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A Multinuclear Nuclear Magnetic Resonance Study of Metal Complexes of the Ligands $Ph_2ECH_2CMe_2CH_2EPh_2$ (E = P, As)

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The two chelating ligands 2,2-dimethyl-1,3-bis(diphenylphosphino)propane (2,2-dm-1,3-dppp) and 2,2-dimethyl-1,3-bis(diphenylarsino)propane (2,2-dm-1,3-dpap) have been synthesized and used to generate the new complexes $Mo(CO)_4$(L-L) $W(CO)_4$(L-L), and $XMn(CO)_3$(L-L) where X = Cl, Br, I, CH_3, and CH_3CO. A rapid chair–chair interconversion of the six-membered metal chelate ring system in the molybdenum and tungsten complexes results in the apparent equivalence of the phenyl groups (^{13}C NMR), methyl groups (^{1}H and ^{13}C NMR), and methylene protons (^{1}H NMR). The assignment of a facial configuration to each of the manganese complexes is based on infrared spectra in the 2000-cm^{-1} region, a single ^{31}P resonance for complexes of 2,2-dm-1,3-dppp, and the inequivalence of the 2-methyl groups (^{1}H and ^{13}C NMR), the phenyl groups (^{13}C NMR), and the geminal methylene hydrogens (^{1}H NMR). The ^{1}H and ^{13}C NMR spectra of the manganese complexes are interpreted on the basis of a single preferred chair conformation. Specific assignments for the ^{1}H and ^{13}C NMR resonance signals of the dissimilar 2-methyl groups are based upon the observation of four-bond planar W-coupling of the equatorial 2-methyl protons to phosphorus ($^4J_{HP} \simeq 3$ Hz) and Karplus-type three-bond coupling between phosphorus and the equatorial 2-methyl carbon ($^3J_{CP} \simeq 10.5$ Hz). Phosphorus coupling to the axial 2-methyl carbon ($^4J_{CP} = 2.5$ Hz) and protons is considerably weaker.

Introduction

Although the use of ^{13}C NMR in studies of organometallic transition-metal complexes is becoming increasingly more common,[1-5] published ^{13}C NMR studies have focused on metal carbonyl ligands and π-bonded organic groups and to a large degree have neglected assignments for the organic parts of σ-donor ligands such as tertiary phosphines and arsines. For the many known complexes of chelating bis(tertiary phosphines and arsines),[6] the major NMR-active nuclei studied have been ^{1}H and/or ^{31}P.[7-13] We have now synthesized a series of complexes of the new ligands $Ph_2ECH_2CMe_2CH_2EPh_2$ with E = P, As and have found their ^{1}H, ^{31}P, and ^{13}C NMR spectra to be readily interpreted. This paper reports the results of this study and points out how concepts used in analyzing spectra of substituted cyclohexanes can be applied to six-membered chelate ring systems.

Experimental Section

Ligands. The two new ligands 2,2-dimethyl-1,3-bis(diphenylphosphino)propane (2,2-dm-1,3-dppp) and 2,2-dimethyl-1,3-bis(diphenylarsino)propane (2,2-dm-1,3-dpap) were prepared according to the general procedure of Hewertson and Watson.[14] The 2,2-dimethyl-1,3-dibromopropane used in the ligand preparations was synthesized according to the procedure of Whitmore and co-workers.[15] Analyses and physical properties for the ligands are given in Table I.

Complexes. New complexes reported in this work were synthesized by previously reported well-known procedures. Analytical data, physical properties and methods of synthesis are listed in Table I. The irradiation procedures were carried out in pyrex Schlenk tubes by using unfiltered radiation from an external mercury lamp. The solutions were kept cool by means of a water-cooled cold-finger probe inserted directly into the reaction mixture. All thermal reactions and irradiation procedures were carried out in nitrogen-flushed systems, and the evolution of carbon monoxide was monitored volumetrically. The complexes of the new ligands reported here are analogous to many other previously reported complexes of ligands such as diphos and diars in terms of air stability, color, and solubility in various solvents.

Spectra. Infrared spectra were recorded on a Perkin-Elmer Model 283 grating spectrometer calibrated with polystyrene. NMR spectra were recorded on Hitachi Perkin-Elmer R20A (60-MHz) and JEOLCO FX90Q (90-MHz) spectrometers. The INEPT experiment was carried out on an IBM WP200SY instrument. The ^{13}C spin-echo experiment with gated broad-band decoupling was performed on an IBM NR80 instrument.

Spectral Results and Interpretation

Infrared Spectra. The metallocarbonyl CO stretching bands for the new complexes are given in Table II. Cis structures are readily assigned for the molybdenum and tungsten complexes.[16] The manganese complexes are assigned facial structures on the basis of the similarity of their spectra to those of previously reported analogues.[16,17] The one iron complex reported has a spectrum similar to that reported for $Fe(CO)_3$(diphos).[18]

^{31}P{^{1}H} NMR. Values of the chemical shifts of the proton-decoupled ^{31}P resonances for four of the complexes made in this work are given in Table III. The ^{31}P spectrum of $W(CO)_4$(2,2-dm-1,3-dppp) is like that reported for other tungsten complexes[19] and consists of one strong sharp signal and two weaker satellites arising from ^{183}W–^{31}P coupling with $^1J_{W-P} = 224.6$ Hz. In contrast, the ^{31}P spectra of the manganese complexes consist of broad singlet resonance signals. Quadrupolar coupling of the manganese and/or halogen nuclei to phosphorus could account for the observed broadening. The single resonance line for each manganese complex is indicative of a facial arrangement of the ligands. This conclusion is

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Table I. Synthetic Procedures, Analyses, and Physical Properties of New Compounds

compd	synthetic procedure	yield, %	color	mp, °C	elemental anal., found (calcd) % C	elemental anal., found (calcd) % H
$Ph_2PCH_2CMe_2CH_2PPh_2$ (2,2-dm-1,3-dppp)	*a*	42	white	86–87	78.68 (79.07)	6.85 (6.86)
$Ph_2AsCH_2CMe_2CH_2AsPh_2$ (2,2-dm-1,3-dpap)	*a*	30	white	85–85.5	65.65 (65.92)	5.71 (5.72)
$Mo(CO)_4$(2,2-dm-1,3-dppp)	*b*	58	yellow	201–203	60.96 (61.12)	4.73 (4.66)
$Mo(CO)_4$(2,2-dm-1,3-dpap)	*c*	55	yellow	196–197	53.54 (53.10)	4.17 (4.15)
$W(CO)_4$(2,2-dm-1,3-dppp)	*c*	44	yellow	191–194	54.01 (53.83)	3.95 (4.11)
$W(CO)_4$(2,2-dm-1,3-dpap)	*c*	45	yellow	211–213	48.01 (48.09)	4.00 (3.67)
$Mn(CH_3CO)(CO)_3$(2,2-dm-1,3-dppp)	*d*	48	yellow	193–194 dec	65.24 (65.60)	5.17 (5.34)
$Mn(CH_3CO)(CO)_3$(2,2-dm-1,3-dpap)	*d*	12	yellow	167–170	57.80 (57.48)	4.93 (4.68)
$Mn(CH_3)(CO)_3$(2,2-dm-1,3-dppp)	*d*	33	yellow	195–198 dec	*f*	*f*
$Mn(CH_3)(CO)_3$(2,2-dm-1,3-dpap)	*d*	76	yellow	181–185 dec	58.17 (58.08)	4.98 (4.87)
$MnCl(CO)_3$(2,2-dm-1,3-dppp)	*b*	91	yellow	191–196 dec	62.85 (62.50)	4.91 (4.92)
$MnCl(CO)_3$(2,2-dm-1,3-dpap)	*b*	81	yellow	184 dec	54.89 (54.69)	3.95 (4.11)
$MnBr(CO)_3$(2,2-dm-1,3-dppp)	*b*	94	yellow-orange	200–204 dec	59.86 (59.65)	4.85 (5.18)
$MnBr(CO)_3$(2,2-dm-1,3-dpap)	*b*	69	orange	194 dec	51.24 (51.43)	3.89 (4.05)
$MnI(CO)_3$(2,2-dm-1,3-dppp)	*b*	43	red-orange	201–205 dec	53.95 (54.41)	3.91 (4.28)
$MnI(CO)_3$(2,2-dm-1,3-dpap)	*b*	85	red-orange	188–190 dec	46.19 (48.39)	3.74 (3.81)
$Fe(CO)_3$(2,2-dm-1,3-dppp)	*e*	46	yellow	149–151 dec	65.96 (66.22)	5.59 (5.21)

[a] Reference 14. [b] Thermal reaction: methylcyclohexane solvent; recrystallization from benzene/hexane. [c] Photochemical reaction: THF solvent; recrystallization from THF/CH_3OH. [d] Reference 7. [e] Reference 18. [f] Characterization based on agreement of physical and spectral properties with those of analogous complexes reported elsewhere[7,14,18] or in this paper.

Table II. Infrared Spectra in the 2000-cm^{-1} Region[a]

compd	$\bar{\nu}$, cm^{-1}			
L-L = 2,2-dm-1,3-dppp				
$Mo(CO)_4$(L-L)	2018 m	1932 m	1914 s	1906 s
$W(CO)_4$(L-L)	2018 m	1929 m	...	1902 s
fac-$MnCH_3(CO)_3$(L-L)	1997 s	1920 m	1875 m	
fac-$Mn(CH_3CO)(CO)_3$(L-L)	2010 s	1920 s, br		
fac-$MnCl(CO)_3$(L-L)	2029 s	1964 m	1905 m	
fac-$MnBr(CO)_3$(L-L)	2026 s	1964 m	1904 m	
fac-$MnI(CO)_3$(L-L)	2022 s	1961 m	1906 m	
$Fe(CO)_3$(L-L)	1990 s	1918 m	1890 m	
L-L = 2,2-dm-1,3-dpap				
$Mo(CO)_4$(L-L)	2023 m	1930 s	1917 s	1900 s
$W(CO)_4$(L-L)	2021 m	1926 s	1910 s	1897 s
fac-$MnCH_3(CO)_3$(L-L)	1996 s	1920 m	1884 m	
fac-$Mn(CH_3CO)(CO)_3$(L-L)	2000 s	1914 s, br		
fac-$MnCl(CO)_3$(L-L)	2028 s	1960 m	1908 m	
fac-$MnBr(CO)_3$(L-L)	2025 s	1961 m	1906 m	
fac-$MnI(CO)_3$(L-L)	2021 s	1958 m	1909 m	

[a] Mo and W complexes in methylcyclohexane; Mn and Fe complexes in dichloromethane.

Table III. $^{31}P\{^1H\}$ NMR Data for $Ph_2PCH_2CMe_2CH_2PPh_2$ Complexes

compd	resonance position,[a] MHz	δ[b]	δ[c]
free ligand (L-L)	36.271 425	0	−25.3
$W(CO)_4$(L-L)	36.272 340	25.28[d]	0
$MnCl(CO)_3$(L-L)	36.273 466	56.38	+31.1
$MnBr(CO)_3$(L-L)	36.273 376	53.90	+28.6
$MnI(CO)_3$(L-L)	36.273 259	50.66	+25.4

[a] $DCCl_3$ solution. Resonance positions are referenced to ^1H of Me_4Si at 89.603 877 MHz by using ^2D external lock on $DCCl_3$ as suggested by: Mann, B. E. In "NMR and the Periodic Table"; Harris, R. H., Mann, B. E., Eds.; Academic Press: New York, 1978; p 101. [b] Referenced to free ligand. [c] Referenced to external 85% H_3PO_4. [d] $^1J_{WP}$ = 224.6 Hz.

consistent with the IR data and ^1H and ^{13}C NMR spectra still to be discussed. A direct relationship between the electronegativities of the halogens and the ^{31}P chemical shifts for the halomanganese complexes is seen as the chemical shifts follow the trend Cl > Br > I.

^{1}H NMR. The ^1H NMR data for the new ligands and complexes prepared in this study are summarized in Table IV, and all assignments are based upon a chair configuration for the six-membered chelate ring system shown in Figure 1. The $M(CO)_4$(L-L) complexes, where M is Mo or W and (L-L) is either of the two new ligands 2,2-dm-1,3-dppp and 2,2-dm-1,3-dpap, are fluxional as a result of rapid chair ↔ chair interconversion.[20] For the complexes with the arsenic ligand both the methyl groups and methylene protons exchange equatorial and axial sites quite rapidly on the NMR time scale. No slowing of the exchange was perceptible down to −80 °C. Spectra of the fluxional complexes with the phosphorus donor ligands are complicated by coupling to phosphorus. The signal for the methylene protons is the apparent doublet expected for an $X_2AA'X'_2$ spin system where X = X' is ^1H and A = A' is ^{31}P. According to Harris,[21] the separation between the two strong lines in the apparent doublet is equal to $|^nJ_{AX} + {}^{n+2}J_{AX'}|$. For the particular ligand system employed here, $n = 2$ and the four-bond ^1H–^{31}P coupling is assumed to occur through the metal atom and not through the aliphatic chain bridging the donor atoms of the chelating ligand. With respect to this assumption, it should be noted that four-bond H–P coupling was not observed for the free ligand. The CH_3 resonance for the fluxional $M(CO)_4$(2,2-dm-1,3-dppp) is broader than the CH_3 resonance for the arsenic analogue. Inasmuch as broadening due to $^4J_{HH}$ coupling should be about the same for the two systems, the extra breadth for the CH_3 signal of the phosphorus compound must result from $^4J_{HP}$ coupling. If so, the upper limit for this $^4J_{HP}$ would be about 1.5 Hz. As will be shown below, $^4J_{HP}$ coupling of this type in a nonfluxional system must be included in the analysis of the spectra of the halomanganese complexes.

An examination of the structure of $XMn(CO)_3$(L-L) complexes in the effectively locked configuration shown in Figure 1 reveals the following facts: (a) the methyl groups should be chemical shift nonequivalent; (b) the geminal CH_2 protons should be chemical shift nonequivalent and in the absence of coupling to other nuclei constitute an AB spin system; (c) the two phenyl groups bound to a particular donor atom are also symmetry nonequivalent. The particular conformation suggested for the manganese complexes with the halogen atoms pointing over the chelate ring is based on the reports of crystal structure of related complexes.[22,23] Although a ring system such as that studied here cannot assume a chair configuration

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Table IV. ^{1}H NMR Spectral Data for $Ph_2ECH_2CMe_2CH_2EPh_2$ (E = P, As) Complexes[a]

	δ					$\lvert {}^2J_{HP} + {}^4J_{HP} \rvert$			
compd	CH_3(ax)	CH_3(eq)	CH_2(A)	CH_2(B)	$^2J_{H_{ax}H_{eq}}$	N_A	N_B	$\lvert {}^4J_{CH_3(eq)P} \rvert$	solvent
L-L = 2,2-dm-1,3-dppp									
(L-L)	1.11 (1)		2.41 (2)[b]						CH_2Cl_2
$Mo(CO)_4$(L-L)	0.83 (1)		2.44[c]			7.1			$CDCl_3$
$W(CO)_4$(L-L)[d,e]	0.84 (1)		2.55[c]			7.9			$CDCl_3$
fac-$Mn(CH_3)(CO)_3$(L-L)[d]	0.38 (1)	1.04 (3)	2.40		not measurable	not measurable		2.4	$CDCl_3$
fac-$Mn(CH_3CO)(CO)_3$(L-L)[f]	0.69 (1)	1.39 (3)	unresolvable		not measurable	not measurable		3.0	$CDCl_3$
fac-$MnCl(CO)_3$(L-L)[e]	0.37 (1)	1.09 (3)	3.21 (2)[g]	2.27 (2)[g]	14.1	7.6	15.5	2.8	$CDCl_3$
fac-$MnBr(CO)_3$(L-L)[e]	0.30 (1)	1.13 (3)	3.36 (2)[g]	2.35 (2)[g]	14.2	6.8	15.0	2.8	$CDCl_3$
fac-$MnI(CO)_3$(L-L)[e]	0.20 (1)	1.19 (3)	3.48 (2)[g]	2.50 (2)[g]	14.0	6.7	14.5	3.2	$CDCl_3$
$Fe(CO)_3$(L-L)	0.39 (1)		2.17			9.4			CS_2
L-L = 2,3-dm-1,3-dpap									
(L-L)	1.12 (1)		2.33 (1)						CH_2Cl_2
$Mo(CO)_4$(L-L)	0.99 (1)		2.31 (1)						CS_2
$W(CO)_4$(L-L)[e]	1.01 (1)		2.45 (1)						$CDCl_3$
fac-$Mn(CH_3)(CO)_3$(L-L)[h]	0.52 (1)	1.20 (1)	2.26 (1)						$CDCl_3$
fac-$Mn(CH_3CO)(CO)_3$(L-L)[i]	0.63 (1)	0.98 (1)	2.96 (2)[j]	2.27 (2)[j]	12.6				C_6H_6
fac-$MnCl(CO)_3$(L-L)[e]	0.43 (1)	1.18 (1)	3.02 (2)[j]	2.25 (2)[j]	12.6				$CDCl_3$
fac-$MnBr(CO)_3$(L-L)[e]	0.38 (1)	1.20 (1)	3.15 (2)[j]	2.46 (2)[j]	12.7				$CDCl_3$
fac-$MnI(CO)_3$(L-L)[e]	0.31 (1)	1.22 (1)	3.27 (2)[j]	2.46 (2)[j]	13.0				$CDCl_3$

[a] Chemical shifts are measured against internal Me_4Si at $\delta = 0$; J values are ±0.3 Hz or better; signal multiplicities are given in parentheses. Data are at 60 MHz except for compounds indicated by *e*, which were measured at 90 MHz. [b] $\lvert {}^2J_{HP} \rvert = 3.1 \pm 0.2$ Hz. [c] Apparent doublet. [d] CH_3Mn at $\delta = -0.68$ (3) with $^3J_{HP} = 90$ Hz. [e] 90-MHz data. [f] CH_3CO at $\delta = 1.95$ (1). [g] Doublet of apparent triplets; Figure 2B. [h] CH_3Mn at $\delta = -0.66$ (1). [i] CH_3CO at $\delta = 2.35$ (1). [j] See Figure 2A and text.

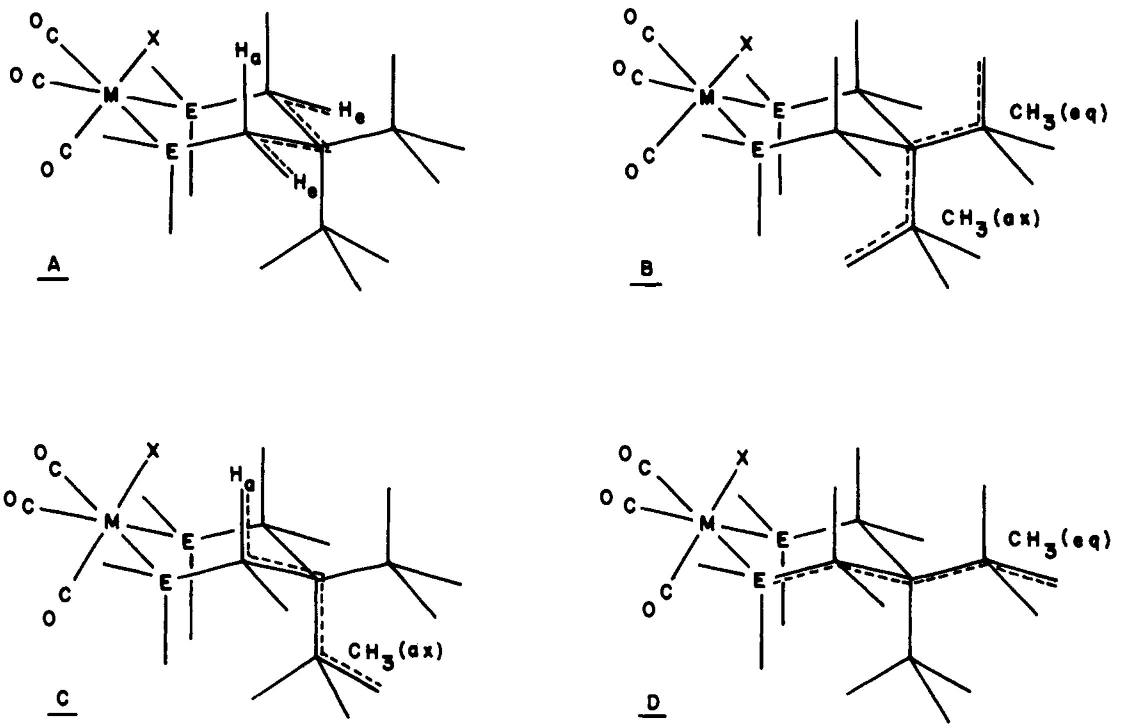

Figure 1. Illustration of the types of W-coupling possible in the six-membered chelate ring system $M–EPh_2–CH_2–CMe_2–CH_2–EPh_2$, where E = P, As (phenyl groups omitted in the diagrams): (A) CH_2(eq)–CH_2(eq) coupling; (B) CH_3(ax)–CH_3(eq) coupling; (C) CH_2(ax)–CH_3(ax) coupling; (D) E═P—CH_3(eq) coupling.

with the same bond and dihedral angles as cyclohexane, the structure is expected to be close enough to permit the defining of axial and equatorial positioning of the various ring substituents.

^{1}H NMR spectra of two manganese complexes prepared in this work are shown in Figure 2 and a summary of data on all manganese complexes is given in Table IV. Each spectrum is typified by the presence of two methyl resonance signals separated by 0.4–1.0 ppm. The more highly shielded of the two methyl resonance signals for complexes with 2,2-dm-1,3-dpap is the broader and is assumed to be that of the axial methyl group. The breadth of methyl signals has been accorded significance in reported studies on the ^{1}H NMR spectra of various substituted six-membered ring systems.[23-25] Invariably, axial methyl resonance signals are reported to be broader than those of equatorial methyl groups.[24-26] This broadening results from long-range coupling.

An empirical rule has been formulated which states that coupling over four bonds will be seen when the coupling atoms are coplanar with the three intervening bonds and the geometry of the bonds is an M or W.[27,28] The three types of W-coupling

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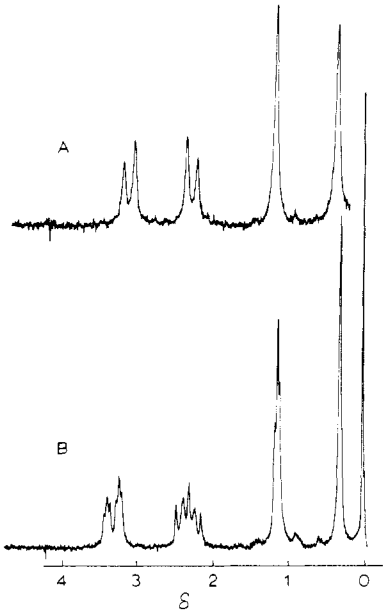

Figure 2. ^1H NMR spectra (90 MHz) of *fac*-$MnBr(CO)_3(Ph_2ECH_2CMe_2CH_2EPh_2)$ in $CDCl_3$ (Me_4Si at $\delta = 0$): (A) E = As; (B) E = P.

between hydrogen atoms possible for the diarsine chelate ring are illustrated in Figure 1. While it is true that coplanarity of the indicated coupling paths may not be as strict as in cyclohexane rings, the development of this argument does lead to a consistent assignment of chemical shifts for the diarsine and diphosphine complexes. The possibility of coupling between the two methyl groups exists and should lead to equivalent broadening of both signals. Coupling between the axial CH_3 and axial CH_2 can lead to broadening of the axial CH_3 resonance signal without affecting the equatorial CH_3 signal. The W-coupling between the equatorial methylene hydrogens will not affect the methyl groups. An examination of the spectrum of the 2,2-dm-1,3-dppp complex in Figure 2 reveals splitting of the lower field methyl resonance and no splitting of the higher field resonance. On the assumption that there is no interchange of relative chemical shifts for the methyl groups in the two very similar complexes, the small but additional coupling can only be related to the presence of the two equivalent ^{31}P nuclei with $^4J_{HP} = 2.8$ Hz. An examination of the fourth type of W-coupling in Figure 1 illustrates quite clearly that the geometry allows W-coupling of the ^{31}P nuclei only to the equatorial CH_3 groups and not to the axial CH_3. In support of this assignment is the observation that $^4J_{HP} = 2.3–2.7$ Hz for coupling between a ring phosphorus atom and an equatorial methyl group in 1,3,2-dioxaphosphorinanes. Coupling over the same distance to an axial methyl group is only 0.8 Hz.[29] It is interesting to note that for the isomer of 4,6-dimethyl-2-oxo-2-phenoxy-1,3,2-dioxaphosphorinane in which the methyl groups are anti oriented, the axial methyl group is the more shielded[29] while in the 3,3-dimethyl analogue the equatorial methyl group is reported to be more shielded.[30] Thus, a reliance on chemical shifts as a means of determining axial or equatorial positioning of substituents is dangerous.

The resonance signals for the CH_2 protons of the 2,2-dm-1,3-dpap complexes as seen in Figure 2 constitute a classical AB quartet. Calculations for the chemical shifts were carried out according to a well-known procedure,[31] and the results are tabulated together with the appropriate $^2J_{HH}$ values in Table IV. Coupling of the CH_2 protons to the ^{31}P nuclei is apparent in the spectra of the 2,2-dm-1,3-dppp complexes as each component of the expected AB quartet from hydrogen–hydrogen coupling is converted to an apparent triplet. The A portion of the spectrum consists of two well-separated apparent triplets with N_A values of 6.7–7.6 Hz.[21] In contrast, the B portion of the spectrum has an apparent five-line pattern, which must arise from coincidental overlap of two apparent triplets. N_B values of approximately 15 Hz were measured from the separation between the first and third and between the third and fifth lines of the five-line pattern.[21] As was pointed out in the case of the fluxional $M(CO)_4(L-L)$ complexes, the N values are equal to $|^2J_{HP} + {}^4J_{HP}|$. Although equatorial methylene hydrogen resonance signals are found to be deshielded by 0.1–0.7 ppm relative to those of axial protons in cyclohexanes, definitive assignments for the geminal methylene protons in the $XMn(CO)_3(L-L)$ are not possible. The average geminal coupling constants $^2J_{H_{ax},H_{eq}}$ for the 2,2-dm-1,2-dppp and 2,3-dm-1,3-dpap halomanganese complexes are 14.1 ± 0.1 and $12.8 = 0.2$ Hz, respectively, and are appropriate for tetrahedral carbon. The larger coupling for the complexes of 2,2-dm-1,3-dppp may be indicative of a slightly compressed CH_2 bond angle brought about by steric constraints that are released in the arsine complex owing to the difference in size of the donor atoms. A significant difference is noted between the N values of the methylene protons in the $XMn(CO)_3$(2,2-dm-1,3-dppp) complexes. If, as is normally the case, the $^2J_{HP}$ contribution to N is significantly greater than that of $^4J_{HP}$, this difference in N values could be a reflection of a difference in the two P–C–H bond angles. Alternatively, the significant difference in N values could be a reflection of different signs for the two $^4J_{HP}$ coupling constants. However, without additional spectral and structural data, further speculation regarding assignments and bond angles for the ring in general and the methylene protons in particular is not warranted.

^{13}C NMR. A summary of the ^{13}C NMR data obtained in this study is given in Table V. Discussion of the data can be simplified by taking advantage of the natural division of the ^{13}C spectra into aliphatic, aromatic, and carbonyl regions.

^{13}C-Aliphatic Region. The simplest proton-decoupled ^{13}C spectrum among those of the complexes studied here is that of $W(CO)_4$(2,2-dm-1,3-dpap) as it consists of three signals corresponding to the two symmetry-equivalent methylene carbons, the quaternary carbon, and the two time-equivalent methyl carbons. An off-resonance ^1H-decoupling experiment led to definite chemical shift assignments. In particular, the δ 39.25 signal becomes a triplet, thus locating the CH_2 resonance; the δ 35.77 signal remains a singlet as would be expected for the quaternary carbon; the δ 33.98 signal becomes a quartet and thereby is assigned to the methyl groups. With this information, the ^{13}C spectrum of the compound without proton decoupling is readily analyzed to give $^1J_{CH_3} = 126.5$ Hz and $^1J_{CH_2} = 131.5$ Hz. The values are in excellent agreement with tabulated values.[31] The $^{13}C\{^1H\}$ spectrum of $W(CO)_4$(2,2-dm-1,3-dppp) is complicated by coupling to the phosphorus nuclei. Both the methyl and quaternary carbon atoms form AX_2 spin sets with the phosphorus nuclei and yield 1:2:1 triplets with $^3J_{PC} = 7.3$ Hz and $^2J_{PC} = 2.7$ Hz, respectively. Coupling between the methylene carbon and phosphorus nuclei yields an apparent triplet. Inasmuch as these nuclei comprise an AXX′ spin set (A = ^{13}C, X = X′ = ^{31}P), a triplet could result with the separation of the outer lines equal to $|^1J_{CP} + {}^3J_{CP}| = 23.4$ Hz with $^3J_{CP}$ corresponding to coupling

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Table V. $^{13}C\{^1H\}$ NMR Spectral Data for $Ph_2ECH_2CMe_2CH_2EPh_2$ (E = P, As) Complexes[a]

		$W(CO)_4(Ph_2ECH_2CMe_2CH_2EPh_2)$		$Mn(CO)_3X(Ph_2AsCH_2$-$CMe_2CH_2AsPh_2)$			$Mn(CO)_3X(Ph_2PCH_2CMe_2CH_2PPh_2)$		
^{13}C site	$\lvert ^nJ_{CP}\rvert$[b]	δ(E = As)[c,d]	δ(E = P)[e]	δ(Cl)	δ(Br)	δ(I)	δ(Cl)	δ(Br)	δ(I)
				Aliphatic					
CH_3(ax)	$\lvert ^3J\rvert$	{33.98}	{34.34 (t, 7.3)}	30.63	30.43	30.04	31.45 (t, 2.6)	30.99 (t, 2.2)	30.47 (t, <2)
CH_3(eq)	$\lvert ^3J\rvert$			38.08	38.37	38.76	37.97 (t, 10.2)	38.40 (t, 10.6)	38.95 (t, 11.0)
CH_2	$\lvert ^1J + {}^3J\rvert$	39.25	40.45 (at, 23.4)	34.27	34.56	35.70	34.71 (at, 22.2)	35.28 (at, 22.7)	37.00 (at, 23.4)
C	$\lvert ^2J\rvert$	35.77	35.25 (t, 2.6)	36.22	36.42	36.68	34.97 (t, <2)	35.08 (t, <2)	35.41 (t, 1.8)
				Aromatic					
C-1	$\lvert ^1J + {}^3J\rvert$	138.22	138.32 (int, 41.0)	136.47	136.73	136.83	135.39 (at, 34,4)	135.39 (at, 34.0)	135.30 (at, 33.7)
C-2 (C-6)	$\lvert ^2J + {}^4J\rvert$	131.56	131.69 (at, 11.7)	132.24	132.20	132.14	131.98 (at, 8.8)	131.88 (at, 8.8)	131.85 (at, 8.1)
C-3 (C-5)	$\lvert ^3J + {}^5J\rvert$	128.73	128.31 (at, 8.8)	128.31	128.21	127.98	127.98 (at, 8.8)	127.88 (at, 8.8)	127.69 (at, 9.5)
C-4	$\lvert ^4J\rvert$	129.48	129.54 (s)	129.28	129.28	129.28	129.48 (s)	129.41 (s)	129.38 (s)
C-1′	$\lvert ^1J + {}^3J\rvert$			138.16	138.03	138.00	138.26 (at, 44.0)	138.13 (at, 45.4)	137.93 (at, 46.2)
C-2′ (C-6′)	$\lvert ^2J + {}^4J\rvert$			133.35	133.31	133.18	132.18 (at, 10.3)	133.83 (at, 10.3)	133.93 (at, 10.3)
C-3′ (C-5′)	$\lvert ^3J + {}^5J\rvert$			128.76	128.70	128.63	128.34 (at, 8.1)	128.27 (at, 8.8)	128.21 (at, 8.8)
C-4′	$\lvert ^4J\rvert$			130.16	130.09	130.00	130.55 (s)	130.55 (s)	130.48 (s)
				Carbonyl					
cis (P)	^2J	202.08	202.96 (t, 6.6)	*f*	*f*	*f*	*f*	*f*	*f*
trans (P)	^2J	205.73	205.93 (d, 16.1)	*f*	*f*	*f*	222.5 (br)		226.0 (br)

[a] δ values are in ppm from ^{13}C of internal Me_4Si. $\lvert J\rvert$ values are in Hz. All data are on $CDCl_3$ solutions. [b] J_{CP} values are in Hz, and band shapes are given in parentheses for complexes of 2,2-dm-1,3-dppp. Abbreviations: s, singlet; d, doublet, t, triplet; at, apparent triplet; int., "5"-fine-line pattern described in text. [c] Assignments based on off-resonance experiment: δ 33.98 (quartet); δ 35.77 (singlet); δ 39.25 (triplet); C-1 (singlet); C-2, C-3, C-4 (doublet). [d] From hydrogen-coupled spectrum: $^1J_{CH}(CH_3) = 126.5$ Hz; $^1J_{CH}(CH_2) = 131.5$ Hz. [e] From hydrogen-coupled spectrum: $^1J_{CH}(CH_3) = 126.3$ Hz; $^1J_{CH}(CH_2) = 125.8$ Hz. [f] Not readily observable.

through the metal atom.[21,32] Alternatively, three bond ^{13}C–^{31}P coupling could be seen through the aliphatic carbon chain. In the latter case, a doublet of doublets might be anticipated. The spectrum of the uncomplexed ligand reveals just such a doublet of doublets with coupling constants of 9.2 and 17.7 Hz. Certainly the possibility exists that the apparent triplet seen for the tungsten complex arises from near coincidence of two lines of a doublet of doublets if $^1J_{CP} \cong {}^3J_{CP} \cong 11.7$ Hz. However, we prefer to assign this triplet as an apparent triplet arising from coupling through the metal atom and will employ this approach in the remainder of the paper. Analysis of the spectrum of the W compound without proton-decoupling yielded $^1J_{CH_3} = 126.3$ Hz and $^1J_{CH_2} = 125.8$ Hz.

The $^{13}C\{^1H\}$ spectra of the manganese complexes all consist of four signals, excluding coupling to phosphorus, and provide clear evidence of the nonequivalence of the methyl groups in these facial complexes. Inasmuch as the ideal ratio of these signals is 2:1:1:1, complete and definite spectral assignments for these complexes are impossible without additional information. With use of chemical shift positions observed in the $^{13}C\{^1H\}$ spectrum of $BrMn(CO)_3$(2,3-dm-1,3-dpap) and with $^1J_{CH} = 126$ Hz, the ^{13}C spectrum of this compound can be reasonably predicted as shown in Figure 3. Fortunately, there is no $^2J_{CH}$ coupling possible in this ring system and $^3J_{CH}$ is generally very small. Thus, the use of only $^1J_{CH}$ in making a prediction for the spectrum is reasonable. The analysis clearly determines the chemical shift position for the CH_2 and quaternary carbon atoms. However, a specific assignment of the two methyl carbon quartets to the axial and equatorial methyl groups cannot be made directly. On the basis of an argument to be presented below, the $^{13}CH_3$ signals at δ 30.0 and 38.8 are assigned to the axial and equatorial groups, respectively.

The $^{13}C\{^1H\}$ spectrum of $IMn(CO)_3$(2,2-dm-1,3-dppp) shown in Figure 4 reveals clearly the strong coupling of two types of aliphatic carbon atoms to the ^{31}P nuclei. Broadening of the other two signals is most likely a result of weaker coupling to the ^{31}P nuclei. The strong triplet, actually an apparent triplet, centered at δ 37.00 can be assigned as the $^{13}CH_2$ resonance position. This spin system is of the AXX′ type, and the separation of the outer lines is $\lvert ^1J_{CP} + {}^3J_{CP}\rvert$. On the assumption that the lowest and highest field signals are those of the CH_3 group as was determined from the spectrum of the arsine complex shown in Figure 3, the remaining resonance at δ 35.41 is that of the quaternary carbon atom. On the basis of these assignments and with a constant $^1J_{CH} = 126$ Hz, the ^{13}C hydrogen-coupled spectrum was approximated. As shown in Figure 4, the stick spectrum and actual ^{13}C spectrum match quite closely. Alternative assignments give poor agreement between observation and prediction. Incontrovertible evidence for these ^{13}C chemical shift assignments was provided by two separate experiments. A spin-echo experiment employing gated broad-band proton decoupling clearly differentiated those carbon nuclei carrying an odd number of hydrogen atoms (atomatic CH and CH_3) from those with either no or an even number of hydrogen atoms (aromatic C–P; aliphatic quaternary C and CH_2).[33] A trace of the aliphatic region under these experimental conditions is shown in Figure 5A. The aliphatic CH_2 and quaternary carbon signals are absolutely defined by the results of an INEPT experiment[34] shown in Figure 5B. As can be readily seen, the δ 35.4 signal disappears under INEPT conditions, a phenomenon which can occur only for the quaternary carbon atom owing to the absence of polarization transfer. Thus, the stronger δ 37.00 resonance with the same phase shift must be the $^{13}CH_2$ signal.

In contrast to the uncertainty associated with assignments of the axial vs. equatorial $^{13}CH_3$ resonance signals for complexes of the arsine ligand, specific assignments are possible for the 2,2-dm-1,3-dppp complexes. Karplus[35] has shown a correlation to exist between $^3J_{HH}$ values and the dihedral angle of the two planes defined by the three adjoining bonds in organic compounds. This correlation is known to apply to other nuclei and in particular to three-bond coupling between carbon and phosphorus.[36,37] A model of the halomanganese

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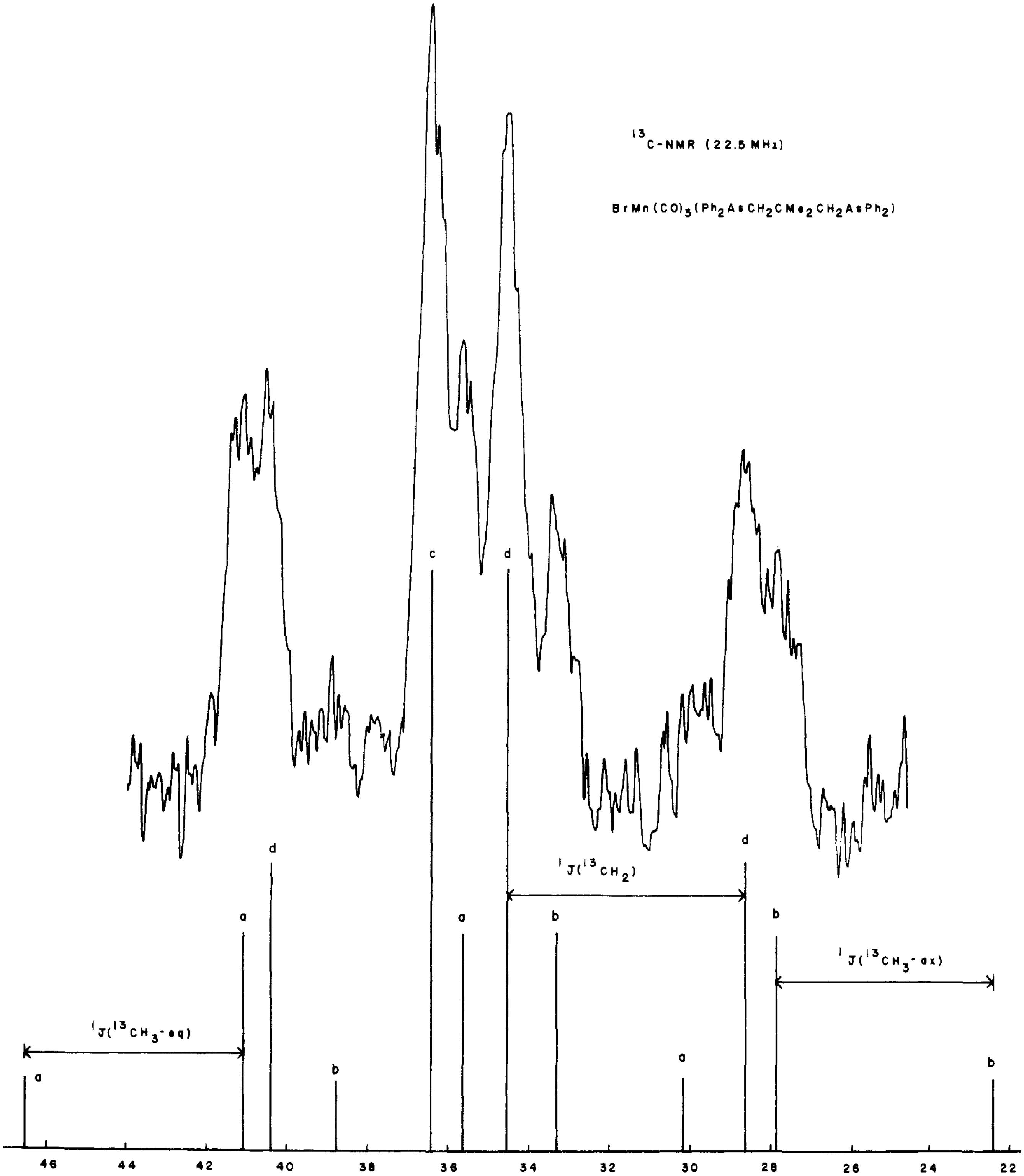

Figure 3. ^{13}C NMR spectrum (22.5 MHz) in the aliphatic carbon region for *fac*-$BrMn(CO)_3(Ph_2AsCH_2CMe_2CH_2AsPh_2)$ in $CDCl_3$ (Me_4Si internal standard at $\delta = 0$): a, CH_3(eq); b, CH_3(ax); c, C (quaternary); d, CH_2.

complexes of the diphosphine ligand reveals the dihedral angles for the $P-C-C-C_{ax}$ and $P-C-C-C_{eq}$ three-bond systems to be about 90 and 170°, respectively. These angles are close to the minimum and maximum in the Karplus curve and suggest $^3J_{C_{ax}P}$ should be small and $^3J_{C_{eq}P}$ considerably larger. Thus, the triplet at δ 38.95 is assigned to the equatorial $^{13}CH_3$ with $^3J_{CP} = 11.0$ Hz; the signal centered at δ 30.47 must be that of the axial $^{13}CH_3$ with $^3J_{CP} < 2$ Hz.

Several trends in the ^{13}C spectra of the manganese complexes are apparent. Both $\delta(CH_2)$ and $\delta(C_q)$ follow the order I > Br > Cl, a trend which is opposite to the electronegativity order for the halogens. The changes in $\delta(CH_2)$ as a function of the halogen for the phosphorus ligand complexes are greater than for the arsine complexes and in both sets of complexes are greater than changes for $\delta(C_q)$. As a result, whereas $\delta(CH_2) < \delta(C_q)$ for the arsine ligand complexes and the chloro complex with the diphosphine, a chemical shift reversal of these two signals occurs for the bromo and iodo complexes with the diphosphine.

Exactly why the ^{31}P chemical shifts of the $XMn(CO)_3$-(2,2-dm-1,3-dppp) complexes parallel the electronegativities of the halogens and the chemical shifts of the ^{13}C nuclei in

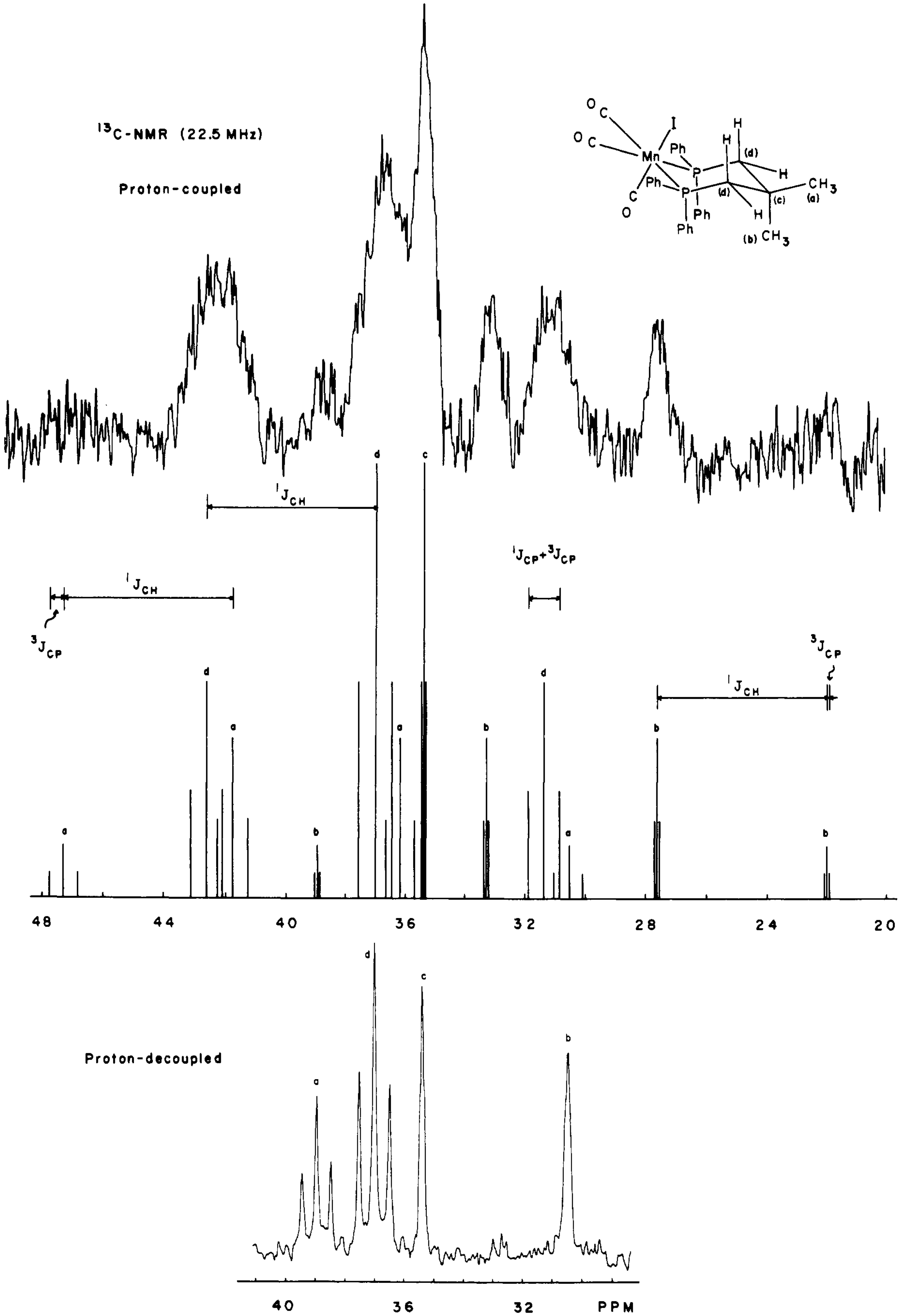

Figure 4. ^{13}C NMR spectra (22.5 MHz) of *fac*-$IMn(CO)_3(Ph_2PCH_2CMe_2CH_2PPh_2)$ in $CDCl_3$ with Me_4Si as internal standard at $\delta = 0$: top spectrum, proton coupled; bottom spectrum, proton decoupled. Assignments: a, CH_3(eq); b, CH_3(ax); c, C (quaternary); d, CH_2.

the carbon chain connecting the ligand donor atoms do not is an interesting question. Although there are insufficient published data with which to compare the present observations, the fact that the chemical shifts for $\delta(CH_2)$ and $\delta(C_q)$ do parallel the size of the halogen does seem to be significant. The chemical shift difference between the ^{13}C resonance for the equatorial and axial methyl groups also follows the order I > Br > Cl. Once again, the effect is greater with the

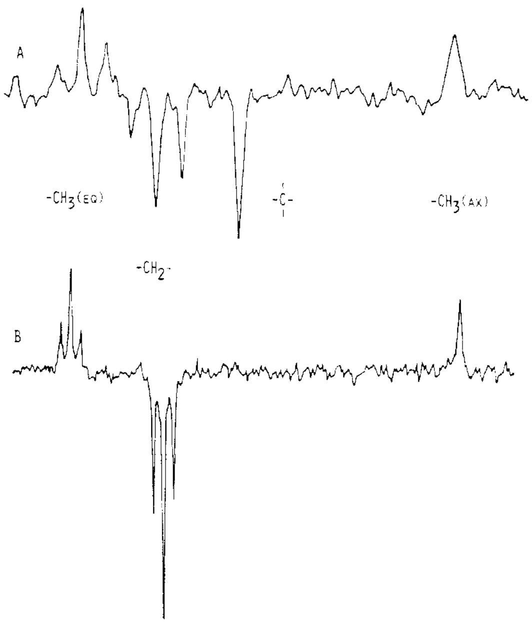

Figure 5. ^{13}C NMR spectra of *fac*-$IMn(CO)_3(Ph_2PCH_2CMe_2CH_2PPh_2)$ in $CDCl_3$: (A) 20.1-MHz spectrum with use of modified sequence shown in ref 33; (B) 50.3-MHz spectrum—INEPT program.

phosphine donor ligand than with the arsine donor ligand. Inasmuch as phosphorus is smaller than arsenic, halogen–chelate ring and halogen–phenyl steric interactions would be greater in the phosphine complexes, and these in turn would lead to more pronounced effects on chemical shifts with increasing size of the halogen than would be expected for the arsine complexes. It is interesting to note that the average of the two $\delta(^{13}CH_3)$ values is a constant in each series; the values are δ 34.4 and 34.7 for the arsine and phosphine complexes, respectively.

^{13}C-Aromatic Region. Although the ^{13}C resonance signals of aryl phosphorus donor ligands have been frequently neglected, some reports including total analysis have been given.[38] Analyses for the aromatic carbon ^{13}C region of the complexes reported here are summarized in Table V. As can be expected, ^{13}C spectra of the two fluxional tungsten complexes are characterized by equivalence of the aromatic groups bound to the donor atoms. In contrast, two distinctly separate sets of phenyl resonance signals are observable for the halomanganese complexes owing to the absence of a symmetry plane containing the chelate ligand donor atoms and the manganese. The chemical shifts of C-1 and C-4 in all cases are readily apparent from observation of the intensity of the spectral lines. The choice of the most deshielded signal for C-4 in $W(CO)_4$(2,2-dm-1,3-dpap) was evident from the doubling of this signal in an off-resonance spectrum and lack of doubling for C-1. For all of the complexes with 2,3-dm-1,3-dppp, C-1 was assigned as the signal showing the strongest coupling to phosphorus. Also, in the spin-echo gated broad-band decoupling experiment described earlier, this signal showed the same phase shift as the methylene and aliphatic quaternary carbon atoms. The chemical shift assignments for C-2 (C-6) and C-3 (C-5) are made on the assumption that δ(C-2(6)) should be greater than δ(C-3(5)). This ordering agrees with an ordering reported earlier.[38]

A special comment regarding the shape of the ^{13}C aromatic resonance signals is necessary. The spin set comprising any one ^{13}C atom and the two ^{31}P nuclei is described as AXX′ (A = ^{13}C, X = X′ = ^{31}P), and the line shape is very dependent upon the relative values of the three coupling constants $^2J_{XX'}$, $^nJ_{AX}$, and $^{n+2}J_{AX}$. The shape of the signal is an apparent sharp triplet with the separation of the outer lines equal to $|^nJ_{AX} + {}^{n+2}J_{AX}|$ when $^2J_{XX'}$ is large. For $^2J_{XX'} = 0$, the system degenerates to a real doublet with a separation of $^nJ_{AX}$. For intermediate $^2J_{XX'}$ values, the spectrum consists of five lines with the separation of the second and fourth lines equal to $|^nJ_{AX} + {}^{n+2}J_{AX}|$.[32] The J values given in Table V were assigned on this basis. With one important exception, the ^{13}C resonance signals for C-1, C-2 (C-6), and C-3 (C-5) for the complexes with 2,2-dm-1,3-dppp are apparent triplets. ^{31}P coupling to C-4 is effectively nonexistent, and the signal is a singlet. The exception to the general observation of triplets for C-1 is seen in the spectrum of $W(CO)_4$(2,2-dm-1,3-dppp) in which a five-line signal is seen for C-1. Apparently $^2J_{PP'}$ is quite small (10–15 Hz), and because of the large value of $|^1J_{CP} + {}^3J_{CP'}|$ the uncommon line shape is evident. For C-2 and C-3, the signals resemble classical apparent triplets because the respective $|^2J_{CP} + {}^4J_{CP'}|$ and $|^3J_{CP} + {}^5J_{CP'}|$ are much smaller than $|^1J_{CP} + {}^3J_{CP'}|$. Others have reported that for C-1 in $M(CO)_4(Ph_2PCH_2CH_2PPh_2)$, where M is Mo or W, the signal shape is a doublet and thereby $^2J_{PP'}$ is effectively zero.[38]

A tentative identification of the signal sets for the axial and equatorial phenyl groups in the complexes of 2,2-dm-1,3-dppp is possible. An examination of the chair structure proposed for these complexes shows C-1 of an equatorial phenyl group to be correctly positioned for strong Karplus-type coupling over three bonds to the distant phosphorus atom, P′. In contrast, $^3J_{CP'}$ between C-1 of an axially positioned phenyl group and P′ should approach zero. Experimentally one set of $|^1J_{CP} + {}^3J_{CP'}|$ values averages 45 Hz and the other averages 34 Hz. On the assumption that $^1J_{CP}$ is nearly the same for the axial and equatorial phenyl groups, the larger N values might correspond to the larger $^3J_{CP'}$ and thus identify the signals of the equatorial phenyl group. This argument assumes the signs of the two coupling constants are the same.

^{13}C-Metallocarbonyl Region. Although the major emphasis of the current study focused on ^1H, ^{31}P, and ^{13}C NMR properties of complexes of the two new ligands $Ph_2ECH_2CMe_2CH_2EPPh_2$, some data in the metallocarbonyl ligands were obtained are are included in Table V. The assignments of cis and trans ^{13}C signals follow those from earlier studies.[2]

Discussion. The two ligands $Ph_2ECH_2CMe_2CH_2EPh_2$ were originally synthesized because of their potential as structural probes for defining structures of complexes in which isomers could arise. As shown earlier in this paper, this goal has been achieved for $XMn(CO)_3$(L-L) complexes as both the ^1H and ^{13}C NMR spectra of these complexes indicate unequivocally a common facial configuration for the complexes. In summarization of the results, the presence of dissimilar methyl groups was illustrated by both ^1H and ^{13}C NMR. In the ^1H spectra, AB quartets for the methylene protons are indicative of nonequivalent geminal hydrogen atoms. Two groups of phenyl resonance signals in the ^{13}C spectra yield still one more piece of evidence defining the facial structures. Of course, the infrared data, which can be misleading for $XMn(CO)_3$(L-L) complexes, and the ^{31}P data also support the facial configuration.

Other than defining the geometry of coordination at manganese in the $XMn(CO)_3$(L-L) complexes, the NMR results reported here are of still further importance for two reasons. First, the results indicate that both the concept of W-coupling and application of the Karplus correlation find applicability to analysis of spectra of six-membered chelate ring systems. Second, the results illustrate further the importance of considering $^2J_{PP'}$ in the interpretation of both the ^1H and ^{13}C

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NMR spectra of *cis*-bis(phosphine) complexes.[39,40] Certainly the effect of $^2J_{PP'}$ is seen in both types of spectra and when properly recognized leads to no real interpretation problems. Admittedly, ^1H spectra of $X_nAA'X'_n$ systems do lead to more complex spectra than ^{13}C spectra which are of an AXX′ type, but the two types of spectra are complementary.

Registry No. (2,2-dm-1,3-dppp), 80326-98-3; (2,2-dm-1,3-dpap), 80326-99-4; $Mo(CO)_4$(2,2-dm-1,3-dppp), 80327-49-7; $Mo(CO)_4$(2,2-dm-1,3-dpap), 80327-48-6; $W(CO)_4$(2,2-dm-1,3-dppp), 80327-47-5; $W(CO)_4$(2,2-dm-1,3-dpap), 80327-46-4; $Mn(CH_3CO)(CO)_3$(2,2-dm-1,3-dppp), 80327-65-7; $Mn(CH_3CO)(CO)_3$(2,2-dm-1,3-dpap), 80327-64-6; $Mn(CH_3)(CO)_3$(2,2-dm-1,3-dppp), 80327-63-5; $Mn(CH_3)(CO)_3$(2,2-dm-1,3-dpap), 80327-62-4; $MnCl(CO)_3$(2,2-dm-1,3-dppp), 80327-61-3; $MnCl(CO)_3$(2,2-dm-1,3-dpap), 80327-60-2; $MnBr(CO)_3$(2,2-dm-1,3-dppp), 80327-59-9; $MnBr(CO)_3$(2,2-dm-1,3-dpap), 80327-58-8; $MnI(CO)_3$(2,2-dm-1,3-dppp), 80327-57-7; $MnI(CO)_3$(2,2-dm-1,3-dpap), 80327-56-6; $Fe(CO)_3$(2,2-dm-1,3-dppp), 80327-55-5.

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(Pentamethylcyclopentadienyl)cobaltaboranes Derived from the $B_5H_8^-$ and $B_9H_{14}^-$ Ions: Studies in Synthesis and Structure[1]

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The reactions of $B_5H_8^-$ and $B_9H_{14}^-$ ions (both generated from B_5H_9 and NaH in THF solution under different conditions) with $CoCl_2$ and $Li^+[C_5(CH_3)_5]^-$ in THF were examined. The two reaction systems generate entirely different cobaltaborane products, which were isolated as air-stable, colored crystalline solids and characterized by ^{11}B and ^1H FT NMR spectroscopy at 115.5 and 360 MHz, respectively, by unit- and high-resolution mass spectrometry and infrared spectra, and (in five cases) by X-ray diffraction studies which are reported in the following two papers. From the $B_9H_{14}^-$ reaction four products were characterized, all of which are 10-vertex CoB_9 or Co_2B_8 nido cages analogous to $B_{10}H_{14}$; the major species, 6-$[C_5(CH_3)_5]CoB_9H_{13}$, was obtained in 25% yield. Minor products were 6,9-$[C_5(CH_3)_5]_2Co_2B_8H_{12}$, 5,7-$[(C_5(CH_3)_5]_2Co_2B_8H_{12}$, and the 6-chloro derivative of the latter compound. The $B_5H_8^-$ reaction generates a larger and structurally more diverse series of products, none in greater than 5% yield. The major products obtained after a 2-h reaction period at room temperature are 2-$[C_5(CH_3)_5]CoB_4H_8$, 1,2-$[C_5(CH_3)_5]_2Co_2B_4H_6$, and 1,2,3-$[C_5(CH_3)_5]_3Co_3B_4H_4$, all of which are analogous to cyclopentadienyl complexes obtained in the reaction of $B_5H_8^-$ with $CoCl_2$ and $C_5H_5^-$ reported earlier. Minor products, which do *not* have known C_5H_5 counterparts, consist of 1,2-$[C_5(CH_3)_5]_2Co_2B_5H_7$, $[C_5(CH_3)_5]_2Co_2B_5H_9$, and 5,9-$[C_5(CH_3)_5]_2Co_2B_8H_{12}$. The structures deduced for these species are, respectively, pentagonal bipyramidal (closo), nido, and nido; the last species is isomeric with the Co_2B_8 complexes obtained from $B_9H_{14}^-$. Thermal rearrangement of 2-$[C_5(CH_3)_5]CoB_4H_8$, a nido cage analogous to B_5H_9, gave the 1-isomer. Thermolysis of 1,2-$[C_5(CH_3)_5]_2Co_2B_5H_7$ resulted in loss of hydrogen to give $[C_5(CH_3)_5]_2Co_2B_5H_5$, a 2*n*-electron cage system that has been assigned a capped-octahedral geometry.

Interactions of transition-metal cations with the $B_5H_8^-$ anion have proved to be a remarkably fertile source of metallaborane clusters. In earlier work,[2] the reaction of $CoCl_2$, NaB_5H_8, and NaC_5H_5 in cold tetrahydrofuran (THF) was found to give, following workup in air, a series of crystalline, air-stable, structurally interesting cobaltaboranes of general formula $[(C_5H_5)Co]_n(BH)_mH_p$ where $1 \leq n \leq 4$. This reaction generated the first known examples of *closo*-metallaboranes (exclusive of metallacarboranes), of electron-hyperdeficient (hypercloso) metallaboranes, of tetrametallic boron clusters, and of partial incorporation of a cyclopentadienyl ring into a boron cage. In addition, two of the products $[(C_5H_5)_2Co_2B_4H_6$ and $(C_5H_5)_3Co_3B_3H_5]$ were shown to have face-bridging hydrogen atoms associated with the metals,[2,3] a feature not previously established in boron chemistry although it had been postulated in certain metallacarboranes from NMR data. In all of these cases, molecular structures of key compounds have been established by X-ray crystallography,[3-7] and the results in general are in agreement with the Wade electron-counting rules for clusters[8] (an exception, however, is $(C_5H_5)_4Co_4B_4H_4$[6]).

These findings on the $CoCl_2/B_5H_8^-/C_5H_5^-$ reaction system pointed to several lines of further study, including (1) interactions of other metal cations with $B_5H_8^-$ and $C_5H_5^-$, (2) reactions of metal cations with $B_5H_8^-$ in the *absence* of $C_5H_5^-$ or other ligands, and (3) reactions in which another coordinating ligand is employed in place of $C_5H_5^-$. With respect to (1), we have reported that $FeCl_2$[9] and $NiBr_2$[10] in the presence of $B_5H_8^-$ and $C_5H_5^-$ generate isolable metallaboranes that differ markedly in composition and structure from those obtained with $CoCl_2$ and from each other. Studies relating to the second point are in progress; complexes formed from $B_5H_8^-$ and metal halides of iron, cobalt, nickel, ruthenium, and rhodium are ionic and difficult to characterize, but THF solutions containing these species exhibit significant catalytic activity in the homogeneous hydrogenation of alkynes and alkenes under mild conditions.[11]

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