

Synthesis and Spectra of Cationic Bis(tertiary phosphine) Derivatives of Cycloheptatrienylium-molybdenum and Cyclopentadienyliron Complexes

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Summary

Reaction of $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3][\text{PF}_6]$ and $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_3\text{CN}][\text{PF}_6]$ with ditertiary phosphine ligands afforded products of three types; the monosubstituted complexes $[(\text{Ring})\text{M}(\text{CO})_2\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2][\text{PF}_6]$ (Ring = $\eta\text{-C}_7\text{H}_7$, M = Mo, n = 1; Ring = $\eta\text{-C}_5\text{H}_5$, M = Fe, n = 1 and 2), the chelated complexes $[(\text{Ring})\text{M}(\text{CO})\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2][\text{PF}_6]$ (Ring = $\eta\text{-C}_7\text{H}_7$, M = Mo, n = 1 and 2; Ring = $\eta\text{-C}_5\text{H}_5$, M = Fe, n = 1 and 2), and the dinuclear complex $\{[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_2]_2-\mu\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\}[(\text{PF}_6)_2]$. Spectroscopic properties, including ^{31}P NMR, are reported.

Introduction

We recently reported the preparation of several useful intermediate complexes of the type $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_2\text{-L}][\text{PF}_6]$ in which L is a tertiary phosphine, arsine or

stibine ligand [1]. Since complexes of this type were with one exception unknown, the work was extended to include the bidentate phosphines bis(diphenylphosphino)methane (dpm) and bis(diphenylphosphino)ethane (dpe). The products included examples of the ditertiary phosphines behaving as monodentate, bidentate chelate, and bidentate bridging ligands. This variety of coordination patterns provides useful new ^{31}P NMR data complementing our work on $(\text{OC})_3\text{Mo}(\text{dpm})_2$ isomers [2], and bearing on the general problem of the influence of chelate ring size on ^{31}P chemical shifts.

Experimental

Melting points were determined using a microscope with Kofler hot stage. Analytical results (Table 1) were obtained by the Microanalytical Laboratory of this department. Table 1 lists as footnotes molar conductivities of selected ionic derivatives.

Infrared spectra of the carbonyl stretching region were measured by means of a Perkin-Elmer Model 337 spectrometer at a scanning rate of $39\text{ cm}^{-1}\text{ min}^{-1}$, and recorded in expanded form (1 cm of chart $\approx 10\text{ cm}^{-1}$) on an external recorder. Spectra were calibrated with bands of gaseous CO and DBr, and are considered accurate to $\pm 1\text{ cm}^{-1}$. Band positions quoted in Table 2 refer to the midpoint at half-height.

Proton NMR spectra were measured on Varian A56/60 or A56/60a instruments using tetramethylsilane as an internal standard. The NMR data are included in Table 2.

TABLE I

YIELDS, COLORS, MELTING POINTS, MICROANALYTICAL DATA AND CONDUCTIVITY^a

Compound	Yield (%)	Color	M.P. (°C)	Calcd. %		Found %	
				C	H	C	H
$[C_7H_7Mo(CO)_2Ph_2PCH_2PPh_2][PF_6]^b$	30	red	242-245	52.87	3.78	52.50	3.60
$[C_7H_7Mo(CO)Ph_2PCH_2PPh_2][PF_6]$	43	red-brown	231-233	53.24	3.93	53.03	3.88
$[C_7H_7Mo(CO)Ph_2PC_2H_4PPh_2][PF_6]^c$	40	red-brown	228-231	53.84	4.12	53.73	4.60
$[C_7H_7Mo(CO)_2Ph_2PC_2H_4PPh_2][(PF_6)_2]^d$	16	orange-red	220 dec.	44.99	3.26	44.94	3.30
$[C_5H_5Fe(CO)_2Ph_2PCH_2PPh_2][PF_6]$	79	yellow	200-205	54.41	3.85	53.84	3.97
$[C_5H_5Fe(CO)_2Ph_2PC_2H_4PPh_2][PF_6]$	71	pale yellow	198-199	55.00	4.05	54.18	4.15
$[C_5H_5Fe(CO)Ph_2PCH_2PPh_2][PF_6]$	88	orange-yellow		54.70	3.98	54.71	4.09
$[C_5H_5Fe(CO)Ph_2PC_2H_4PPh_2][PF_6]$	58	yellow	191-194	55.51	4.22	55.06	4.32

^a Conductivity measurements quoted in footnotes b-d were performed on ca. 10^{-3} M solutions in nitromethane at 25° using a Phillips conductivity bridge, model PR9500.

^b $87.9 \text{ cm}^2 \text{ ohm}^{-1} \text{ mole}^{-1}$.

^c $71.4 \text{ cm}^2 \text{ ohm}^{-1} \text{ mole}^{-1}$.

^d $172.7 \text{ cm}^2 \text{ ohm}^{-1} \text{ mole}^{-1}$.

TABLE 2

CARBONYL STRETCHING FREQUENCIES^a AND ¹H NMR DATA

Compound	Frequencies (cm ⁻¹)	Chemical Shift (τ Value) ^b	
		C ₇ H ₇ or C ₅ H ₅	CH ₂
[C ₇ H ₇ Mo(CO) ₂ Ph ₂ PCH ₂ PPh ₂][PF ₆]	2025(10.0) 1978(8.2)	4.22 d (2.3)	6.3(9.0, 2.0)
[C ₇ H ₇ Mo(CO)Ph ₂ PCH ₂ PPh ₂][PF ₆]	1963	4.30 t (2.7)	d
[C ₇ H ₇ Mo(CO)Ph ₂ PC ₂ H ₄ PPh ₂][PF ₆]	1958	4.40 t (2.3)	7.2 br
[(C ₇ H ₇ Mo(CO) ₂ Ph ₂ PC ₂ H ₄ PPh ₂)] ₂ [(PF ₆) ₂] ^c	2018(10.0) 1937(8.8)	4.74 t (1.1)	8.20 br
[C ₅ H ₅ Fe(CO) ₂ Ph ₂ PCH ₂ PPh ₂][PF ₆]	2055(9.9) 2012(10.0)	4.85 d (1.6)	6.5(11, 1.7)
[C ₅ H ₅ Fe(CO) ₂ Ph ₂ PC ₂ H ₄ PPh ₂][PF ₆]	2058(10.0) 2010(10.0)	4.86 d (1.6)	7.2 br
[C ₅ H ₅ Fe(CO)Ph ₂ PCH ₂ PPh ₂][PF ₆]	1983	4.92 t (1.4)	e
[C ₅ H ₅ Fe(CO)Ph ₂ PC ₂ H ₄ PPh ₂][PF ₆]	1981	4.92 t (1.5)	7.5 br

^a Dichloromethane solutions, except where noted. Figures in parenthesis are relative band intensities.

^b Measured in CD₃CN relative to TMS. P-C₆H₅ τ values not given. Figures in parenthesis are J values in Hz. Key: d = doublet, t = triplet, br = broad.

^c IR measured in CH₃CN solution.

^d AB pattern with H_A = 4.8, H_B = 5.6, J_{AB} = 16 Hz, ¹J_{P-CH₂} = 10 Hz.

^e AB pattern with H_A = 4.9, H_B = 5.5, J_{AB} = 16 Hz, ¹J_{P-CH₂} = 12 Hz.

Proton-decoupled phosphorus-31 NMR spectra were obtained on a Bruker HFX-90 operating at 36.4 MHz using a deuterium lock and a sealed capillary of P_4O_6 as an external standard. The chemical shift values are quoted relative to 85% H_3PO_4 which was taken to be 112.5 ppm upfield from P_4O_6 .

Tricarbonyl(η -cycloheptatrienyl) molybdenum(I) hexafluorophosphate and acetonitriledicarbonyl(η -cyclopentadienyl)iron(I) hexafluorophosphate were prepared by established methods [3],[4]. Bis(diphenylphosphino)methane and bis(diphenylphosphino)ethane were purchased from Strem Chemicals Inc., and were used without further purification. Ethanol used as reaction solvent was "95%" grade; all other solvents used were reagent grade. All reactions were performed under a nitrogen atmosphere.

Preparation of $[(\eta-C_7H_7)Mo(CO)_2Ph_2PCH_2PPh_2][PF_6]$

Dpm (1.8 g, 4.8 mmol) and $[(\eta-C_7H_7)Mo(CO)_3][PF_6]$ (2.0g, 4.8 mmol) were stirred at 50-55° in 100 ml of acetone for 0.5 h. The IR spectrum in the carbonyl stretching region showed that some starting material was still present, and thus an additional 0.5 g of ligand was added. After a further 15 min, the solvent was removed on a rotary evaporator using water aspiration. The resulting oil was chromatographed over a Florisil column (2.5 x 20 cm). Dichloromethane eluted a yellow band which was recrystallized from dichloromethane-ethanol to yield 0.5 g of pale yellow crystals. This compound was identified as a mixture of *fac* and *mer* isomers of $(CO)_3Mo(Ph_2PCH_2PPh_2)_2$ by comparisons with authentic samples [2]

A second red band consisting of $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_2\text{Ph}_2\text{PCH}_2\text{PPh}_2][\text{PF}_6]$ was eluted with dichloromethane:acetonitrile (4:1) and was recrystallized from dichloromethane to give 1.1 g (30% yield) of red crystals.

Use of a twofold excess of ligand, under otherwise identical reaction conditions and purification procedures, resulted in 1.6 g (35% yield) of $(\text{CO})_3\text{Mo}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2$ as the major product.

Preparation of $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})\text{Ph}_2\text{PCH}_2\text{PPh}_2][\text{PF}_6]$

Dpm (1.6 g, 4.2 mmol) was added to a hot ethanol solution (100 ml) of $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3][\text{PF}_6]$ (2.0 g, 4.8 mmol) and the mixture refluxed for 1.5 h. The red reaction mixture was allowed to cool to room temperature and the precipitated solid was filtered and washed with cold ethanol and dichloromethane. Recrystallization from acetonitrile-ether afforded needle-like red crystals; 1.9 g, 43% yield.

Preparation of $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2][\text{PF}_6]$ and $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_2]_2\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2[(\text{PF}_6)_2]$.

Dpe (1.5 g, 3.8 mmol) and $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3][\text{PF}_6]$ (1.5 g, 3.6 mmol) in 70 ml of ethanol were refluxed for 3 h. The brown reaction mixture was filtered and the brown solid residue washed with 25 ml of hot ethanol and the washings added to the filtrate. The residue was then washed with several portions of dichloromethane and recrystallized from acetonitrile-ether affording orange-red crystals of $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_2]_2\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2[(\text{PF}_6)_2]$.

The filtrate was allowed to cool at -20° overnight affording a brown solid. This was filtered, washed with cold ethanol and ether and recrystallized from dichloromethane-ether to give the red-brown $[(\eta-C_7H_7)Mo(CO)Ph_2PC_2H_4PPh_2][PF_6]$; 1.1 g, 40% yield.

The yield of the binuclear complex can be improved by addition of less than the stoichiometric amount of ligand. For example, dpe (1.0 g, 2.5 mmol) and $[(\eta-C_7H_7)Mo(CO)_3][PF_6]$ (1.5 g, 3.6 mmol) reacted, as described above, to yield 0.7 g (16% yield) of $\{[(\eta-C_7H_7)Mo(CO)_2]_2Ph_2PC_2H_4PPh_2\}[(PF_6)_2]$.

Preparation of $[(\eta-C_5H_5)Fe(CO)_2Ph_2PCH_2PPh_2][PF_6]$

A solution of bis(diphenylphosphino)methane (1.2 g, 3.1 mmol) and $[(\eta-C_5H_5)Fe(CO)_2CH_3CN][PF_6]$ (1.0 g, 2.8 mmol) in 120 ml ethanol was refluxed for 5 h. The solvent was removed on a rotary evaporator using water aspiration, the residue chromatographed on Florisil with dichloromethane as solvent and eluent. Recrystallization from dichloromethane-petroleum ether (60° - 80°) afforded the analytical sample, 1.4 g, 72% yield.

Preparation of $[(\eta-C_5H_5)Fe(CO)_2Ph_2PC_2H_4PPh_2][PF_6]$

A solution of dpe (1.2 g, 3.0 mmol) and $[(\eta-C_5H_5)Fe(CO)_2CH_3CN][PF_6]$ (1.0 g, 2.8 mmol) in 120 ml ethanol was refluxed overnight. The solution was filtered while hot and allowed to cool to room temperature; brown-yellow crystals separated. These were washed liberally with benzene, then

with ether, and recrystallized from dichloromethane-petroleum ether (60°-80°) to give 1.4 g (71% yield) of yellow needles.

The chelated complexes, $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{Ph}_2\text{PCH}_2\text{PPh}_2][\text{PF}_6]$ and $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2][\text{PF}_6]$ were prepared similarly using toluene as reaction solvent.

Results and Discussion

When a mixture of dpm and $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3][\text{PF}_6]$ was gently heated in acetone for a short time, two compounds formed which were separated by column chromatography. One was the yellow mixture of isomers of *fac*- and *mer*- $(\text{OC})_3\text{Mo}(\text{dpm})_2$, which we have obtained by another route and characterized elsewhere [2]. The second was a red ionic compound, identified by analysis, IR, and NMR as $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_2\text{dpm}][\text{PF}_6]$.

Prolonged refluxing of the reactants in ethanol resulted in the formation of the chelated complex $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})\text{dpm}][\text{PF}_6]$. Carbonyl substitution clearly involves two steps, initial coordination followed by chelation, and the barrier to chelation is reasonably large, as was found in a study of chelation in $(\text{OC})_5\text{M}(\text{dpm})$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) [5].

The monodentate and chelate complexes are readily distinguished spectroscopically. The monodentate dicarbonyl exhibits two carbonyl stretching bands in the infrared, a doublet for the C_7H_7 group in the ^1H NMR, and an AB ^{31}P NMR pattern. The bidentate complex has a single infrared carbonyl stretching band, a triplet resonance for the C_7H_7 protons, and a singlet in the ^{31}P NMR.

Two products were isolated from the reaction of dpe with $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3][\text{PF}_6]$. The first was identified as the chelate complex $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})\text{dpe}][\text{PF}_6]$. Its IR and ^1H NMR compared well with the same compound prepared by Beall and Houk [6]. Attempts to isolate a monodentate complex of dpe were not successful, although IR evidence for its formation during the reaction was obtained.

The second compound formed in the dpe reaction was insoluble in dichloromethane and could thus be separated from the first. Its ^{31}P NMR spectrum showed a single peak at -35.7 ppm, in the range found for monodentate coordinated dpm, but well removed from the range found for chelated dpe (*cf.* later discussion). It is also close to the value of -31.2 ppm reported for the $-\text{Ph}_2\text{P}$ end of the ligand in $(\text{CO})_5\text{Mo}(\mu\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{PPhEt})\text{Mo}(\text{CO})_5$ [7]. This favors the binuclear structure $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_2(\mu\text{-dpe})\text{Mo}(\text{CO})_2(\eta\text{-C}_7\text{H}_7)]^{2+}$ for the cation. Its conductivity in nitromethane is $172.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$, which is typical of 1:2 electrolytes [8]. Values for 1:1 electrolytes such as $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_2\text{L}][\text{PF}_6]$ range from $63\text{-}80 \text{ ohms}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ [1].

Although our initial studies involved only the molybdenum complexes, it seemed desirable to investigate other systems in which a potentially bidentate ligand acts also as a monodentate ligand. We found that the known salt $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_3\text{CN}][\text{PF}_6]$ [4] reacted with dpm or dpe to provide the complexes of interest. In toluene at 110° , the chelated monocarbonyl salts $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2][\text{PF}_6]$ ($n = 1, 2$) were formed. Both complexes had earlier been prepared by other routes [9] [10].

TABLE 3

PHOSPHORUS-31 SPECTRAL DATA AND ASSIGNMENTS^a

Compound	CHEMICAL SHIFT (PPM) ^b					J _{p-p} ^e
	δ(P _a)	δ(P _b)	δ(P _c)	Δ _{coord} ^c	Δ _{chel} ^d	
Ph ₂ PCH ₂ PPh ₂ ^{f, g}	21.4/21.7	-	-	-	-	-
[C ₇ H ₇ Mo(CO) ₂ Ph ₂ PCH ₂ PPh ₂][PF ₆] ^f	24.9	-33.6	-	-55.0	-	97.7(J _{ab})
[C ₅ H ₅ Fe(CO) ₂ Ph ₂ PCH ₂ PPh ₂][PF ₆] ^g	24.6	-60.3	-	-82.0	-	90.0(J _{ab})
[C ₇ H ₇ Mo(CO)Ph ₂ PCH ₂ PPh ₂][PF ₆] ^f			-6.9		26.7	
[C ₅ H ₅ Fe(CO)Ph ₂ PCH ₂ PPh ₂][PF ₆] ^g			8.9		69.2	
<i>fac</i> -(CO) ₃ Mo(Ph ₂ PCH ₂ PPh ₂) ₂ ^{f, h}	25.2	-30.0	-3.0	-51.4	27.0	34.2(J _{ab})
<i>mer</i> -(CO) ₃ Mo(Ph ₂ PCH ₂ PPh ₂) ₂ ^{f, h}	24.3	-44.7	-1.8	-66.1	42.9	24.4(J _{bc}) 64.4(J _{ab})
			-20.8(P _d)		23.9	25.6(J _{bc}) 72.4(J _{bd})
Ph ₂ PC ₂ H ₄ PPh ₂ ^f	12.9					24.4(J _{cd})
[C ₅ H ₅ Fe(CO) ₂ Ph ₂ PC ₂ H ₄ PPh ₂][PF ₆] ^f	~11 ^l	-61.8	-	-74.7		36.0(J _{ab})
[C ₇ H ₇ Mo(CO)Ph ₂ PC ₂ H ₄ PPh ₂][PF ₆] ^f			-68.3			-34.7 ^k
[C ₅ H ₅ Fe(CO)Ph ₂ PC ₂ H ₄ PPh ₂][PF ₆] ^f			-92.3			-32.3
[C ₇ H ₇ Mo(CO) ₂ Ph ₂ PC ₂ H ₄ PPh ₂][PF ₆] ₂ ^g		-35.7				-48.0

- a P_a and P_b refer to the uncoordinated and coordinated phosphorus atoms of the ditertiary phosphine respectively. P_c and P_d refer to the phosphorus atoms when the ditertiary phosphine is acting as a chelate.
- b Relative to 85% H_3PO_4 , with negative values downfield from reference. PF_6 resonance not included.
- c Coordination shift defined as $\delta_{\text{coord}} - \delta_{\text{free ligand}}$.
- d Chelation shift defined as $\delta_{\text{chelate}} - \delta_{\text{coord}}$.
- e $|^2J_{pp}|$ or $|^3J_{pp}|$ where $J_{ab} = J(P_a-P_b)$; $J_{bc} = J(P_b-P_c)$; $J_{bd} = J(P_b-P_d)$.
- f In CD_2Cl_2
- g In CD_3CN
- h Reference [2].
- i Observed as a very broad resonance (see text).
- k Using δ_{coord} as -33.6, the value for $[(\eta-C_7H_7)Mo(CO)_2Ph_2-PCH_2PPh_2][PF_6]$, since singly coordinate dpe was not measured.

In ethanol at 78°, these phosphines reacted with the acetonitrile cation forming exclusively the monodentate complexes $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2][\text{PF}_6]$ ($n = 1, 2$). This method of synthesis affords higher yields than an earlier reaction [11], and avoids the handling of perchlorate salts.

Influence of Chelate Ring Size on ^{31}P Chemical Shifts

Data on ^{31}P chemical shifts of monodentate and chelate forms of the ditertiary phosphine ligands are presented in Table 3. The coordination shift ($\delta_{\text{coord}} - \delta_{\text{free ligand}}$) is in all cases negative, i.e., there is a shift to lower field upon coordination, the amount of the shift being dependent on the metal.

The chelation shift ($\delta_{\text{chelate}} - \delta_{\text{coord}}$) is defined, following Connor *et. al.* [5], as the difference in ^{31}P chemical shift between the coordinated phosphorus atom of the monodentate complex, and the phosphorus atoms of the chelated complex. It is meaningful to define the chelation shift in this way when the coordination shifts in the corresponding monodentate complexes are available or can be estimated. In the four-membered ring derivatives of dpm, the chelation shift is in all cases positive, that is, the chemical shift in the chelate is *upfield* from that of the corresponding monodentate complex. We have noted the same trend in the complexes *fac*- and *mer*-(OC) $_3\text{Mo}(\text{dpm})_2$ [2], which are included in Table 3 for comparison. Examination of published ^{31}P NMR data on (CO) $_4\text{W}(\text{dpm})$ [12] using the reported [13] shift of the coordinated Ph_2P group in

$(\text{CO})_5\text{W}\{(\text{i-C}_3\text{H}_7)\text{PhPCH}_2\text{CH}_2\text{PPh}_2\}$ as δ_{coord} , shows a positive chelation shift in this four-membered ring complex as well. In the latter complex, the upfield shift due to chelation is sufficiently large that the chemical shift in the chelate is the same as that in the free dpm ligand.

In contrast, the five-membered chelate complexes of Table 3 have negative chelation shifts (chemical shift of chelate downfield from corresponding monodentate complexes) as do other reported five-membered ring ditertiary phosphine complexes [5].

A single example can be cited which suggests that with six-membered rings, the chelation shift may be positive; this example is provided by the bis(diphenylphosphine)propane (dpp) compound, $(\text{CO})_4\text{W}(\text{dpp})$ [12], again taking the coordinated Ph_2P group in $(\text{CO})_5\text{W}\{(\text{i-C}_3\text{H}_7)\text{PhPCH}_2\text{CH}_2\text{PPh}_2\}$ as a reasonable value for δ_{coord} .

More examples will be required to establish firmly this curious alternating effect in chelation shift: positive in 4-membered rings, negative in 5-membered rings, and apparently positive in 6-membered rings. Since the internal angle at phosphorus in reported structures increases smoothly from 96.3° in $(\text{CO})_4\text{Mo}(\text{dpm})$ [14] to 108° in $(\text{CO})_4\text{Cr}(\text{dpe})$ [15] to 114° in $(\text{dpp})\text{Ir}(\text{CH}_3)(\text{C}_8\text{H}_{18})$ [16], there is no obvious explanation based on ring strain.

The ^{31}P spectra of all but one of the monodentate complexes examined showed the anticipated two pairs of doublets. The exception was $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2]^-$ [PF_6], in which the signal due to the uncoordinated phosphorus atom was a broad and unresolved signal. The

usual doublet ($J = 38.0$ Hz) was observed for the coordinated phosphorus atom. The spectrum did not change down to -40° . It is of interest that in the case of $(CO)_5M(Me_2PCH_2CH_2PMe_2)$ complexes ($M = Mo, W$) the resonance of the coordinated phosphorus was broad while that of the uncoordinated phosphorus was resolved; for $M = Cr$, neither phosphorus resonance could be resolved [5].

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