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- (22) In the infrared spectra of thiocarbamatometal complexes a shoulder of the strong band due to $\nu(\text{C}=\text{O})$ above 1500 cm⁻¹ has been often assigned to $\nu(\text{C}^{\equiv}\text{N})$, but any shoulder assignable to $\nu(\text{C}^{\equiv}\text{N})$ has not occurred in most complexes in this work. A partial double-bond character of the C[≡]N bond would be expected from the assumption that the $\nu(\text{C}^{\equiv}\text{N})$ mode is highly coupled with the $\nu(\text{C}=\text{O})$ in the thiocarbamate complexes.
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Poly(tertiary phosphines and arsines). XI. Phosphorus-31 Nuclear Magnetic Resonance Studies on Some Metal Complexes of Poly(tertiary phosphines)¹

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Proton noise-decoupled pulsed Fourier transform phosphorus-31 NMR spectra of metal complexes of the di(tertiary phosphine) $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$, the symmetrical tri(tertiary phosphines) $\text{R}'\text{P}(\text{CH}_2\text{CH}_2\text{PR}_2)_2$ (R and R' = methyl or phenyl), the unsymmetrical tri(tertiary phosphine) $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$, and the tripod tetra(tertiary phosphines) $\text{P}(\text{CH}_2\text{CH}_2\text{PR}_2)_3$ (R = methyl or phenyl) are reported and discussed on the basis of known structures of the metal complexes. Uncomplexed and complexed phosphorus atoms in complexes such as biligate monometallic (triphos)W(CO)₄, monoligate monometallic C₃H₅Fe(CO)(triphos)(COCH₃), biligate monometallic (tetraphos)Cr(CO)₄, and triligate monometallic (tetraphos)Cr(CO)₃ can easily be differentiated by this method. The anomalously large downfield shift of phosphorus atoms in five-membered chelate rings is increased if the phosphorus atom belongs to two or three fused five-membered chelate rings. Thus the center phosphorus atom in the tetraligate monometallic tripod tetra(tertiary phosphine) complexes [(tetraphos)NiCl][PF₆], which belongs to three fused five-membered chelate rings, exhibits downfield coordination chemical shifts in excess of 150 ppm. In [(triphos)PtCl]⁺ derivatives the ¹J(Pt-P) for the phosphorus atom trans to chlorine is lower than that found in corresponding complexes of monodentate phosphines apparently because this phosphorus atom is part of two fused five-membered chelate rings.

Introduction

This paper surveys the proton noise-decoupled pulsed Fourier transform phosphorus-31 NMR spectra of previously reported^{3,4} metal complexes of phenylated poly(tertiary phosphines) as well as presently reported⁵ metal complexes of methylated poly(tertiary phosphines). Attention was focused on the metal complexes of di-, tri-, and tripod tetra(tertiary phosphines), since the phosphorus-31 NMR spectra of most of the metal derivatives of the more complicated linear tetra-⁴ and hexa(tertiary phosphine)⁶ ligands exhibited complexities which could not be unequivocally unraveled from the spectra of presently available complexes. Our techniques in this work are similar to those used recently by Mynott, Pregosin, and Venanzi⁷ for their study of tungsten carbonyl complexes of tri- and tripod tetra(tertiary phosphines) of different types from those used in our project.

Experimental Section

The phosphorus-31 NMR spectra (Tables I-IV) were taken in the indicated solvents using a Jeolco PFT-100 spectrometer operating at 40.3 MHz in the Fourier transform mode with proton noise decoupling and a deuterium lock. The samples were placed in 10-mm NMR tubes also containing a concentric 5-mm tube of 85% phosphoric acid, used as an external standard, and a capillary of deuterium oxide for the lock. A pulse width of 90° was used with a repetition rate of 3 sec. Approximately 1000 such pulses were used to obtain a typical spectrum. However, in particularly favorable cases, notably the free ligands, as few as 100 pulses could be used, whereas in a few less soluble compounds (or for unequivocal identification of ¹⁹⁵Pt satellites—see Table V) as many as 10,000 pulses were used. An 8 K transform with a spectral width of 10 kHz (i.e., 248 ppm) was routinely used such that the resolution was limited to 2.44 Hz. The chemical shifts are reported in ppm above the external 85% phosphoric acid standard. Coordination chemical shifts (Tables I-IV) are reported in ppm relative to the corresponding phosphorus in the free

Table I. Phosphorus-31 NMR Data on Metal Complexes of the Unsymmetrical Di(tertiary phosphine) $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$

Compd	Solvent	Chem shifts		Coord chem shifts		$J(\text{P-P}')$, Hz
		$(\text{CH}_3)_2\text{P}$	$(\text{C}_6\text{H}_5)_2\text{P}$	$(\text{CH}_3)_2\text{P}$	$(\text{C}_6\text{H}_5)_2\text{P}$	
Pm-Pf	C_6H_6	+48.4	+13.5			25
(Pm-Pf)Cr(CO) ₄	CH_2Cl_2	-55.0	-81.2	-103.4	-94.7	15
(Pm-Pf)Mo(CO) ₄	CH_2Cl_2	-26.3	-57.1	-74.7	-70.6	7
(Pm-Pf)W(CO) ₄	CH_2Cl_2	-7.9	-42.2	-56.3	-55.7	<2
(Pm-Pf)NiCl ₂	CH_2Cl_2	-48.6	-58.4	-97.0	-71.9	76
(Pm-Pf)PdCl ₂	CH_2Cl_2	-58.8	-64.5	-107.2	-78.0	10
(Pm-Pf)PtCl ₂	CH_2Cl_2	-30.8	-42.2	-79.2	-55.7	<2
[CpFeCO] ₂ (Pm-Pf)	CH_2Cl_2	-43.8	-65.4	-91.2	-78.9	<i>a</i>

^a The resonances were too broad for determination of this coupling constant.

Table II. Phosphorus-31 NMR Data on Metal Complexes of the Tri(tertiary phosphines) $\text{R}'\text{P}(\text{CH}_2\text{CH}_2\text{PR}_2)_2$

Compd	Solvent	Chem shifts		Coord chem shifts		$J(\text{P-P})$, Hz
		R'P	R ₂ P	R'P	R ₂ P	
MeP(CH ₂ CH ₂ PMe ₂) ₂	C_6H_6	+34.8	+49.0			22
(Pm-Pm-Pm)Cr(CO) ₃	CH_2Cl_2	-106.1	-57.5			22
(Pm-Pm-Pm) ₂ [Cr(CO) ₄] ₃	CH_2Cl_2	-69.3	-56.0, -34.1, -18.4	-140.9	-106.5	20, 20, 20, 8
[(Pm-Pm-Pm)NiCl][PF ₆]	Me ₂ CO	-102.9	-37.2	-137.7	-86.2	50
[(Pm-Pm-Pm)PdCl]Cl	EtOH	-104.0	-36.1	-138.8	-85.1	9
[(Pm-Pm-Pm)PtCl]Cl	<i>n</i> -BuOH	-76.7	-33.3	-110.5	-82.3	<2
PhP(CH ₂ CH ₂ PMe ₂) ₂	C_6H_6	+18.1	+48.8			22
(Pm-Pf-Pm)Cr(CO) ₃	CH_2Cl_2	-114.9	-56.9	-133.0	-105.7	19
(Pm-Pf-Pm)Mo(CO) ₃	CH_2Cl_2	-87.0	-28.7	-105.1	-77.5	7
[(Pm-Pf-Pm)NiCl]Cl	CH_2Cl_2	-115.0	-39.0	-131.1	-87.8	56
[(Pm-Pf-Pm)NiCl][PF ₆]	CH_2Cl_2	-111.6	-37.9	-129.7	-86.7	52
[(Pm-Pf-Pm)PdCl]Cl	CH_2Cl_2	-114.4	-35.4	-132.5	-84.2	10
[(Pm-Pf-Pm)PtCl]Cl	CH_2Cl_2	-88.3	-32.2	-106.7	-81.0	<2
[CpFe(Pm-Pf-Pm)]I	CH_2Cl_2	-120.4	-76.1	-138.5	-124.9	37
(Pm-Pf-Pm)Mn(CO) ₂ Br	CH_2Cl_2	-124	-59.3	-142	-108.1	<i>a</i>
MeP(CH ₂ CH ₂ PPh ₂) ₂	C_6H_6	+33.6	+13.6			16
(Pf-Pm-Pf)NiCl ₂	CH_2Cl_2	-101.4	-48.5	-135.0	-62.1	44
PhP(CH ₂ CH ₂ PPh ₂) ₂	CH_2Cl_2	+16.5	+12.9			27
(Pf-Pf-Pf)Cr(CO) ₃	CH_2Cl_2	-110.2	-77.9	-126.7	-90.8	12
(Pf-Pf-Pf)Mo(CO) ₃	CH_2Cl_2	-82.4	-55.3	-98.9	-68.2	~6
(Pf-Pf-Pf)W(CO) ₃	CH_2Cl_2	-71.8	-40.3	-88.3	-53.2	~6
(Pf-Pf-Pf)W(CO) ₄	CH_2Cl_2	-39.6	-30.5, +13.2	-56.1	-43.4, +0.3	39, 36
[(Pf-Pf-Pf)NiCl][PF ₆]	CH_2Cl_2	-109.2	-47.1	-125.7	-70.0	50
[(Pf-Pf-Pf)PdCl][PF ₆]	CH_2Cl_2	-109.5	-45.7	-126.0	-68.6	10
[(Pf-Pf-Pf)PtCl][PF ₆]	CH_2Cl_2	-86.0	-41.9	-102.5	-54.8	<2
CpFe(CO)(Pf-Pf-Pf)C(O)Me	CH_2Cl_2	A: -69.5	+12.7	-85.0		
CpFe(CO)(Pf-Pf-Pf)C(O)Me	CH_2Cl_2	B: +15.5	-74.8, +12.7		-87.7	

^a These resonances were too broad and weak for $J(\text{P-P}')$ to be determined.

Table III. Phosphorus-31 NMR Data on Metal Complexes of the Unsymmetrical Tri(tertiary phosphine) $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{P}(\text{CH}_3)_2$

Compd	Solvent	Chem shifts			Coord chem shifts			Coupling constants, Hz		
		PhP	PPh ₂	PMe ₂	PhP	PPh ₂	PMe ₂	$J(\text{PhP-PPh}_2)$	$J(\text{PhP-PMe}_2)$	$J(\text{PPh}_2\text{-PMe}_2)$
PhP(CH ₂ CH ₂ -PMe ₂)(CH ₂ -CH ₂ PPh ₂)	C_6H_6	+17.9	+13.5	+49.0				27	22	0
(Pm-Pf-Pf)Cr(CO) ₃	CH_2Cl_2	-114.0	-82.4	-53.6	-131.9	-95.9	-102.6	11	18	25
(Pm-Pf-Pf)Mo(CO) ₃	CH_2Cl_2	-86.0	-58.8	-25.6	-103.9	-72.3	-74.6	<2	22	5
[(Pm-Pf-Pf)NiCl][PF ₆]	CH_2Cl_2	-109.9	-42.6	-42.6	-127.8	-56.1	-91.6	52	52	<i>a</i>
[(Pm-Pf-Pf)NiCl][PF ₆]	(CD ₃) ₂ CO	-110.8	-42.5	-41.3	-128.7	-56.0	-90.3	52	52	~143
[(Pm-Pf-Pf)PdCl]Cl	CH_2Cl_2	-113.2	-42.7	-42.5	-130.1	-56.2	-91.5	10	10	<i>a</i>
[(Pm-Pf-Pf)PtCl]Cl	CH_2Cl_2	-86.9	-38.6	-37.5	-104.8	-52.1	-86.5	<2	<2	<i>a</i>
[CpFe(Pm-Pf-Pf)]I	CH_2Cl_2	-123.1	-104.3	-68.7	-141.0	-117.8	-117.7	29	39	44

^a This coupling constant cannot be determined owing to the equivalence or near equivalence of the chemical shifts of the end PPh₂ and PMe₂ phosphorus atoms.

ligand. Unless otherwise specified, the reported coupling constants are absolute values, since our experiments did not determine the sign of the coupling constant.

Some of the hexafluorophosphate salts examined in this work

exhibited sharp lines separated by constant intervals of 711 ± 2 Hz in addition to the resonances listed in Tables II-IV. These can be assigned to the strongest components of the 1:6:15:20:15:6:1 PF₆⁻ septet (lit.⁸ $^1J(\text{P-F})$ (in PF₆⁻) = 707 Hz).

Table IV. Phosphorus-31 NMR Data on Metal Complexes of the Tripod Tetra(tertiary phosphines)

Compd	Solvent	Chem shifts		Coord chem shifts		$J(\text{P}-\text{P}')$, Hz
		Center P	PR_2	Center P	PR_2	
$(\text{Me}_2\text{PCH}_2\text{CH}_2)_3\text{P}$	C_6H_6	+20.1	+48.9			20
$[\text{P}(\text{Pm})_3\text{NiCl}][\text{PF}_6]$	CH_2Cl_2	-153.5	-36.7	-173.6	-85.6	32
$(\text{Ph}_2\text{PCH}_2\text{CH}_2)_3\text{P}$	CH_2Cl_2	+17.5	+13.1			27
$[\text{P}(\text{Pf})_3\text{NiCl}][\text{PF}_6]$	CH_2Cl_2	-140.1	-32.1	-157.6	-45.2	28
$\text{P}(\text{Pf})_3\text{Cr}(\text{CO})_3$	CH_2Cl_2	-114.5	-78.7, -78.7, +12.7	-132.0	-91.8, -91.8, -0.4	14, 14, 32
$\text{P}(\text{Pf})_3\text{Cr}(\text{CO})_2$	CH_2Cl_2	-78.9	-65.2, +12.8, +12.8	-96.4	-78.3, -0.3, -0.3	
$\text{MeC}(\text{O})\text{Mn}(\text{CO})_3\text{P}(\text{Pf})_3$	CH_2Cl_2	-83.2	-81.7, +12.6, +12.6	-100.7	-94.8, -0.5, -0.5	
$[\text{CpMn}(\text{NO})\text{P}(\text{Pf})_3][\text{PF}_6]$	CH_2Cl_2	-96.9	-93.8, +13.5, +13.5	-114.4	-106.9, +0.4, +0.4	
$\text{CpFe}(\text{CO})\text{P}(\text{Pf})_3\text{I}$	CH_2Cl_2	-96.5	-93.6, +12.5, +13.3	-114.0	-106.7, -0.6, +0.2	

Table V. Platinum-Phosphorus Coupling Constants of Some Platinum Tri(tertiary phosphine) Complexes

Compd	Solvent	$J(\text{Pt}-\text{P})$, Hz	
		P trans to P	P trans to Cl
$(\text{Pm}-\text{Pm}-\text{Pm})\text{PtCl}_2$	<i>n</i> -BuOH	2344	3024
$(\text{Pm}-\text{Pf}-\text{Pm})\text{PtCl}_2$	CH_2Cl_2	2337	3242
$(\text{Pm}-\text{Pf}-\text{Pf})\text{PtCl}_2$	CH_2Cl_2	2390, 2390	3118
$[(\text{Pf}-\text{Pf}-\text{Pf})\text{PtCl}][\text{PF}_6]$	CH_2Cl_2	2483	3025

The metal complexes of the phenylated poly(tertiary phosphines) $\text{C}_6\text{H}_5\text{P}[\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2$ (abbreviation Pf-Pf-Pf)³ and $\text{P}[\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_3$ (abbreviation P(-Pf)³)⁴ were samples which remained from the previous work. The integrity of the metal carbonyl derivatives from this source was checked by their infrared spectra in the $\nu(\text{CO})$ region. All of the compounds from this source for which spectra are reported in Tables II and IV had the same colors as when originally reported.

The metal complexes of the methylated poly(tertiary phosphines) $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ (abbreviation Pm-Pf), $\text{CH}_3\text{P}[\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2$ (abbreviation Pm-Pm-Pm), $\text{C}_6\text{H}_5\text{P}[\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2$ (abbreviation Pm-Pf-Pm), and $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ (abbreviation Pm-Pf-Pf) were prepared and characterized by procedures reported elsewhere.⁵ The nickel(II) complexes of $\text{CH}_3\text{P}[\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_2$ (abbreviation Pf-Pm-Pf) and $\text{P}[\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]_3$ (abbreviation P(-Pm)³) were prepared from nickel(II) chloride hexahydrate and the ligand in ethanol solution using procedures similar to those reported for related complexes.^{4,5}

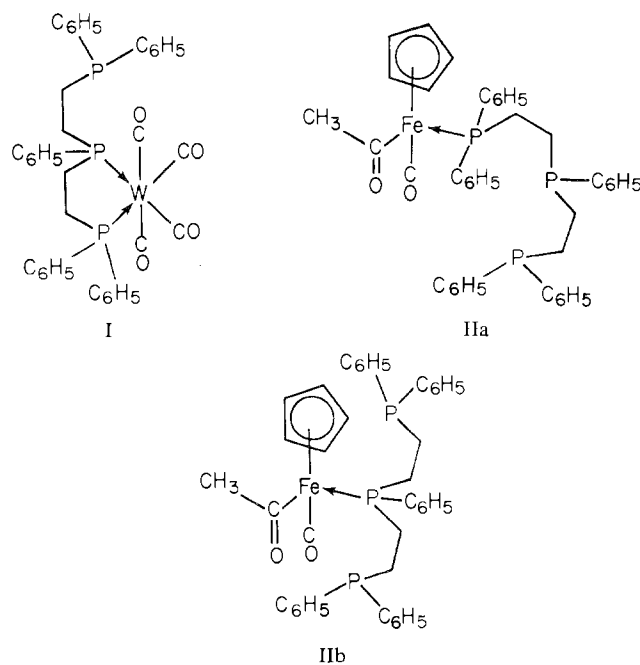
Discussion

The ligand $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$, like the ligands $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{OP}(\text{C}_6\text{H}_5)_2$ and $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{OP}(\text{C}_6\text{H}_5)_2$ studied by Grim et al.,⁹ is a bidentate ligand with nonequivalent phosphorus atoms. The phosphorus-phosphorus coupling constants in metal complexes of $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ can therefore be determined directly from the proton-decoupled ³¹P NMR spectra. The values of $J(\text{P}-\text{P}')$ in the (Pm-Pf)-M(CO)₄ complexes of Cr, Mo, and W (15, 7, and <2 Hz) are consistently smaller than those reported⁹ for the corresponding $[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{OP}(\text{C}_6\text{H}_5)_2]\text{M}(\text{CO})_4$ complexes (46, 35, and 31 Hz) by 30 ± 2 Hz. This is consistent with the transmission of $J(\text{P}-\text{P}')$ in (Pm-Pf)M(CO)₄ both through the ligand backbone and through the metal atom as was postulated⁹ for the metal complexes $[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{OP}(\text{C}_6\text{H}_5)_2]\text{M}(\text{CO})_4$. A similar effect is probably responsible for the decrease in coupling constants in the (Pm-Pf)MCl₂ derivatives in the series Ni, Pd, and Pt.

Most of the complexes of the tri(tertiary phosphines) in Table II contain triligate monometallic ligands. Such complexes can be readily identified by their characteristic proton-decoupled phosphorus-31 NMR spectra, which exhibit a lower field triplet and a higher field doublet, provided, of course, that the two ends of the tri(tertiary phosphine) are equivalent. For example, all of the (triphos)MCl₂ derivatives exhibit this triligate monometallic pattern in their proton-decoupled phosphorus-31 NMR spectra indicating formulations as the ionic triligate monometallic derivatives $[(\text{triphos})\text{MCl}]^+\text{Cl}^-$, rather than the nonionic biligate mo-

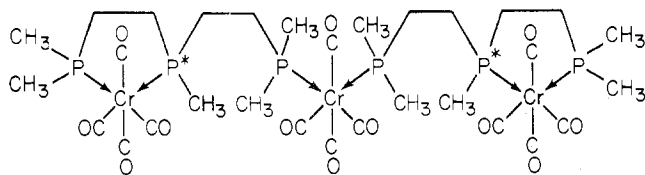
nometallic derivatives (triphos)MCl₂ with one uncomplexed phosphorus atom in accord with other information such as conductivity data. An authentic biligate monometallic derivative in Table II is (Pf-Pf-Pf)W(CO)₄ (I), in which the uncomplexed end phosphorus atom has a phosphorus-31 chemical shift nearly unchanged from that of the free ligand similar to the uncomplexed phosphorus atom in Venanzi's complex (QP)W(CO)₃.⁷

The monoligate monometallic complex $\text{C}_5\text{H}_5\text{Fe}(\text{CO})\text{-(Pf-Pf-Pf)}(\text{COCH}_3)$ can exist as isomer IIa, in which an end phosphorus atom is bonded to the iron atom, or isomer IIb, in which the center phosphorus atom is bonded to the iron atom. The phosphorus-31 NMR spectrum of this complex exhibits two distinct resonances separated by 5 ppm in the region assigned to complexed phosphorus atoms of the tri(tertiary phosphine) ligand. This thus indicates that our sample of $\text{C}_5\text{H}_5\text{Fe}(\text{CO})\text{-(Pf-Pf-Pf)}(\text{COCH}_3)$ must be a mixture of the two isomers IIa and IIb, a fact that would be difficult to demonstrate unequivocally by any technique other than phosphorus-31 NMR spectroscopy.

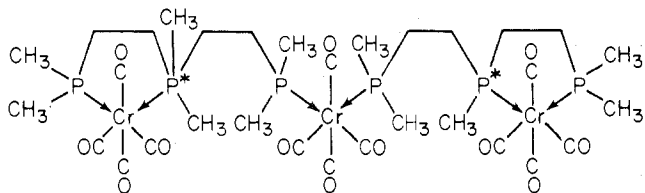


Another unusual tri(tertiary phosphine) complex is the chromium carbonyl derivative $(\text{Pm}-\text{Pm}-\text{Pm})_2[\text{Cr}(\text{CO})_4]_3$, obtained from $\text{C}_7\text{H}_8\text{Cr}(\text{CO})_4$ and the methylated tri(tertiary phosphine). The phosphorus-31 NMR spectrum can be interpreted on the basis of a mixture of the meso isomer IIIa and the *dl* isomer IIIb. The resonance at -69.3 ppm can be assigned to the two equivalent (and asymmetric) center phosphorus atoms of the two tri(tertiary phosphine) ligands (P* in IIIa and IIIb). The resonance at -56.0 ppm can be assigned to the two equivalent end phosphorus atoms bonded to the outer chromium units. The remaining resonances at

-34.1 and -18.4 ppm can be assigned to the phosphorus atoms bonded to the center chromium unit. The presence of these last two resonances can be attributed to a mixture of meso and *dl* diastereoisomers. The fine structure of these four resonances in $(\text{Pm-Pm-Pm})_2[\text{Cr}(\text{CO})_4]_3$ is consistent with coupling of each of the two center phosphorus atoms to three of the four end phosphorus atoms by about 20 Hz and to the fourth end phosphorus atom by about 8 Hz.



IIIa



IIIb

The nonequivalence of the two ends of the tri(tertiary phosphine) $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ should make three generally different phosphorus-phosphorus coupling constants directly observable in the phosphorus-31 NMR spectrum. In the metal carbonyl complexes *fac*-(Pm-Pf-Pf) $\text{M}(\text{CO})_3$ (M = Cr and Mo) these three different coupling constants are directly observable by normal methods. Despite the fact that all three pairs of phosphorus atoms in *fac*-(Pm-Pf-Pf) $\text{M}(\text{CO})_3$ are in mutual *cis* positions, the three phosphorus-phosphorus coupling constants are quite different (Table III). However, the couplings $J(\text{PhP-PPH}_2)$ and $J(\text{PhP-PMe}_2)$ have pathways both through the metal atom and through the ethane bridge whereas the coupling $J(\text{Ph}_2\text{P-PMe}_2)$ has only a pathway through the metal atom; this could account for some of the differences.

The proton-decoupled phosphorus-31 NMR spectrum of $[(\text{Pm-Pf-Pf})\text{NiCl}][\text{PF}_6]$ as originally taken in dichloromethane was unusual since both end phosphorus atoms appeared to be equivalent despite the fact that one is bonded to two methyls and the other to two phenyls. The only reasonable explanation is accidental equivalence of the chemical shifts of the two end carbons of the tri(tertiary phosphine) ligand in $[(\text{Pm-Pf-Pf})\text{NiCl}][\text{PF}_6]$. If the spectrum of $[(\text{Pm-Pf-Pf})\text{NiCl}][\text{PF}_6]$ is taken in acetone- d_6 rather than dichloromethane, the two end phosphorus atoms of the ligand become slightly nonequivalent and the phosphorus NMR spectrum exhibits an ABX pattern.¹⁰ The X resonance exhibits five rather than six lines, but if the center line is assigned to the overlapping $5' \rightarrow 3'$ and $6' \rightarrow 4'$ transitions,¹⁰ then both J_{AX} and J_{BX} are 52 Hz, in accord with the value found in the spectrum of this nickel complex run in dichloromethane solution and analyzed as a first-order AX₂ system.¹⁰ The second-order ABX nature of the $[(\text{Pm-Pf-Pf})\text{NiCl}][\text{PF}_6]$ spectrum in acetone- d_6 solution allows estimation of the trans $|J(\text{P-P}')|$ coupling constant as 143 Hz.

The chemical shift difference of the nonequivalent end phosphorus atoms in the analogous palladium complex $[(\text{Pm-Pf-Pf})\text{PdCl}]\text{Cl}$ in dichloromethane solution is extremely small but detectable from increased complexity of the end phosphorus resonance beyond a simple 1:2:1 triplet. The chemical shift difference of the nonequivalent phosphorus atoms in the platinum complex $[(\text{Pm-Pf-Pf})\text{PtCl}]\text{Cl}$ is sufficient for two distinct end phosphorus resonances to be observed, complete with accompanying ¹⁹⁵Pt satellites. Analysis

of the spectrum of this platinum complex was simplified by values of $|J(\text{P-P}')|$ below the 2-Hz resolution limit as was also found for the other square-planar platinum complexes examined in this work.

The chemical shift differences between the nonequivalent end phosphorus atoms of the remaining metal complexes of the unsymmetrical tri(tertiary phosphine) $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ (Table III) were much larger than those in the nickel, palladium, and platinum complexes discussed above (i.e., at least 25 ppm). Unambiguous assignments of the end phosphorus resonances in the complexes (Pm-Pf-Pf) $\text{M}(\text{CO})_3$ (M = Cr and Mo) and $[\text{C}_5\text{H}_5\text{Fe}(\text{Pm-Pf-Pf})\text{I}]$ could be made by comparisons of their chemical shifts with the chemical shifts of the end phosphorus resonances in the corresponding metal complexes of the symmetrical tri(tertiary phosphines) $\text{R}_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)\text{CH}_2\text{CH}_2\text{PR}_2$ (R = CH₃ and C₆H₅) (Table II).

The tripod tetra(tertiary phosphines) in the complexes listed in the Table IV function as bidentate, tridentate, or tetradentate ligands. The phosphorus-31 NMR spectra of these three complex types are distinctly different. For the bidentate and tridentate complexes of the tripod tetra(tertiary phosphine), which contain two and one uncomplexed phosphorus atoms, respectively, the expected resonances for the uncomplexed phosphorus atom(s) are observed within 1 ppm of the end phosphorus resonance of the free tripod tertiary phosphine ligand.

Grim et al.⁹ have noted an anomalously large downfield shift upon coordination of di(tertiary phosphines) to form five-membered chelate rings. A similar effect is found in our work, which, because of the PCH₂CH₂P structural unit in all of our ligands, involves ligands forming only five-membered chelate rings. For example, the coordination chemical shifts of the (C₆H₅)₂P end in (Pm-Pf) $\text{M}(\text{CO})_4$ complexes of Cr, Mo, and W (-95, -71, and -56 ppm) are very close to the anomalously high downfield coordination chemical shifts reported by Grim et al.⁹ for the 1,2-bis(diphenylphosphino)ethane complexes (Pf-Pf) $\text{M}(\text{CO})_4$ of Cr, Mo, and W (-92, -67, and -53 ppm). Fusion of two five-membered chelate rings as in the triligate monometallic tri(tertiary phosphine) complexes examined in this work causes an even larger anomalous downfield shift of the resonance of the center (i.e., bridgehead) phosphorus atom, which is common to both chelate rings. This effect is best illustrated by a comparison of the chemical shifts of the center phosphorus atoms in the two tungsten carbonyl complexes of the same tri(tertiary phosphine) (Pf-Pf-Pf) $\text{W}(\text{CO})_4$ and (Pf-Pf-Pf) $\text{W}(\text{CO})_3$. Thus, in the biligate monometallic complex (Pf-Pf-Pf) $\text{W}(\text{CO})_4$ with only one five-membered chelate ring, the coordination chemical shift of the center ligand phosphorus atom is -56.1 ppm, whereas in the triligate monometallic complex (Pf-Pf-Pf) $\text{W}(\text{CO})_3$ with two fused five-membered chelate rings, the downfield coordination chemical shift of the center ligand phosphorus atoms increases to -88.3 ppm. The most extreme example of this effect is found in the tripod tetra(tertiary phosphine) complexes $[(\text{tetra-phos})\text{NiCl}][\text{PF}_6]$, where the center phosphorus atom of the tripod tetra(tertiary phosphine), which is common to *three* five-membered chelate rings, exhibits coordination chemical shifts in excess of -150 ppm. In general, the coordination chemical shifts of the center ligand phosphorus atom in the tripod tetra(tertiary phosphine) complexes listed in Table IV correlate well with the number of chelate rings to which this center phosphorus atom belongs and thus provide confirmation of the number of phosphorus atoms of the tripod tetra(tertiary phosphine) ligand bonded to the metal atom in these complexes.

The platinum-phosphorus coupling constants have been determined in several $[(\text{triphos})\text{PtCl}]^+$ complexes from their ¹⁹⁵Pt satellites (Table V). The $|J(\text{Pt-P})|$ values for the

phosphorus atoms trans to other phosphorus atoms (i.e., the end phosphorus atoms of the tri(tertiary phosphine) ligands) occur in the range 2337–2483 Hz which is within the range found¹¹ for similar phosphorus atoms trans to other phosphorus atoms in monodentate phosphine-square-planar platinum(II) complexes of the types *trans*-L₂PtCl₂ and [L₃PtCl]⁺. However, the $|^1J(\text{Pt-P})|$ values for the phosphorus atoms trans to chlorine (i.e., the center phosphorus atoms of the tri(tertiary phosphine) ligands) occur in the range 3024–3242 Hz, which is appreciably below the 3490–3675-Hz range found¹¹ for similar phosphorus atoms trans to chlorine in monodentate phosphine square-planar platinum(II) complexes of the types *cis*-L₂PtCl₂ and [L₃PtCl]⁺. We suspect that the strain of the two fused five-membered chelate rings weakens the bond from the platinum to the phosphorus common to these chelate rings with resultant lowering of the corresponding $|^1J(\text{Pt-P})|$ coupling constant.

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Registry No. Pm-Pf, 42495-77-2; (Pm-Pf)Cr(CO)₄, 54823-50-6; (Pm-Pf)Mo(CO)₄, 54823-51-7; (Pm-Pf)W(CO)₄, 54823-52-8; (Pm-Pf)NiCl₂, 54823-53-9; (Pm-Pf)PdCl₂, 54823-54-0; (Pm-Pf)PtCl₂, 54823-55-1; [CpFeCO]₂(Pm-Pf), 54823-48-2; Pm-Pm-Pm, 42495-85-2; (Pm-Pm-Pm)Cr(CO)₃, 54823-60-8; (Pm-Pm-Pm)₂[Cr(CO)₄]₃ (IIIa), 54823-49-3; [(Pm-Pm-Pm)NiCl][PF₆], 54823-57-3; [(Pm-Pm-Pm)PdCl]Cl, 54823-58-4; [(Pm-Pm-Pm)-PtCl]Cl, 54823-59-5; Pm-Pf-Pm, 42495-81-8; (Pm-Pf-Pm)Cr(CO)₃,

54823-28-8; (Pm-Pf-Pm)Mo(CO)₃, 54823-29-9; [(Pm-Pf-Pm)-NiCl]Cl, 54823-30-2; [(Pm-Pf-Pm)NiCl][PF₆], 54823-32-4; [(Pm-Pf-Pm)PdCl]Cl, 54823-33-5; [(Pm-Pf-Pm)PtCl]Cl, 54823-34-6; [CpFe(Pm-Pf-Pm)]I, 54823-35-7; (Pm-Pf-Pm)Mn(CO)₂Br, 54823-36-8; Pm-Pm-Pf, 36892-73-6; (Pm-Pm-Pf)NiCl₂, 54823-24-4; Pm-Pf-Pf, 23582-02-7; (Pm-Pf-Pf)Cr(CO)₃, 33847-58-4; (Pm-Pf-Pf)Mo(CO)₃, 33847-60-8; (Pm-Pf-Pf)W(CO)₃, 33847-61-9; (Pm-Pf-Pf)W(CO)₄, 54823-23-3; [(Pm-Pf-Pf)NiCl][PF₆], 33847-47-1; [(Pm-Pf-Pf)PdCl][PF₆], 33847-48-2; [(Pm-Pf-Pf)PtCl][PF₆], 33847-50-6; CpFe(CO)(Pm-Pf-Pf)C(O)Me (IIa), 54823-37-9; CpFe(CO)(Pm-Pf-Pf)C(O)Me (IIb), 34675-94-0; Pm-Pf-Pf, 54823-20-0; (Pm-Pf-Pf)Cr(CO)₃, 54823-38-0; (Pm-Pf-Pf)Mo(CO)₃, 54823-39-1; [(Pm-Pf-Pf)NiCl][PF₆], 54823-41-5; [(Pm-Pf-Pf)-PdCl]Cl, 54823-42-6; [(Pm-Pf-Pf)PtCl]Cl, 54823-43-7; [CpFe(Pm-Pf-Pf)]I, 54823-44-8; P-(Pm)₃, 42495-87-4; [P-(Pm)₃NiCl][PF₆], 54823-46-0; P-(Pm)₃, 23582-03-8; [P-(Pm)₃NiCl][PF₆], 33881-21-9; P-(Pm)₃Cr(CO)₃, 34652-28-3; P-(Pm)₃Cr(CO)₄, 33864-98-1; MeC(O)Mn(CO)₃P(-Pm)₃, 33849-32-0; [CpMn(NO)P(-Pm)₃][PF₆], 34676-46-5; CpFe(CO)P(-Pm)₃I, 54823-47-1; (Pm-Pm-Pm)₂[Cr(CO)₄]₃ (IIIb), 54868-46-1; ³¹P, 7723-14-0.

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Poly(tertiary phosphines and arsines). XII. Some Metal Complexes of Methylated Di- and Tri(tertiary phosphines)^{1,2}

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Metal complexes of the di(tertiary phosphine) (CH₃)₂PCH₂CH₂P(C₆H₅)₂ of the types (diphos)MCl₂ (M = Ni, Co, Pd, and Pt), (diphos)M(CO)₄ (M = Cr, Mo, and W), [(diphos)₂RhCl₂]⁺, and (diphos)Fe₂(CO)₂(C₅H₅)₂ have been prepared by standard methods. Metal complexes of the tri(tertiary phosphines) R'³P(CH₂CH₂PR₂)₂ (R' = C₆H₅, R = CH₃; R' = CH₃, R = CH₃ and C₆H₅) and (CH₃)₂PCH₂CH₂P(C₆H₅)CH₂CH₂P(C₆H₅)₂ of the types [(triphos)MCl]⁺ (M = Ni, Pd, and Pt), (triphos)M(CO)₃ (M = Cr, Mo, and W), (triphos)Mn(CO)₂Br, (triphos)Mn(CO)₂C(O)CH₃, and [C₅H₅Fe(triphos)]⁺ have been prepared by standard methods. In general, tractable metal complexes of methylated tri(tertiary phosphines) with uncomplexed -CH₂CH₂P(CH₃)₂ groups could not be prepared. The proton NMR spectra of the dimethylphosphino groups in metal complexes of methylated poly(tertiary phosphines) indicate that a single nonplanar five-membered chelate ring, such as that found in metal complexes of the di(tertiary phosphine) (CH₃)₂PCH₂CH₂P(C₆H₅)₂, can undergo rapid inversion on the NMR time scale whereas two fused nonplanar five-membered chelate rings, such as those found in triligate monometallic complexes of tri(tertiary phosphines), remain rigid even on the NMR time scale.

Introduction

The discovery of the base-catalyzed addition of phosphorus-hydrogen bonds to vinylphosphorus compounds⁵ has made available numerous poly(tertiary phosphines) with PCH₂CH₂P structural units. Previous papers of this series^{6–8} have surveyed metal complexes of phenylated tri-, tripod tetra-, linear tetra-, and hexa(tertiary phosphines). This paper describes some metal complexes of the partially methylated di(tertiary phosphine) (CH₃)₂PCH₂CH₂P(C₆H₅)₂ and the tri(tertiary

phosphines) (CH₃)₂PCH₂CH₂P(C₆H₅)CH₂CH₂PR₂ (R = CH₃ and C₆H₅) as well as the completely methylated tri(tertiary phosphine) CH₃P[CH₂CH₂P(CH₃)₂]₂. These ligands with -CH₂CH₂P(CH₃)₂ units were of interest in order to determine the effect on metal complex formation of a more basic and less bulky dimethylphosphino group relative to the diphenylphosphino group. An example of a previously reported⁹ drastic effect when dimethylphosphino groups are substituted for diphenylphosphino groups in a di(tertiary