7, with the Co(II) complex covalency, arbitrarily set at 1.00.
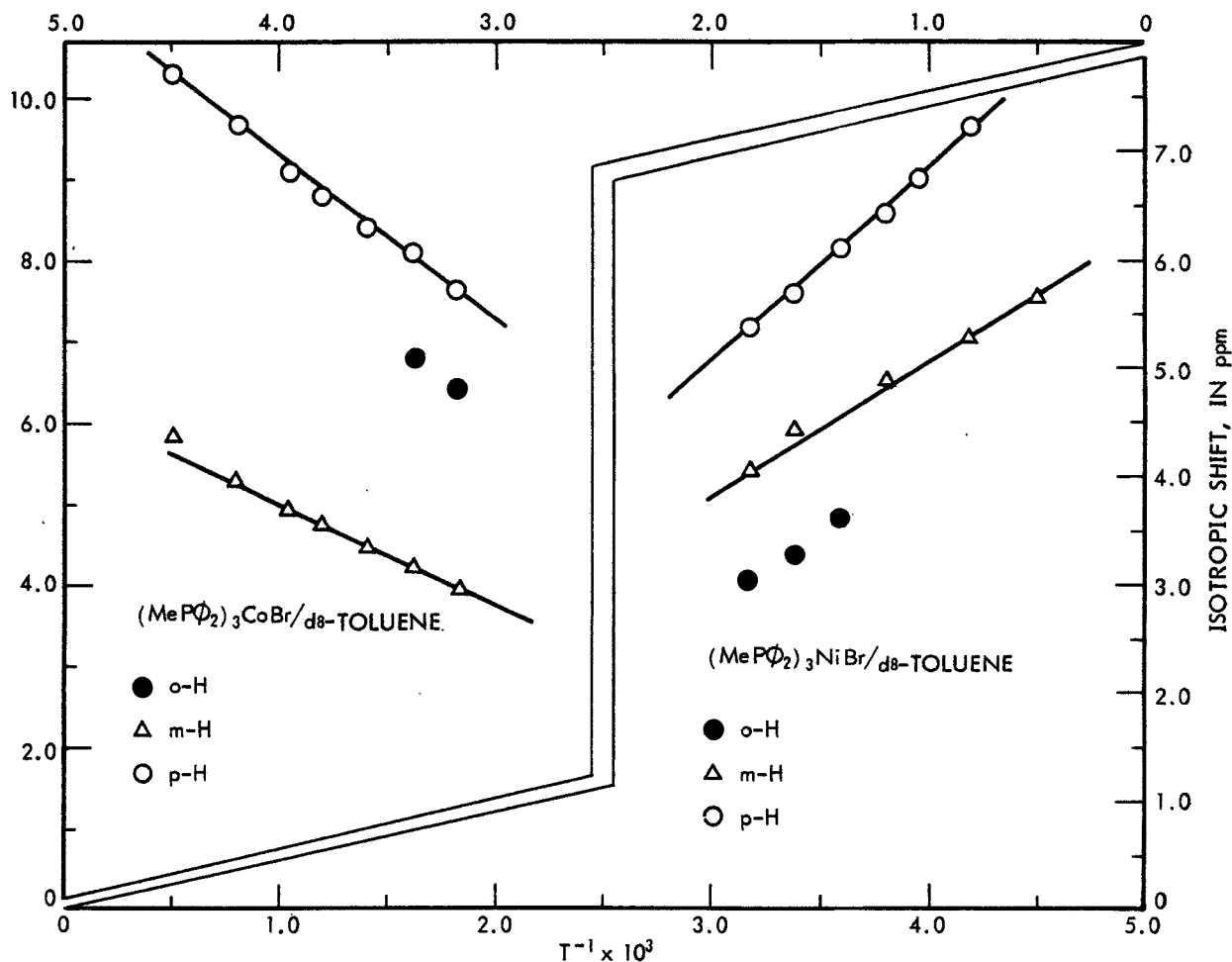[d] Taken from Ref. 19

FIGURE 2   *Curie Plot for (Me Pφ₂)₃ MBr Complexes*

resonances for the coordinated and free ligand up to 42°, with no observable line broadening effects from ligand exchange. For the Ni(I) complex, $(MeP\phi_2)_3NiBr$, though an averaged ligand resonance is observed at 20° in the presence of excess ligand, lowering the temperature to $-35°$ slows the exchange process such that narrow, separate resonances for free and coordinated ligand are displayed. The order of ligand lability for the monovalent species, Ni>Co, is the same as reported[33] for the divalent complexes.[34] For the Co(O) complex, the benzene solvent prevented low temperature measurements, and the sample decomposed above 55°. The change in shifts, ΔH, with temperature in the range 5 to 55° yields a product $\Delta H.T$ which varies by only $\sim5\%$, so that the Curie law can be assumed to hold.

The p-H spin density, ρ, is obtained from the McConnell relationship,[6, 7]

$$\rho = \frac{A.2S}{Q},\qquad(2)$$

where $Q = -63$ MHz and $2S =$ total number of unpaired spins. Insamuch as the same ligand basis functions are assumed for all complexes, this spin density can be taken as an index of the covalency by normalizing to unit spin occupation of the appropriate t_2 d orbitals on the metal.[35] Only *relative* covalencies can be determined from the p-H spin densities, since the coefficient of the *para* carbon in the ligand MO is not known. The *relative* covalencies for the complexes of interest, with the Co(II) complex arbitrarily set to 1.00, are given in

Table 3 along with the spin densities calculated from equation (2).

As indicated above, if the spin delocalization occurs through $d\pi$-$d\pi$ bonding, the relative covalency should increase[17] significantly upon reducing the metal ion; if the spin transfer occurs via the lone pair and σ-π non-orthogonality, the relative covalency should decrease[16] on lowering the metal valence state. The lack of any significant change in covalency on reduction suggests that both mechanisms are probably operative in the lower valence state.

The calculated relative covalencies in Table 3 clearly show that for both cobalt and nickel, reduction of the divalent complex, $M^{+2} \rightarrow M^{+1}$, results in a very small increase in the apparent covalency. Due to the possibility of 10% dipolar shift contributions and a comparable effect due to going from two to three phosphine ligands, the M^{+2} and M^{+1} complexes exhibit comparable covalencies. The fact that the relative covalencies did not decrease suggests that the $d\pi$-$d\pi$ spin transfer mechanism must be operative in the M^{+1} complexes, though not dominant, while the spin transfer mechanism in the M^{+2} complexes must arise primarily from σ bonding. Upon further reducing the monovalent cobalt complex, $M^{+1} \rightarrow M^0$, the relative covalency increases significantly, indicating that in the zero valent state, the dominant spin transfer mechanism is indeed $d\pi$-$d\pi$ bonding.[2-4]

We therefore conclude that $d\pi$-$d\pi$ bonding is the dominant spin transfer mechanism only in the zero valent cobalt complex, though it is probably also operative to some extent in both monovalent complexes. In the complexes of the divalent ions of cobalt and nickel, [10-12, 19] as well as for the analogous iron complexes,[36] the contact shifts must result primarily from M-P σ bonding and the ligand σ-π non-orthogonality, with $d\pi$-$d\pi$ bonding apparently unimportant. A similar conclusion[4] as to the probable absence of significant $d\pi$-$d\pi$ bonding in Pt(II) phosphine complexes has been reached on the basis of a detailed analysis of the Pt^{195}-P^{31} spin-spin coupling constants;[37] however, the presence or even dominance of such $d\pi$-$d\pi$ bonding in low valent platinum complexes cannot be discounted.[4]

In calculating the relative covalencies for the different oxidation states,[7] we assumed that the form of the ligand MO's, whether involving the σ lone pair or the phosphorus $d\pi$ orbitals, remain essentially unchanged with metal oxidation state. However, caution must be exercised in too strict a reliance on the calculated relative covalencies involving $d\pi$-$d\pi$ bonding. The reason is that π bonding through d orbitals in a tetrahedral configuration (about the phosphorus) does not lend itself to "normal" conjugation.[8, 38] Instead, the competitive π bonding[8] of the dissimilar groups about the phosphorus results in the π bonding with the phosphorus d orbital being optimized for one or the other set of attached groups. This effect has been illustrated in the ligand spin redistribution in nickel(II) chelates with mixed aminotroponeimine[39] ligands. Thus for complexes in "normal" oxidation states, M^{+2}, the M-P $d\pi$-$d\pi$ interaction is very weak, while the P-C $d\pi$-$p\pi$ interaction is probably more significant. As the M-P $d\pi$-$d\pi$ bonding increases upon successive reductions of the metal ion, the P-C $d\pi$-$p\pi$ interaction or covalency will *decrease*. Therefore the phenyl π shifts are not a direct measure of the relative extents of $d\pi$-$d\pi$ bonding, even if this is the dominant spin transfer mechanism in both complexes being compared. However, since the P-C $d\pi$-$p\pi$ interaction decreases while the M-P $d\pi$-$d\pi$ interaction increases upon reducing the metal ion, the increase in the calculated covalency, [as for the $Co(I) \rightarrow Co(O)$], will necessarily *under-estimate* the relative increase in $d\pi$-$d\pi$ covalency in the lower valence state.

ACKNOWLEDGEMENTS

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