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Bis(μ-5,5-dimethyl-1,3,2-dioxaphosphorinano)-diiron Hexacarbonyl: A Fluxional Molecule Exhibiting Two Types of Proton Site Exchange

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The new compound $(\mu\text{-}\overline{POCH_2C(CH_3)_2CH_2O})_2Fe_2(CO)_6$ has been synthesized and characterized by infrared spectroscopy, ^1H NMR spectrometry, mass spectrometry, and Mössbauer spectroscopy. The ^1H NMR spectrum reveals the heterocyclic, organophosphorus rings to be fluxional down to temperatures less than −75 °C. The $\overline{Fe–P–Fe–P}$ ring is shown to be fluxional at high temperatures with a coalescence temperature near 60 °C in toluene-d_8 and acetone-d_6.

Introduction

Interest in the stereochemistry of phosphorus heterocycles, especially of 1,3,2-dioxaphosphorinanes, increased at a rapid pace in the 1960s.[1] Although the preferred conformation of the 1,3,2-dioxaphosphorinane ring is a rigid chair,[2] exceptions to this stereochemistry are known.[3,4] Previous work has shown the rigid-chair conformation to persist when a metal carbonyl group is attached either axially[5–7] or equatorially[8] at phosphorus. In comparison, stereochemical nonrigidity of the 1,3,2-dioxaphosphorinane ring is noted when two identical groups are attached to phosphorus.[9,10] Thus, it is of interest to determine the effect that two large metal carbonyl groups attached to phosphorus might have upon the conformation and/or fluxionality of a 1,3,2-dioxaphosphorinane ring. With respect to this point, we have isolated the new compound, bis(μ-5,5-dimethyl-1,3,2-dioxaphosphorinano)-diiron hexacarbonyl, $[(\mu\text{-DMP})Fe(CO)_3]_2$, Figure 1, and found this particular 1,3,2-dioxaphosphorinano ring to be stereochemically nonrigid in solution. In addition, the methylene protons within each heterocyclic ring in $[(\mu\text{-DMP})Fe(CO)_3]_2$ undergo dynamic group exchange of a type reported for other bridging dialkylphosphido derivatives of iron carbonyl.[11,12] However, Dean[13] in a companion paper on the crystal structure of this compound noted that a chair conformation is found for each heterocyclic ring in the solid state with one iron atom axially oriented and the other equatorially positioned at phosphorus.

Experimental Section

Reactions and isolation procedures were carried out routinely under a nitrogen atmosphere. ^1H NMR (60 MHz) spectra were obtained with a Hitachi Perkin-Elmer R20A spectrometer. The 220-MHz spectra were obtained in the FT mode with a Varian spectrometer. Infrared spectra in the 2000-cm^{-1} region were recorded on a Perkin-Elmer 621 spectrophotometer. Mössbauer spectra were obtained with an Austin Scientific Associates instrument utilizing a ^{57}Co-in-copper source. Elemental analyses were performed by the Baron Consulting Co., Orange, Conn.

Bis(μ-5,5-dimethyl-1,3,2-dioxaphosphorinano)-diiron Hexacarbonyl. A mixture of 7.9 g of triiron dodecacarbonyl,[14] 1.9 g of 2-chloro-1,3,2-dioxaphosphorinane,[15] and 50 mL of dry benzene was heated at reflux for 45 min. The solution was allowed to cool to room temperature whereupon approximately 5 g of a yellow solid precipitated. The solid was collected by filtration and washed with two 25-mL portions of petroleum ether (bp 20–40 °C). The benzene filtrate was chromatographed on a 2.5 × 40 cm column of alumina. Elution with benzene gave two yellow bands, the first being the previously reported (2-chloro-1,3,2-dioxaphosphorinane)tetracarbonyliron.[5] The second band contained a solid identical with the yellow solid obtained above. The two solid fractions were combined and recrystallized twice from hexane to give bis(μ-5,5-dimethyl-1,3,2-dioxaphosphorinano)-diiron hexacarbonyl as a yellow, extremely air-stable, microcrystalline powder, mp 182–184 °C dec, in up to 50% yield. Anal. Calcd for $C_{16}H_{20}Fe_2O_{10}P_2$: C, 35.26; H, 3.66; mol wt 545.97. Found: C, 35.01; H, 3.86; mol wt 550 (cryoscopic, C_6H_6), 546 (complex multiplet, mass spectrum). Infrared spectrum (hexane): 2066 (m), 2026 (vs), 2005 (s), 1978 (m), 1954 (m) cm^{-1}.

2,2,5,5-Tetramethyl-1,3,2-dioxaphosphorinanium Iodide. A solution of 3.0 g of freshly distilled 2,5,5-trimethyl-1,3,2-dioxaphosphorinane in 25 mL of diethyl ether was stirred vigorously as 4.0 g of methyl iodide was added dropwise. The resulting precipitate was filtered under nitrogen, washed with two 25-mL portions of hexane, and dried in a stream of nitrogen. The yield of hygroscopic white solid, mp 134 °C dec, was nearly quantitative. The salt appears stable under a nitrogen atmosphere but decomposes slowly under vacuum. Anal. Calcd for $C_7H_{16}IO_2P$: C, 28.92; H, 5.54. Found: C, 28.96; H, 5.69.

2-Hydroxy-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane Monohydrate. A procedure described by McConnell and Coover[16] gave this compound in good yield; mp 174 °C. Anal. Calcd for $C_5H_{13}O_5P$: C, 32.60; H, 7.06. Found: C, 32.68; H, 7.06.

Results and Discussion

Characterization of $[(\mu\text{-DMP})Fe(CO)_3]_2$. The reaction between triiron dodecacarbonyl and 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane yields both (2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane)tetracarbonyliron, (2-Cl-DMP)Fe(CO)$_4$,[5] and bis(μ-5,5-dimethyl-1,3,2-dioxaphosphorinano)-diiron hexacarbonyl, $[(\mu\text{-DMP})Fe(CO)_3]_2$, Figure 1. Longer reaction times yield more of the bridged complex which has been characterized by infrared, Mössbauer, and mass spectral methods and by variable temperature 60- and 220-MHz ^1H NMR. The mass spectrum shows the parent ion $[(\mu\text{-DMP})Fe(CO)_3]_2^+$ at an *m/e* value of 546, corresponding to the compound with both iron atoms of mass 56, the most abundant isotope of iron. Readily assignable peaks corresponding to the loss of six successive molecules of carbon monoxide are also observed. Further losses correspond to degradation of the heterocyclic ring, with loss of two 5-methyl groups being the only readily discernible feature of subsequent cracking. No evidence for $Fe(CO)_3[P(OCH_2)_2C(CH_3)_2]^+$ fragments was observed, and lines of only weak intensity corresponding to ions for $Fe[P(OCH_2)_2C(CH_3)_2]^+$ were noted. The ^{57}Fe Mössbauer spectrum of $[(\mu\text{-DMP})Fe(CO)_3]_2$ is consistent with a structure in which the iron atoms experience the same chemical environment. The observed isomer shift of 0.131 mm/s (25 °C) for $[(\mu\text{-DMP})Fe(CO)_3]_2$, relative to hydrated sodium nitroprusside, was corrected to −196 °C by adding 0.11 mm/s to yield 0.24 mm/s, a value which compares very favorably with values obtained for other iron complexes with bridging phosphido ligands.[16–18] The observed quadrupole splitting of 0.68 mm/s also compares well with reported values. The general features of the infrared spectrum of $[(\mu\text{-DMP})Fe(CO)_3]_2$, Table I, in the metal carbonyl stretching region resemble those reported for other iron complexes containing bridging phosphido ligands.

^1H NMR Observations. The ^1H NMR spectra of rigid 2-R-5,5-dimethyl-1,3,2-dioxaphosphorinanes, as well as complexes of these phosphorus compounds, usually contain a pair of apparent singlets separated by 0.4–0.8 ppm, which indicate nonequivalence of the 5-methyl groups, and a more complicated set of signals for the methylene protons.[1,5] The ^1H NMR spectra of nonrigid phosphorinanes are significantly

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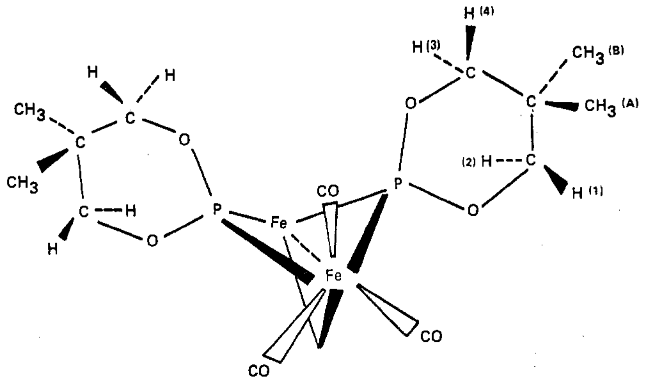

Figure 1. Bis(μ-5,5-dimethyl-1,3,2-dioxaphosphorinano)-diiron hexacarbonyl. The carbonyl ligands on the back iron atom have been omitted for clarity.

Table I. Infrared Spectra of Several Bridging-Phosphido Iron Complexes

Compd	Absorptions, cm^{-1}	Solvent	Ref
[(μ-DMP)Fe(CO)$_3$]$_2$	2066 m, 2026 vs, 2005 s, 1978 m, 1954 m	Hexane	*a*
[(CH$_3$PH)Fe(CO)$_3$]$_2$	2063 w, 2025 s, 1992 m, 1982 m	Heptane	*b*
[(C$_6$H$_5$PH)Fe(CO)$_3$]$_2$	2063 w, 2027 s, 1996 s, 1984 s, 1974 m	Heptane	*b*
[(P(CH$_3$)$_2$Fe(CO)$_3$]$_2$	2050 s, 2010 vs, 1977 vs, 1962 vs	CS$_2$	*c*
[(P(CF$_3$)$_2$Fe(CO)$_3$]$_2$	2098 s, 2068 vs, 2037 vs, 1955 w	CCl$_4$	*d*

[a] This work. [b] P. M. Treichel, W. K. Dean, and W. M. Douglas, *Inorg. Chem.*, **11**, 1609 (1972). [c] R. G. Hayter, *ibid.*, **3**, 711 (1964). [d] J. Grobe, *Z. Anorg. Allg. Chem.*, **361**, 32 (1968).

simpler owing to rapid ring inversion. White[10] reported the ^{1}H NMR spectrum of 2,2,5,5-tetramethyl-1,3,2-dioxaphosphorinanium tetrafluoroborate to consist of a sharp doublet in the methylene region, a single-ring 5-methyl resonance, and a single doublet for the phosphorus–methyl resonance. Likewise, a simplified spectrum has been noted for 2-hydroxy-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane in water.[8] The reported observations on these two ring systems have been verified in this work at 60 MHz.

The observation of a single, sharp 5-methyl resonance signal for [(μ-DMP)Fe(CO)$_3$]$_2$ in a wide range of solvents at 34 °C, between -75 and $+100$ °C in toluene-d_8, and between -60 and $+54$ °C in acetone-d_6 is evidence that the bridging 5,5-dimethyl-1,3,2-dioxaphosphorinano ligand is fluxional in solution over the indicated temperature ranges. As measured at 220 MHz, the chemical shift for the 5-methyl groups in acetone-d_6 remains constant at 1.100 ± 0.006 ppm relative to internal Me$_4$Si. In toluene-d_8, the same signal remains sharp but shifts quite markedly to lower field with increasing temperature. For example, δ(CH$_3$) equals 0.530 ppm (+16 °C), 0.587 ppm (+42 °C), and 0.654 ppm (+79 °C) as measured at 220 MHz for the indicated temperatures.

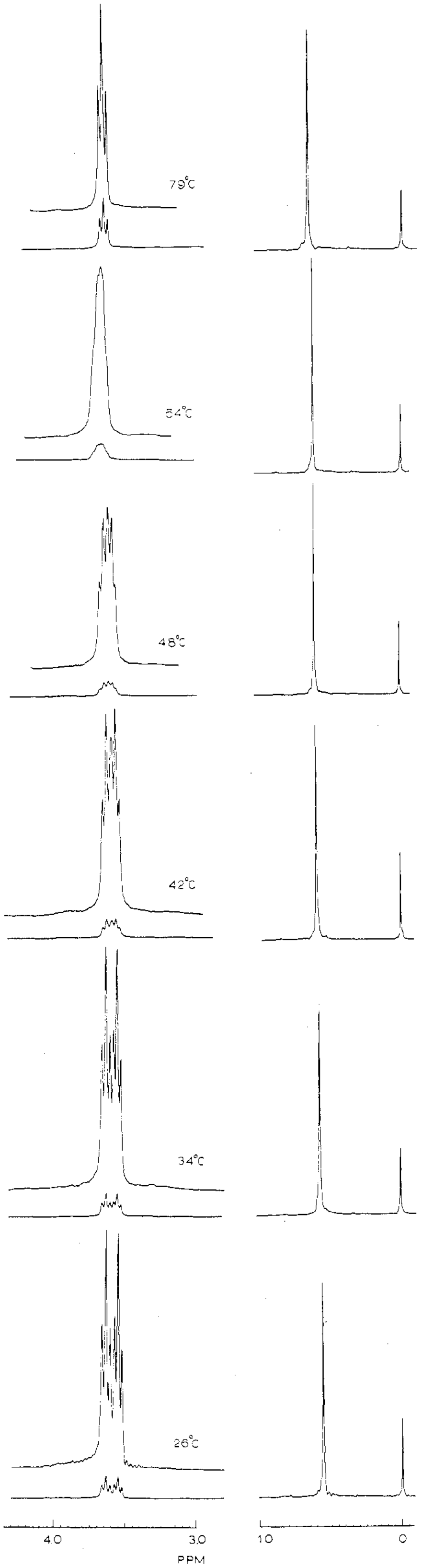

Figure 2. Variable-temperature 220-MHz (FT mode) ^{1}H NMR spectra of [(μ-DMP)Fe(CO)$_3$]$_2$ in toluene-d_8. Me$_4$Si (δ 0) is the internal standard.

The effect of temperature on the methylene resonance signal of [(μ-DMP)$_2$Fe(CO)$_3$]$_2$ is considerably more variable and informative. An examination of Figure 1 suggests that H(1), H(2), H(3), and H(4) would all experience different chemical environments if the phosphorinane ring were in a rigid-chair or even a skew configuration. However, over the temperature range reported here, the equivalence of CH$_3$(A) and CH$_3$(B) requires that the pair H(1) and H(2) on the carbon atom exo to the Fe–P–Fe–P ring also be time equivalent. Likewise H(3) and H(4) on the endo carbon will be time equivalent. The 220-MHz variable-temperature spectra given in Figures 2 and 3 show that this must be the case. Between -60 and about $+40$ °C the methylene resonance signals of the bridging ligand are a pair of deceptively simple triplets. [At 60 MHz, these resonance signals overlap and give rise to a quartet, a pentet, or nondescript multiplet depending upon the temperature and solvent. Chemical shifts and coupling constants were obtained

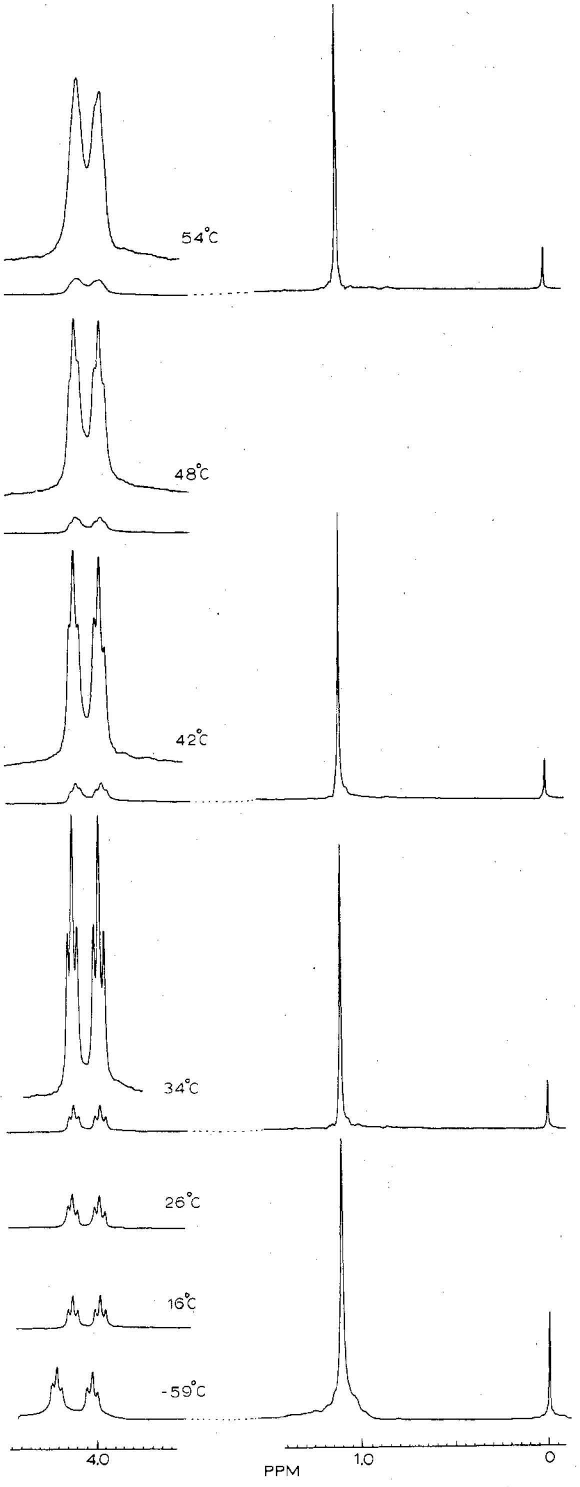

Figure 3. Variable-temperature 220-MHz (FT mode) ^{1}H NMR spectra of $[(\mu\text{-DMP})\mathrm{Fe(CO)_3}]_2$ in acetone-d_6. $\mathrm{Me_4Si}$ (δ 0) is the internal standard.

at 60 MHz in toluene-d_8 and acetone-d_6, and all values agree well with those reported in this paper.] Others have reported deceptively simple triplets for bridging dialkylphosphido ligands in related compounds.[11,12,20,21] The positions of these two triplets are reversed in the two solvents toluene-d_8 and acetone-d_6. To illustrate this point, the two well-separated signals seen at 26 °C in Figures 2 and 3 may be considered. With acetone-d_6 as the solvent, the chemical shifts (ppm) and $J = {}^3J_{\mathrm{HP}} + {}^5J_{\mathrm{HP}}$ (Hz) values are 4.129 (J = 10.9) and 3.985 (J = 12.5); in toluene-d_8 the values are 3.635 (J = 12.4) and 3.548 (J = 11.3). Although the assignment of these two triplets to either the exo or endo pairs of methylene protons is not possible with certainty, the results do show time equivalence of H(1) with H(2) and of H(3) with H(4). The outer-peak separations of 10.9 and 12.2 Hz are attributable primarily to $^3J_{\mathrm{HP}}$; i.e., $^5J_{\mathrm{HP}}$ is small. For comparison, $^3J_{\mathrm{HP}}$ = 12.0 Hz for 2-hydroxy-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane and 11.0 Hz for the 2,2,5,5-tetramethyl-1,3,2-dioxaphosphorinanium ion, both of which are conformationally mobile. Thus, $^2J_{\mathrm{PP}}$ must be very large.

Figure 2 shows that with increasing temperature the apparent triplets observed in toluene-d_8 collapse to a broad nondescript band near 54 °C. At still higher temperatures, a single apparent triplet centered at δ 3.652 ($^3J_{\mathrm{HP}} + {}^5J_{\mathrm{HP}}$ = 11.7 Hz) is seen as a result of flexing of the $\overline{\mathrm{Fe{-}P{-}Fe{-}P}}$ ring which leads to time equivalence of the endo and exo pairs of methylene protons. Owing to the small chemical shift difference between the two apparent triplets prior to coalescence, we cannot state unequivocally exactly what the coalescence temperature is. However, inasmuch as in acetone-d_6 the two triplets are rapidly approaching each other near the boiling point of the solvent, it would seem as though the coalescence temperature must be between 55 and 60 °C. At 60 MHz, the methylene resonance in acetone-d_6 at 58 °C definitely has triplet character. Higher temperature spectra with acetone-d_6 as solvent could not be taken safely. Unfortunately, the available instrumentation did not permit a double-resonance variable-temperature study in which ^{31}P could be uncoupled from the proton resonances and, thus, allow a better determination of the coalescence temperature and activation energies. However, a line-width analysis of the spectra between 30 and 10 °C does suggest that the ΔG^* is equal to 17.3 ± 1.0 kcal/mol for flexing of the $\overline{\mathrm{FeP{-}FeP}}$ ring. We have been unsuccessful in trying to prepare the arsenic analogue of $[(\mu\text{-DMP})\mathrm{Fe(CO)_3}]_2$, a compound which would perhaps give a much clearer picture of the relative energies of the various fluxional processes possible in heterocyclic systems as bridging ligands.

Cotton et al.[12] have commented that site exchange of R groups in $[(\mu\text{-ER}_2)\mathrm{M(CO)_3}]_2$ molecules is a function of M (which determines whether or not there is an M–M bond), E, and the nature of the R groups. Very recently, Clegg[22] has discussed the variation in the flap angle of the $\overline{\mathrm{Fe{-}P{-}Fe{-}P}}$ ring in these compounds and concluded that strongly electron-withdrawing groups on phosphorus tend to give larger flap angles than do alkyl or aryl groups. The cyclic bridging ligand present in the compound of interest in this paper adds another dimension to this area of study because the ligand assumes a chair configuration in the solid state but in solution is fluxional. In addition, the apparent coalescence temperature of 60 °C or less seems to be 10 °C or more lower than has been noted for other related complexes such as $[(\mu\text{-PMe}_2)\text{-}\mathrm{Fe(CO)_3}]_2$ and $[(\mu\text{-P(CF}_3)_2)\mathrm{Fe(CO)_3}]_2$. Neither electronic nor steric effects seem to provide satisfactory answers. In particular, the net electronic effect, as revealed by the CO stretching bands listed in Table I for the complex with the bridging 1,3,2-dioxaphosphorinano system, is midway between that of $\mathrm{PMe_2}$ and $\mathrm{P(CF_3)_2}$ as bridging ligands. Sterically, the constrained nature of the μ-DMP ligands would be expected to minimize cross-ring interactions which might be expected to raise and not lower the coalescence temperature for the flapping of the $\overline{\mathrm{Fe{-}P{-}Fe{-}P}}$ ring. The crystal structure of $[(\mu\text{-DMP})\mathrm{Fe(CO)_3}]_2$ reveals no steric effect between the bridging ligands.[13] Thus, we conclude that the slightly lower coalescence temperature noted for $[(\mu\text{-DMP})\mathrm{Fe(CO)_3}]_2$ may be related to the simultaneous fluxional character of the μ-DMP rings which have a coalescence temperature below −75

°C. Clearly, other complexes with heterocyclic ring systems should be studied to further test this thesis.

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Registry No. Triiron dodecacarbonyl, 12088-65-2; 2-chloro-1,3,2-dioxaphosphorinane, 2428-06-0; $[(\mu\text{-DMP})Fe(CO)_3]_2$, 65150-25-6; 2,2,5,5-tetramethyl-1,3,2-dioxaphosphorinanium iodide, 65150-05-2; 2,2,5,5-tetramethyl-2-iodo-1,3,2-dioxaphosphorinane, 65150-06-3; 2-hydroxy-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane, 873-99-4.

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Preparation and Properties of Hydroxo(methyl)-1,2-bis(diphenylphosphino)ethaneplatinum(II). A Trans-Influence Series Including σ Carbon Donor Ligands Based on Platinum–Phosphorus Coupling Constants

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The monomeric hydroxo(methyl)platinum(II) complex $Pt(OH)(CH_3)(dppe)$ (dppe = 1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$) is obtained from $PtCl(CH_3)(dppe)$ by treatment of the derived labile cation $[Pt(CH_3OH)(CH_3)(dppe)]^+$ with aqueous methanolic sodium hydroxide. It undergoes anation with a variety of acids, including fairly weak carbon acids such as acetone and acetonitrile, and provides a convenient route to unsymmetrical bis(alkyls) of platinum(II), e.g., $Pt(CH_2COCH_3)(CH_3)(dppe)$ and $Pt(CH_2CN)(CH_3)(dppe)$. The values of J_{PtP} trans to X or L derived from the $^{31}P\{^1H\}$ NMR spectra of PtXR(dppe) (X = various anionic ligands and R = methyl or 1-cyclohexenyl), $[Pt(CH_3)L(dppe)]^+$ (L = various neutral ligands), and sundry other neutral complexes of the type PtXY(dppe) permit the establishment of a trans-influence series which includes OH^- and a variety of σ carbon donors. The former has a trans influence comparable with those of typical sulfur donors and higher than those of NO_3^- and $CH_3CO_2^-$. The generally high trans influence of σ carbon donors is lowered by the presence of conjugated electron-withdrawing groups on the ligating carbon atom. Tricyanomethide, $C(CN)_3^-$, binds through nitrogen rather than carbon, and C-bonded triacetylmethyl, $C(COCH_3)_3^-$, is only slightly higher than Cl^- in the trans-influence series, whereas the trans influence of CF_3^- is high and only slightly less than that of CH_3^-. In contrast, Pt–Cl bond length and stretching frequency data indicate the trans influence of CF_3^- to be considerably lower than that of CH_3^-. The discrepancy is thought to arise because the J_{PtP} values primarily reflect changes in hybridization, whereas the Pt–Cl bond parameters are also sensitive to electrostatic effects induced by the electronegative fluorine atoms.

Introduction

In recent years there has been considerable interest in NMR coupling constants in planar platinum(II) complexes, e.g., $^1J(^{195}Pt–^1H)$ in hydrides, $^1J(^{195}Pt–^{13}C)$ in organo derivatives, and $^1J(^{195}Pt–^{31}P)$ in tertiary phosphine complexes. These data have been compared[1] with those available from other spectroscopic techniques and from x-ray diffraction studies to develop the trans-influence series, which permits a relative estimate of the tendency of a ligand to weaken the bond trans to itself in the ground state of a complex.[2]

It is generally assumed that the magnitude of a coupling constant such as $^1J(^{195}Pt–^{31}P)$ is dominated by the Fermi contact term and that it can be expressed by relation 1, where

$$^1J_{PtP} \propto \gamma_{Pt}\gamma_{P}\alpha_{Pt}^2\alpha_{P}^2|\psi_{Pt(6s)}(0)|^2|\psi_{P(3s)}(0)|^2(\Delta E)^{-1} \quad (1)$$

γ_{Pt} and γ_P are the gyromagnetic ratios for the respective nuclei having spin $^1/_2$, α_{Pt}^2 and α_P^2 are the s characters of the bonding orbitals used by the respective atoms in the Pt–P bond, $|\psi_{X(ns)}(0)|^2$ is the electron density of the *ns* orbital at nucleus X (X = Pt, *n* = 6; X = P, *n* = 3), and ΔE is an average singlet–triplet excitation energy. For closely related complexes, variations in $\alpha_P^2|\psi_{P(3s)}(0)|^2$ are likely to be negligible compared with those in the corresponding term involving platinum, and it is further assumed that variations in α_{Pt}^2 are of most importance. This assumption is supported by a comparison of J_{PtP} for analogous planar platinum(II) and octahedral platinum(IV) complexes and by the observation[3] that in complexes such as *cis*-$PtCl(CH_3)(PEt_3)_2$[4] J_{PtP} trans to CH_3 (1719 Hz) is very much less than J_{PtP} trans to Cl (4179 Hz). Since ΔE and $|\psi_{Pt(6s)}(0)|^2$ are common to both couplings, the large

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