

Organometallic Electrochemistry. XVIII.¹ The Effect of Charge on Geometry and Activation Parameters for Fluxional Motion

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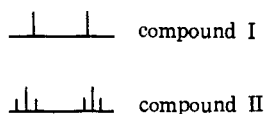
Abstract: An nmr study of a related series of bi- μ -phosphido-dimetallic species has demonstrated that large increases in $J_{PP'}$ occur upon reduction to the singlet-state dianion. These increases are attributed to an increase of the metal-metal distance and a marked decrease in the P-P' distance. In several systems where a dihedral angle exists between the basal planes of the pseudooctahedrally coordinated metal atom sites, and a bent metal-metal bond has been proposed, the inversion frequency of the fluxional molecule is increased upon reduction. Activation parameters are reported.

A previous report in this series² dealt with the electrochemical behavior of a series of bi- μ -phosphido-dimetal carbonyl complexes of structures I and II² (Figure 1). Some workers have ascribed alternative structures to compounds of types I and II.³ The generally recognized structures are given here and are assumed throughout the discussion.⁴

All compounds of structures I and II exhibit electrochemically reversible voltammetric waves with $n = 2$ (n is the number of electrons accepted at a given half-wave potential, $E_{1/2}$, per molecule).² The resulting dianions give no esr signal and are diamagnetic, indicating a singlet ground state. Admixture of neutral (\circ) material and dianion (\ominus) results in the formation of the radical anion (\ominus), suggesting the following equilibrium which has been substantiated by partial electrolysis



Neutral molecules of type I are characterized by ¹H nuclear magnetic resonance (nmr) absorption spectra consisting of two peaks, while neutral molecules of type II are characterized by two triplets.



In the former case, the ³¹P-³¹P nuclear coupling, $J_{PP'}$, is very small and the spectrum is easily interpreted, since the methyl groups occupy equivalent positions. In the latter, $J_{PP'}$ is of considerable magnitude and the non-equivalency of the methyl groups—exo vs. endo—gives rise to the characteristic spectrum.⁵

Upon reduction to the radical anion, compounds of types I and II give rise to the characteristic electron spin

resonance (esr) spectra shown in Figures 2 and 3. In both cases, the classical 1:2:1 triplet due to hyperfine coupling with two identical phosphorous atoms is present. Radical anions derived from structure I have each member of the triplet split into a 13-fold multiplet due to the 12 identical protons (CH₃ groups). It is evident that the dihedral angle of neutral molecules of type II is maintained to some extent in the radical anion, since hyperfine interaction with the exo and endo methyl protons (two sets of two CH₃ groups) is drastically different. One set gives rise to sevenfold splitting of each triplet, $a_H = 1.4$ G; the other is unobservable under modulation amplitude conditions of 0.1 G, suggesting an upper limit for a of 0.2 G.

It is known that addition of halogen to compounds of type II^{6b} results in a trans adduct which yields an nmr spectrum consisting of a single 1:2:1 triplet suggestive of equivalent methyl groups. Since halogen addition bears a close resemblance to reduction, it was felt that a study of the nmr spectra of the diamagnetic neutral and dianion species of these systems would be of interest. This paper presents the findings of such a study and reports the fluxional nature of these species. It focuses on the structural changes that occur upon reduction.

Experimental Section

All manipulations involving radical anions and dianions were conducted either in a Vacuum Atmospheres Dry Lab-Dry Train employing an argon atmosphere controlled to a maximum water vapor and oxygen concentration of 1 ppm or by the utilization of standard vacuum-line techniques. The Mössbauer, ir, and esr data were obtained by previously described techniques.¹

Nuclear Magnetic Resonance. The instrumentation used was either the Varian A-60a or the Jeolco C-60H, each equipped with the manufacturer's variable-temperature accessory. Temperatures above and below ambient were calibrated using the chemical shift difference of the C-H and O-H resonances of ethylene glycol and methanol. No correction was made for the slight deviation from linearity of the $\Delta\nu/T^0$ plots. The error limits of the reported temperatures are estimated at $\pm 2^\circ$.

Except where otherwise noted, all spectra were obtained as 1,2-dimethoxyethane (glyme) solutions. Chemical shifts are referred to the solvent and are reported in parts per million from TMS (τ 10.00). The reported line widths (at half-height) and coupling constants are the average of not fewer than five spectra. Instrument sweep widths were calibrated using standard side-band techniques.

The dianion species derived from the phosphido-bridged metal carbonyl complexes were prepared in a 50-ml bulb fitted with an nmr tube, a quartz esr tube, and a break-seal side arm. The com-

(1) For previous papers in this series, see R. E. Dessy, *et al.*, *J. Amer. Chem. Soc.*, **88**, 453, 460, 467, 471, 5112, 5117, 5121, 4963 (1966); **92**, 3947 (1970).

(2) (a) R. E. Dessy and Leonard Wiczorek, *ibid.*, **91**, 4963 (1969); (b) R. E. Dessy, *et al.*, *ibid.*, **90**, 1995, 2001, 2005 (1968), *et seq.*

(3) (a) J. Chatt and D. A. Thornton, *J. Chem. Soc.*, 1005 (1964);

(b) D. T. Thompson, *J. Organometal. Chem.*, **4**, 74 (1965).

(4) (a) L. Dahl and C. Wei, *Acta Crystallogr.*, **16**, 611 (1962); (b) T. Gibb, R. Greatrex, N. Greenwood, and D. Thompson, *J. Chem. Soc.*, 1454 (1968).

(5) (a) R. G. Hayter, *Inorg. Chem.*, **3**, 711 (1964); (b) G. R. Davies, R. H. B. Mais, P. G. Owston, and D. T. Thompson, *J. Chem. Soc.*, **A**, 1251 (1968).

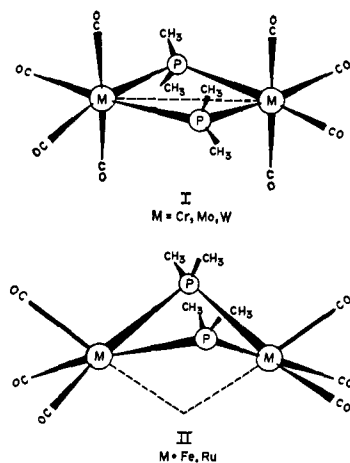


Figure 1.

plex was sealed in the break-seal side arm along with a Teflon-coated stirring bar. Freshly cut potassium was introduced into a small side arm of the bulb's neck in the drybox. After evacuating the bulb on the vacuum line, the potassium was distilled from the neck side arm through a small constriction into the main portion of the bulb where a thin mirror was formed. A quantity of glyme sufficient for the preparation of a 0.5 M solution was bulb-to-bulb distilled into the reaction bulb. The bulb was then sealed at the constriction, thus removing involatile residues from the potassium distillation. On warming the bulb to the glyme melting point, the sample was introduced through the break-seal. The solution was then magnetically stirred for an hour; the sample was stored at -10° . Periodic monitoring of the esr spectrum determined the extent of conversion to the dianion state. Only after exhaustive two-electron reduction to the diamagnetic dianion state could nmr spectra of satisfactory resolution be obtained. Reaction times of 1–2 months were frequently required for the removal of the last esr-detectable traces of radical anion species. When paramagnetic signals were no longer present, the attached nmr tube was filled through a coarse fritted glass disk separating the tube from the bulb and finally sealed off with a torch.

Electrochemistry. The chemical and electrochemical reversibility of the one- and two-electron reductions performed on the reported compounds has been previously reported,² except for I (M = Mo), which displayed a single polarographic wave at -1.9 V relative to a $\text{Ag}|\text{Ag}^+$ (10^{-3} M) reference solution. Controlled-potential electrolysis at -2.0 V demonstrated that the wave represented a two-electron reduction. Irreversible electrochemical reduction of II (M = Ru) was demonstrated by cyclic-voltammetric techniques.

Chemicals. The rigorous drying and purification procedure for 1,2-dimethoxyethane has been described elsewhere.¹ The final transfer of solvent to the reaction bulb was by vacuum-line bulb-to-bulb distillation from a flask containing Na-K eutectic alloy. Several of the radical anion and dianion species were stable at room temperature for periods of up to 2 months in solvent receiving this pretreatment.

Tetramethyldiphosphine was used as obtained from the Strem Chemical Co. Tetraphenyldiphosphine was prepared by the coupling reaction of diphenylchlorophosphine with sodium metal. The metal complexes, I (M = Cr, Mo, and W) and II (M = Fe) were prepared by the published procedures.⁶

II (M = Ru) was obtained from the reaction of tetramethyldiphosphine (3 mmol) and triruthenium dodecacarbonyl (2 mmol) in 10 ml of benzene at reflux under nitrogen. After refluxing for 24 hr, the solvent was removed. The brown residue was dissolved in a minimum quantity of toluene and passed down a short silica gel chromatographic column, eluting with light petroleum ether. When the red band was retained and evaporated to dryness, an orange oil was obtained which slowly crystallized on refrigeration. The compound was recrystallized from a benzene-hexane solution.

All compounds were analyzed satisfactorily for C, H, and N (Galbraith Laboratories, Inc., Nashville, Tenn.).

Immediately prior to any study of these compounds, a final purification by sublimation was performed.

(6) (a) E. Abel, M. Bennett and G. Wilkinson, *J. Chem. Soc.*, 2325 (1959); (b) R. Hayter, *Inorg. Chem.*, 3, 711 (1964).

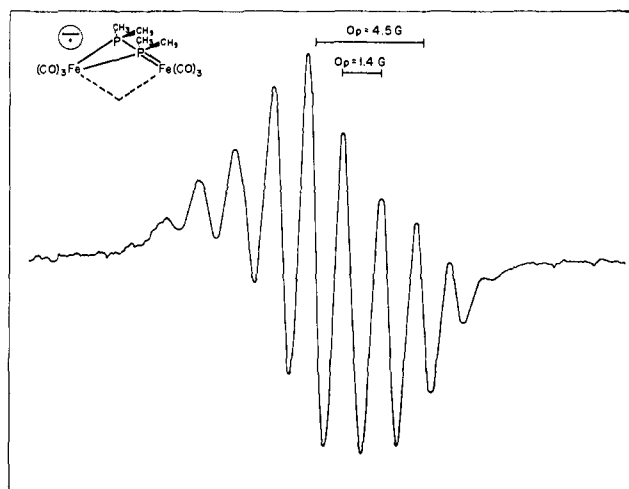


Figure 2.

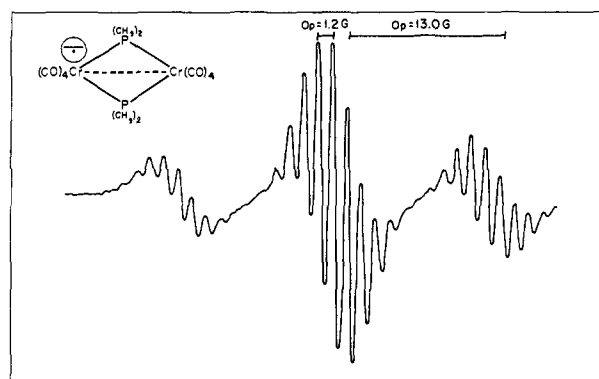


Figure 3.

Results and Discussion

Nuclear Magnetic Resonance Results. Compounds of structure I constitute $X_6AA'X_6'$ ($X = \text{H}$, $A = \text{P}$) spin systems, where $J_{XX'} = 0$, and compounds of structure II constitute $X_3X_3'AA'X_3'X_3''$ systems factorable into two $X_3AA'X_3'$ systems if $^4J_{HH'}$ is taken to be immeasurably small. The nmr spectra of all compounds of structures I and II can therefore be analyzed as $X_n-AA'X_n$ spin systems, which have been discussed in detail.^{7–11} In the analysis of such spin systems it is desirable to provide two composite parameters: $L = J_{XA} - J_{XA'}$ and $N = J_{XA} + J_{XA'}$. Since for the compounds under discussion $^4J_{HP}$ is anticipated to be an order of magnitude smaller than $^2J_{HP}$, the approximation will frequently be made that $L = N$.

The X part of the spectrum arising from an $X_n-AA'X_n$ system where L and N are of similar magnitude has a deceptively simple appearance. When $J_{AA} \ll L$, the spectrum is an apparent doublet, when $J_{AA} \gg L$ an apparent triplet. Intermediate relationships of $J_{AA'}$ and L produce spectra of distorted 1:2:1 triplets with central peaks of variable line width. In general, the narrower the line width of the central peak the larger the magnitude of $J_{AA'}$.

(7) J. P. Fackler, Jr., J. A. Fetchin, J. Mayhew, W. C. Seidel, T. J. Swift, and M. Weeks, *J. Amer. Chem. Soc.*, 91, 1941 (1969).

(8) A. Pidcock, *Chem. Commun.*, 92 (1968).

(9) R. G. Goodfellow, *ibid.*, 114 (1968).

(10) R. K. Harris, *Inorg. Chem.*, 5, 701 (1966).

(11) E. G. Finer and R. K. Harris, *Mol. Phys.*, 12, 457 (1967).

Table I. Nmr Data for Bi- μ -phosphido-Bridged Metal Carbonyl Complexes and Their Dianions

Compound	σ , ppm ^a	N , Hz ^b	Line width at half-height, Hz ^c	$ J_{PP'} $
I (M = Cr)	○ 7.76	10.0	<i>j</i>	0 \pm 5
	⊖ 8.95	7.2	1.56	145 \pm 25 ⁱ
I (M = Mo)	○ 7.73	9.2	<i>j</i>	18 \pm 2 ^m
	⊖ 8.79	7.0	1.62	110 \pm 30 ⁱ
I (M = W)	○ 7.60	9.5	<i>j</i>	19 \pm 2 ^m
	⊖ 8.69	7.1	1.62	110 \pm 30 ⁱ
II (M = Fe)	○ ^d 8.07	11.6	2.50	85 \pm 10 ^m
	8.48	12.0	2.66	80 \pm 10 ^m
	○ ^e 8.27	11.8	2.43	85 \pm 10 ^m
	⊖ ^f 8.70 ^k	<i>i</i>	<i>i</i>	<i>i</i>
	8.96 ^k	<i>i</i>	<i>i</i>	<i>i</i>
	⊖ ^g 8.83	9.8	0.84	>500 ⁿ
II (M = Ru)	○ ^g 8.12	10.7	2.52	80 \pm 10 ^m
	8.41	10.9	2.96	70 \pm 10 ^m
(CH ₃) ₂ PP(CH ₃) ₂ ^h	8.94	14.2	1.02	179.7 ^m

^a Measured from glyme; referred to TMS (τ 10.00). ^b $N = {}^2J_{PH} + {}^4J_{PH}$ = separation of intense outer doublet. ^c For central peak of "virtually coupled triplet." ^d -10° . ^e 110° . ^f -75° . ^g 20° . ^h Reference 11. ⁱ Immeasurable from available spectra. ^j No central peak observed. ^k Estimated chemical shifts in the absence of conformational exchange. ^l Estimated from the height ratio of inner and outer "triplet" peaks. ^m Measured from weak satellite peaks. ⁿ See text.

The separation of the outer two lines of the triplet directly affords the magnitude of N . In addition to the N doublet, $2n$ pairs of lines are also symmetrically arranged about ν_X . The central peak of the apparent triplet is composed of half of the $2n$ pairs of lines.

Various relationships of the spacings of these lines to $J_{AA'}$ have been developed, but only in special cases can these spacings be used to calculate $J_{AA'}$ directly from measurable parameters, due to instrumental limitations of resolution and sensitivity. Indirect methods for obtaining $J_{AA'}$ from the X spectrum have been developed.¹²⁻¹⁴ These methods involve either

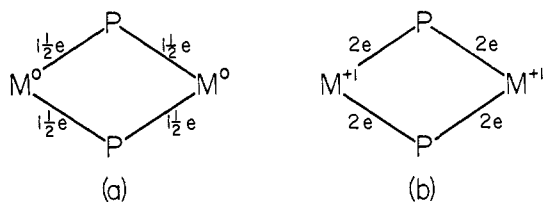


Figure 4.

a hand or computer simulation of the central "triplet" peak, and while these are the only generally available means for determining $J_{AA'}$ they are also the least accurate and, at best, provide only rather crude estimates. Verkade¹²⁻¹⁴ has made considerable use of a double-resonance technique to determine the sign and magnitude of $J_{AA'}$, but the technique requires non-routine instrumentation and concentrations generally greater than those available in the present research.

Wherever possible in this study, $J_{AA'}$ was obtained from the observation of weak satellite lines at high rf power, but in several instances inability to locate these lines required recourse to the less precise simulation methods.

(12) R. D. Bertrand, D. A. Allison, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 71 (1970).

(13) R. D. Bertrand, F. B. Ogilvie, and J. G. Verkade, *ibid.*, **92**, 1908 (1970).

(14) F. B. Ogilvie, J. M. Jenkins, and J. G. Verkade, *ibid.*, **92**, 1916 (1970).

In Table I the ¹H nmr data are summarized. For all compounds studied, an upfield shift is observed on converting the parent compound to its dianion. For the Cr-Mo-W series, this increase ranges from 1.0 to 1.2 ppm, whereas in the case of the Fe compound the averaged values for the exo and endo methyl groups produce a mean shift of 0.56 ppm. A referee has suggested that such upfield shifts may be due to ion-pairing phenomena involving the potassium gegenion. This is plausible, but the authors prefer the following analysis.

All ¹H chemical shifts for the neutral complexes are from about 0.7 to 1.6 ppm downfield from tetramethyldiphosphine, but on reduction to their dianion the chemical shifts all move very close to the diphosphine value of τ 8.94. This uniform trend approaching the diphosphine value is inconsistent with the usually limiting description of the bonding in the di- μ -phosphido complexes in terms of formal valence states, where the metal is considered to possess a formal charge of 1+ and the bridging group a 1- charge (Figure 4b), based largely on the presumed necessity to provide two-electron limiting structure is proposed. Since actual oxidation states involved in these species are unknown and the two structures represent potential canonical forms, there appears to be no harm in using one as a model for discussion of results, since the actual molecular orbital scheme will represent a hybrid. The metal-P ring system then is envisioned as a four-center, six-electron system. The form shown in Figure 4a then better accommodates the observed chemical shift data for the neutral compounds than does the form shown in Figure 4b. The increased electron shielding of the P(CH₃)₂ group on reduction may then arise from a removal of the M-P bond deficiency and a strengthening of M-P framework.

Table II displays the Mössbauer parameters observed for the three charge states of the bridged iron species II.

As would be expected from occupation of a molecular orbital having σ character, the radical anion and dianion have increasingly more negative isomer shifts than the

Table II. Mössbauer Parameters for $[(OC)_3FeP(CH_3)_2]_2$ Species, -196°

Charge state	IS, mm/sec	QS, mm/sec
○	0.25	0.65
⊖	0.19	1.29
⊖	0.10	1.53

^a Referenced to sodium nitroprusside.

neutral parent. Such occupation is also in agreement with the increasing electric field gradient seen around the iron atom.

It was suggested that the short-range P-H coupling, $^2J_{PH}$, dominates the magnitude of the composite coupling parameter, N , for the compounds under consideration. In all cases, conversion of neutral complexes to their respective dianions is accompanied by a decrease in the absolute magnitude of N . Although no theoretical treatment of the P-C-H coupling is available, reported values of J_{PCH} for acyclic compounds indicate that a general trend exists which relates the per cent s character in phosphorus bonding orbitals to the algebraic value of J_{PCH} .¹⁵ It is found that as s character increases, J_{PCH} becomes more negative. From the range of reported values for J_{PCH} , it is observed that all compounds devoid of nonbonding electron pairs on phosphorus possess negative P-C-H couplings. Additionally, the values for N in all *cis*-bis(trimethylphosphine)-substituted metal carbonyls are negative.¹⁶ It is therefore presumed that all of the values of N shown in Table I are negative, and that J_{PCH} is also negative. The change in N on reduction then reflects an increase in algebraic magnitude corresponding to a decrease in s character for the P-C bonds. If this is interpreted as a demonstration of a decreasing C-P-C bond angle, it follows directly that on reduction, the M-P-M angle must increase.

This conclusion is rational from another view also. In the derivatives of structure I, no evidence for hyperfine interactions in the radical ion involving the carbonyl carbons (or the core metal atom of X) has been observed. Although such evidence is to some extent negative in character, the well-defined esr spectra of Figures 2 and 3 suggest that we are dealing with radical anions in which spin density resides largely, if not wholly, in the ligand (if ligand is defined as the non-carbonyl coordinating species).

Using the structure described as Figure 4a as a model for the systems under consideration, the electron-deficient bonding provides a low-lying molecular orbital, largely σ in character, which can be occupied by both electrons injected upon reduction. Occupation of such an orbital should lead to strengthening of the M-P bond, and as charge is distributed to and through the metal atom to the carbonyl moieties, repulsion should lead to an opening of the M-M distance closing of the P-M-P angle, and a consequent decrease in the P-P distance.

In bisphosphine-metal carbonyl complexes $J_{PP'}$ is usually higher for the trans complex (apparent triplet

(15) S. L. Mannatt, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, *J. Amer. Chem. Soc.*, **88**, 2689 (1966).

(16) J. F. Nixon and A. Pidcock, *Annu. Rev. NMR Spectrosc.*, **345** (1969).

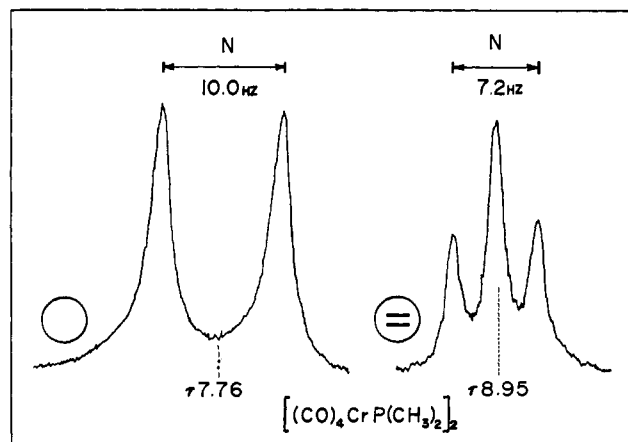


Figure 5.

spectrum) than for the *cis* complex (apparent doublet limiting case), and this has been carefully analyzed and is due to excitation coupling.¹⁶ In the neutral di- μ -phosphido-bridged species, Thompson has pointed out, however, that $J_{PP'}$ appears to increase with decreasing nonbonded P-P distance.⁶ In *cis*-octahedral bisphosphine complexes, a P-M-P angle of approximately 90° produces a nonbonded P-P distance of 3.4 Å (for Cr or Fe), precluding any measurable effect on $J_{PP'}$. Although no X-ray structural analyses have been made on compounds of structures I and II, a P-Fe-P bond angle of 77.6° in $[(CO)_3FeP(CH_3)_2]_2$ has been reported, which reduces the across-space P-P distance to 2.884 Å with a calculated P_{3s} - P_{3s} overlap integral of 0.083.⁶ This is to be compared with an overlap integral of 0.210 for a bonding P-P distance of 2.23 Å. The nmr of this compound is an apparent triplet,⁶ in sharp contrast to the doublet spectrum for structure II, M = Mo, where a P-P distance of 3.8 Å and an overlap integral of 0.018 are estimated. Since upon reduction of the bridged species, the P-M-P angle closes and the P-P distance decreases, it is reasonable that $J_{PP'}$ should increase.

If an M-M bond is assumed in both classes, then the fate of this bond upon reduction is of interest. As previously indicated, the esr signal of the radical anion of structure I shows the expected triplet due to two equivalent P atoms, further split into a 13-fold multiplet. On reduction to the dianion, Figure 5, the nmr spectra changes from the limiting doublet, expected of a low $J_{PP'}$ to the limiting triplet, characteristic of a high $J_{PP'}$. Neither of these facts indicates the nature of the M-M bond. The best test lies in compounds of structure II (M = Fe). In the neutral parent, the dihedral angle between the basal planes is well developed. Upon one-electron reduction, the dihedral angle remains as has been previously deduced. The nmr spectra of both the neutral and dianion species have some interesting temperature characteristics which are exhibited in Figures 6 and 7. At room temperature, the neutral material is characterized by a pair of triplets, due to a $J_{PP'}$ of 85 Hz, and nonequivalent sets of *exo/endo* CH_3 groups. The dianion at room temperature exhibits a single, deceptively simple triplet. Further studies indicate that both species are undergoing conformational exchange, and thus the M-M bond (the dihedral angle) is maintained in the dianion.

If the P-P distance is decreased, there arises the possibility that direct P-P coupling may take place through

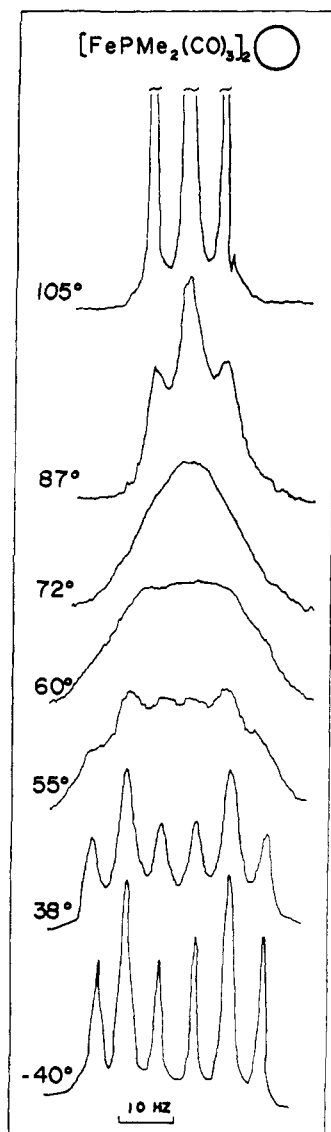


Figure 6.

the overlap of P_{3s} orbitals. The pure s character of such overlap should produce an extremely effective mechanism for spin coupling. Data in Table I demonstrate that on two-electron reduction, $J_{PP'}$ in all cases increases in magnitude, with the increase being more dramatic for II ($M = Fe$) (ca. 500 Hz)¹⁷ and less so for I ($M = Cr, Mo, W$) (ca. 100–150 Hz).

Nixon and Pidcock¹⁶ have treated P–P couplings theoretically and predicted that in all *cis*-substituted biphosphines $J_{PP'}$ will be negative. The data should then be treated as representing an increased P–P coupling *via* one or all of the possible routes open—through space, electronegativity changes, or alteration in π bonding. In light of the recent discussion of Verkade^{12–14} of factors influencing the magnitude of $J_{PP'}$ in biphosphine complexes, it appears unlikely that such large changes in coupling can be ascribed wholly to changes in π bonding in the phosphido bridge upon reduction. In a similar vein, electronegativity changes are not likely to

(17) The line width at half-height for the central triplet peak in II is the same as that of the outer N doublet lines. This circumstance prohibits the measurement of $J_{PP'}$ except by double-resonance techniques. In order for the central peak to be as narrow as the natural width of a single line, $J_{PP'}$ must be in excess of 500 Hz.

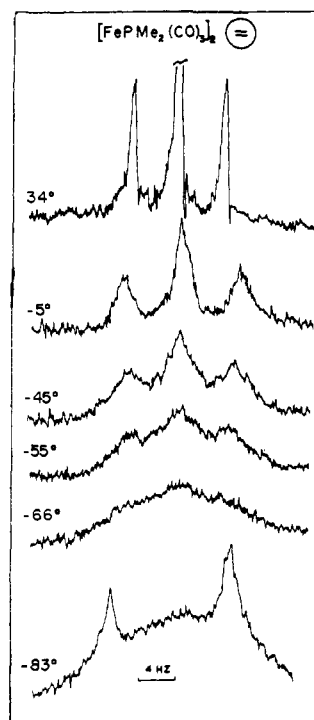


Figure 7.

be the cause of such large changes. Verkade and Nixon have observed that an increase in the electronegativity of the substituents on phosphorus in *cis*-bis(phosphine)metal carbonyls produces an increase in $J_{PP'}$. Plotting substituent electronegativity *vs.* $J_{PP'}$ for *cis*-(R_3P)₂M(CO)₄, where $M = Cr, Mo,$ and W , indicated that an increase of electronegativity of 1.0 produced about a 10-Hz increase in $J_{PP'}$. This effect is likely to be an order of magnitude less than the $J_{PP'}$ observed in this study.

Through-space couplings of F–F and P–F have been reported. A careful analysis of available bond distances, overlap integrals, and the changes that have been demonstrated to occur on reduction indeed point to this phenomena as the source of the increased $J_{PP'}$ upon reduction.

Conformational Exchange. Grobe has reported that the doublet of doublets ¹⁹F nmr spectrum for (CO)₃FeP(CF₃)₂ at 40° (arising from the same exo/endo relationship of CF₃ groups shown in II for CH₃ substitution) reduces to a single well-defined doublet at 120°. We find similar temperature-dependent phenomena for all species of folded structure II, Fe○, Fe⊖ and Ru○ (variable-temperature spectra for these species are shown in Figures 6, 7, and 8). Reversible precipitation of solid material for II ($M = Fe$) ⊖ below –75° and evidence for thermal decomposition of II ($M = Ru$) ○ above 170° precluded a complete study of temperature-dependent behavior for these species. Within the ranges studied, however, it is evident that highly similar phenomena are occurring in all three species.

For II ($M = Fe$), concentrations of 0.1, 0.5, and 1.0 *M* produced no appreciable change in the spectra, showing that the rate-determining step for methyl exchange is not an associative process. The relatively low activation energies of the temperature-dependent phe-

(18) V. J. Grobe, *Z. Anorg. Allg. Chem.*, **361**, 32 (1968).

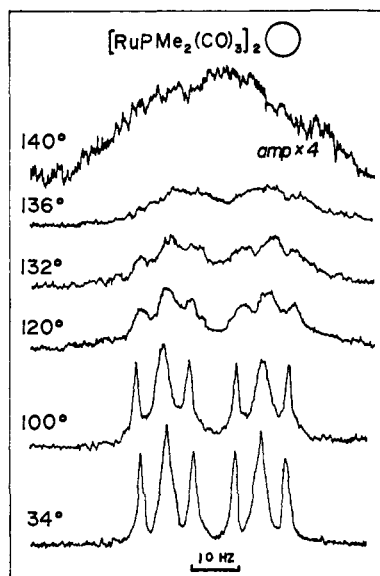


Figure 8.

nomena (reported in Table III) suggest that a bond-breaking step is not involved.

Table III. Kinetic and Thermodynamic Parameters^a

Compound II	T_c , ^a °K	ΔH^\ddagger , ^b kcal/mol	ΔS^\ddagger , ^b eu	k_1 , 0°, ^c l./sec
Fe \circ	338 \pm 2	2.1 \pm 0.2	-45 \pm 1	15.3
Fe \ominus	207 \pm 2	2.2 \pm 0.3	-39 \pm 2	352
Ru \circ	430	5.9 \pm 1.2	-37 \pm 6	0.71

^a Coalescence temperature. ^b Error limits are two standard deviations derived from least-squares fitting. ^c Extrapolated.

Therefore, the methyl exchange must occur *via* an intramolecular pathway not involving bond cleavage. We propose that the molecular motion responsible for the observed temperature-dependent fluxional behavior is the inversion depicted in Figure 9. Thus the static folded form IIa passes through intermediate IIb possessing a planar metal-P ring structure into the folded form IIc equivalent to IIa.

Estimation of kinetic and thermodynamic parameters relating to the proposed inversion in the neutral and dianion species of II may be derived by the use of simplified expressions if two assumptions are made.

(1) **That Forms IIa and IIc Are Equally Populated.** In addition to the clear necessity that this must be true from the equivalence of IIa and IIc, the chemical shift of the resultant, higher temperature multiplet for II (M = Fe, Ru) is the average of the two lower temperature multiplets.

(2) **That the Multiplets May Be Treated as Single Lines with Chemical Shift Equal to the Multiplet Center.** This assumption is approximate, but reasonable, as the multiplet structure does not arise from coupling of spins in the conformationally exchanging groups but rather due to mutual coupling to common nuclei, *viz.*, P and P'.

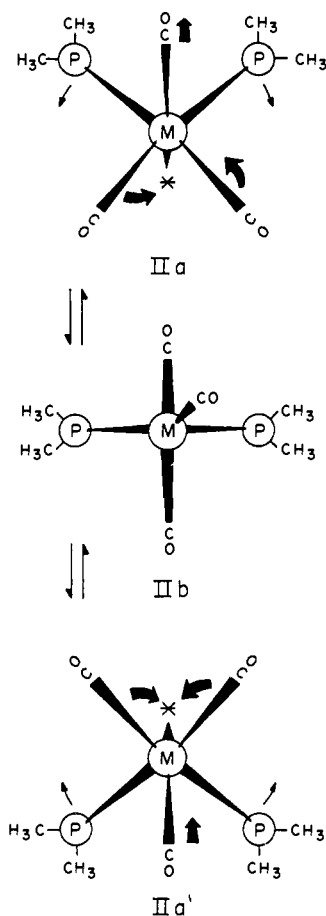


Figure 9.

With these assumptions, the collapsing separation of multiplets for spectra showing two multiplets or the line width changes in the single-transition *N* doublet lines may be used to provide the required parameters. The treatment of the data is essentially that of Gutowsky and Holm,¹⁹ with the modifications and expansions of this treatment utilized by Muetterties and Phillips.²⁰ The results of these calculations are shown in Table III.

The ring motions involved in the iron-containing fluxional systems are characterized by a very low activation enthalpy (approximately 2.2 kcal/mol for both neutral and dianion). Realizing that whatever motion involved in the inversion must involve the M-M bond to some extent, these low values are explicable on the basis of the low bond energies anticipated for such linkages and the fact that inversion of the (M-P)₂ four-membered ring system is probably accomplished *via* a planar configuration in which a large part of the M-M orbital overlap is still retained, thus not requiring any high degree of rupture of the bond.

The ring motions in the iron-containing fluxional systems are characterized by very large negative activation entropies for the dianion (-39 eu) and the neutral material (-45 eu). The observed $\Delta\Delta S^\ddagger$ is reflected in the large difference observed in the coalescence temperature observed for the two species—over 130°—and the extrapolated rates for the butterfly mo-

(19) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(20) E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, **81**, 1084 (1959).

tion at 0° reported in Table III, where it is observed that the dianion is undergoing inversion at a rate 25 times that of the neutral material. The higher activation enthalpy for the Ru-Ru compound (20 times slower in rate than the iron analog) is thought to be due to the higher M-M bond strength ascribed to the former.

While this manuscript was in preparation, Adams and Cotton²¹ reported on a similar fluxional molecule, $[(\text{CH}_3)_2\text{GeCo}(\text{CO})_3]_2$, which possessed nmr properties similar to those presented by Grobe in his classical paper in the area, and the present findings. The observed E^\ddagger was 15 kcal/mol. Cotton elegantly examined the possible routes that could be utilized by such systems and chose to emphasize a pathway involving an intermediate configuration possessing trigonal-bipyramidal configuration about the metal (ignoring the M-M bond) with the pseudothreefold axis in the plane of the (M-Ge)₂ ring. The mechanism is the inverse of the Berry mechanism²² for substitution in trigonal bipyramids and is extremely tempting. Because of the extremely large negative values of the entropy of activation involved in the present case, suggesting a very rigid, organized transition state, the intermediate configuration shown as IIB in Figure 9 is suggested, where the methyl groups are chemically and magnetically equivalent. Further work is obviously necessary to elucidate either mechanism in more detail and to answer the question of whether rotation about the pseudothreefold axis of the (OC)₃Fe end group may be involved.

Cotton-Kraihanzel C≡O stretching force constant data are available on all of the species.² $[(\text{CH}_3)_2\text{PCr}-$

(21) R. D. Adams and F. A. Cotton, *J. Amer. Chem. Soc.*, **92**, 5003 (1970).

(22) (a) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960); (b) G. M. Whitesides and H. L. Mitchell, *J. Amer. Chem. Soc.*, **91**, 5384 (1969); (c) K. E. DeBruin, K. Naumann, G. Zon, and K. Mislow, *ibid.*, **91**, 7031 (1969).

$(\text{CO})_4]_2\cdot^-$ gives $\Delta H_P = 14$ G, $\Delta H_H = 1.3$ G, suggesting high unpaired spin density in the bridging ligand framework; $[(\text{CH}_3)_2\text{PFe}(\text{CO})_3]_2\cdot^-$ gives $\Delta H_P = 4.5$ G, $\Delta H_H = 1.4$ G. We have reported that this spin density in the bridging ligand area affects a drift of charge to and through the metal which alters the C≡O force constants, as indicated in Table IV for the dianion

Table IV

Case		Force constants, mdyne/Å			
		Neutral	Dianion	Δk	
1	$[(\text{CH}_3)_2\text{PCr}(\text{CO})_4]_2$	k_1	15.45	13.01	2.44
		k_2	15.79	14.24	1.55
2	$[(\text{CH}_3)_2\text{PFe}(\text{CO})_3]_2$	k_1	16.53	14.46	2.07
		k_2	15.61	13.21	2.40

singlet state species. Anisotropic σ transmission of charge satisfactorily explains case 1. At the time these data were reported, the anomalous $\Delta k_2 > \Delta k_1$ for case 2 had to be left until some knowledge of geometry was available. It appears that an incomplete opening of the dihedral angle on reduction would account for this reversal, but of course what is needed now is single-crystal data on all charge states. This is obviously a challenge to those workers, like Dahl, who are attempting by this method to evaluate the effect of change of charge on structure.

In this vein, workers interested in this exciting area are referred to an excellent review by Dahl²³ of the effects of M-M bonding in bridged species, and some of the dangers in overinterpreting some classes of data.

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(23) L. F. Dahl, E. R. DeGil and R. D. Feltham, *ibid.*, **91**, 1653 (1969).