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^{31}P Shielding in Phosphine Derivatives of Tricarbonyl-η^5-cyclopentadienylmanganese(I), $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$

DIETER REHDER*

Institut für Anorganische und Angewandte Chemie der Universität, Martin-Luther-King-Platz 6, D-2000 Hamburg 13, F.R.G.

and AHMET KEÇECI

Fen-Edebiyat-Fakültesi, Cukurova Üniversitesi, Adana, Turkey

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Abstract

The ^{31}P NMR parameters $\delta(^{31}P)$, $^nJ(^{31}P–^{31}P)$, coordination shifts $\Delta\delta$ and chelate-ring contributions ΔR are reported and discussed for various $[Mn(Cp)(CO)_{3-n}(PR_3)_n]$ complexes (Cp = η^5-C_5H_5; n = 1, 2), $[Mn(Cp)(CO)_2PP]$, $[\{Mn(Cp)(CO)_2\}_2\mu\text{-}PP]$ and $[Mn(Cp)(CO)PP]$. PR_3 and PP are mono- and bidentate phosphines, respectively. $\Delta\delta$ decreases, mainly as a consequence of decreasing Mn–P π interaction, as the steric requirement of the phosphine increases; the shielding trends in the chelate structures reflect steric and torsional strains: $\Delta\delta$ and ΔR decrease in the series $Ph_2P(CH_2)_nPPh_2$ ($n = 2 > 3 \approx 4 > 1$), and in five-membered rings the ordering is *cis*-$Ph_2PCH{=}CHPPh_2$ > $Ph_2P(CH_2)_2ER_2$ (ER_2 = $AsPh_2$, PEt_2, PPh_2) ≈ *o*-$C_6H_4PPh_2(EPh_2)$ (E = As, P) > $Cy_2P(CH_2)_2PCy_2$ > (*p*-Tol)$_2$P$(CH_2)_2$P(*p*-Tol)$_2$.

Introduction

Irradiation of the complexes $[Mn(Cp)(CO)_3]$ in the presence of phosphines yields $[Mn(Cp)(CO)_2PR_3]$ and $[Mn(Cp)CO(PR_3)_2]$ (R, *e.g.* = Ph [1]), if the ligand is monodentate. Bidentate ligands such as $Ph_2P(CH_2)_2PPh_2$ (dppe) may form dinuclear, ligand–bridged complexes $[\{Mn(Cp)(CO)_2\}_2\mu\text{-dppe}]$ or mononuclear chelates [Mn(Cp)(CO)dppe] [2]. The coordination behaviour of tridentate $R_2P(CH_2)_2PR'(CH_2)_2PR_2$ (R, R' = Ph, Cy) is still more complex, and mono- and dinuclear compounds containing the fragments $\{Mn(Cp)(CO)_n\}$ (n = 0–2) have been described [3, 4]. The ^{31}P NMR spectra of these compounds are of some interest in the context of comparative studies on electronic and steric factors influencing the ^{31}P (and metal) shielding in transition metal complexes [5–8]. In the present study, ^{31}P shift parameters of $[Mn(Cp)(CO)_3]$ complexes containing mono- and bidentate phosphines of varying electronic and steric characteristics will be discussed. ^{55}Mn shielding in these compounds encompasses a narrow range (–2080 to –2270 ppm relative to $[MnO_4]^-$ [8]) and cannot be employed as a parameter to describe alterations of electronic interactions between the bonding partners. This is in contrast with findings for the isoelectronic $[V(Cp)(CO)_4]$ derivatives, but parallels observations in the corresponding niobium system [8].

Experimental

The complexes were obtained as described previously [1, 2, 4, 9] by UV irradiation (high-pressure mercury lamp, Duran ware) of THF or toluene solutions containing *ca.* 1 mmol of $[Mn(Cp)(CO)_3]$ and 1 (bis(phosphines)) or 2 mmol (monodentate phosphines) of the ligand dissolved in *ca.* 30 ml of solvent. The reactions were carried out under N_2 and were monitored by IR and ^{31}P NMR in order to follow up the formation of mono- and di-substituted species. Typical irradiation times for monosubstitution are around 30 to 60 min, for disubstitution 90 to 120 min. In some cases ($Ph_2P(CH_2)_5PPh_2$ (dpppe), $Ph_2P(CH_2)_6PPh_2$ (dpph), $Cy_2P(CH_2)_2PCy_2$ (dcpe), and (*p*-Tol)$_2$P$(CH_2)_2$P(*p*-Tol)$_2$(dtpe)), only small amounts of [Mn(Cp)(CO)PP] were formed even after prolonged irradiation. The complexes [Mn(Cp)(CO)PP] with PP = dppe, $Ph_2P(CH_2)_3PPh_2$ (dppp) and $Ph_2P(CH_2)_4PPh_2$ (dppb) could be isolated in pure form by precipitation from the concentrated reaction mixtures in toluene with n-heptane.

IR spectra of the original solutions were obtained on a Perkin Elmer 577 spectrometer in 0.1 mm KBr cuvettes. $^{31}P\{^1H\}$ NMR spectra (Bruker WH 90,

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*Author to whom correspondence should be addressed.

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TABLE I. ^{31}P NMR[a] and IR Data of Monophosphine Derivatives of [Mn(Cp)(CO)$_3$].

PR$_3$	$\delta(^{31}P)$[b] (ppm)	θ[c] (°)	[Mn(Cp)(CO)$_2$PR$_3$]			[Mn(Cp)(CO)(PR$_3$)$_2$]		
			$\delta(^{31}P)$	$\Delta\delta$[d]	ν(CO) (cm^{-1})	$\delta(^{31}P)$	$\Delta\delta$[d]	ν(CO) (cm^{-1})
PH$_2$Ph	−125.3	101	+14.7	140.0	1940 1878	+0.2	125.5	1851
PMe$_3$	−60.8	118	+48.0	108.8	1928 1860	e		1831
P(iBu)$_3$	−48.4	145	+73.9	121.3	1928 1858	(28.8)[e]	(77.2)	(1827)[e]
PEt$_3$	−22.7	132	+77.7	100.4	1930 1860	+70.1	92.8	1820
PEtPh$_2$[f]	−13.7	141	+85.5	99.2	1918 1857	+86.8	100.5	1818
PPh$_3$	+5.3[g]	145	+92.2[h]	86.9		+92.0[h]	86.7	
P(iPr)$_3$	+19.4	160	+99.7[i]	80.3	1925 1858	e		e
P(tBu)$_3$	+63.1	182	+137.5	74.4	1918 1850	e		e
P(OEt)$_3$	+135.5	109	+204.0	68.5	1945 1875	+209.9	74.7	e

[a] At room temperature, except for PEtPh$_2$ (230 K) in THF. [b] For the free phosphine in the reaction mixture. [c] Tolman's cone angle [10]. [d] Coordination shift $\Delta\delta = \delta$(coordinated PR$_3$) − δ(free PR$_3$). [e] Not observed or not assigned unambiguously. [f] Reference for ΔR^1 (*cf.* Table II). [g] Ref. 11. [h] Ref. 12, in CH$_2$Cl$_2$; the value given for [Mn(η^5-C$_5$H$_4$Me)(CO)$_2$PPh$_3$] in ref. 11 is +96.0 ppm. [i] See also ref. 12 (δ = +98.9 in CH$_2$Cl$_2$).

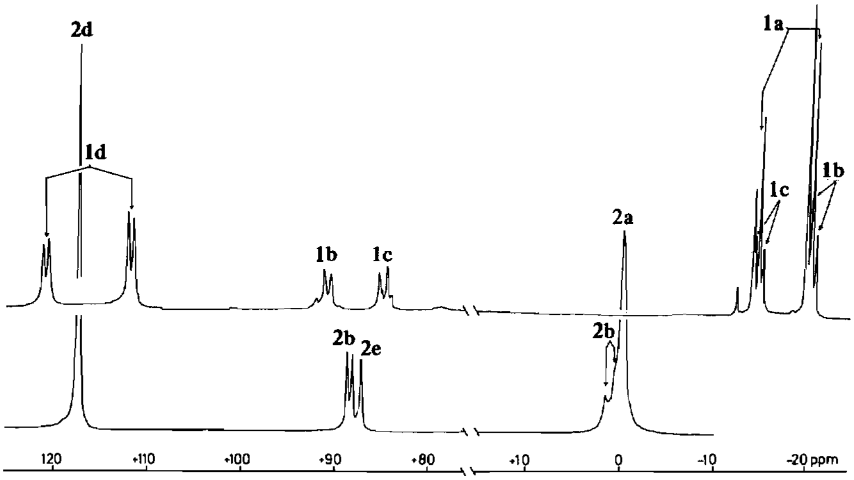

Fig. 1. ^{31}P{^{1}H} NMR spectra (230 K) of the photoproducts from the systems [Mn(Cp)(CO)$_3$]/Ph$_2$P(CH$_2$)$_2$PEt$_2$ (**1**) and [Mn(Cp)(CO)$_3$]/Cy$_2$P(CH$_2$)$_2$PCy$_2$ (**2**). a: Unreacted ligand; **1b**: {Mn}PPh$_2$(CH$_2$)$_2$PEt$_2$, **1c**: {Mn}PEt$_2$(CH$_2$)$_2$PPh$_2$, **2b**: {Mn}PCy$_2$(CH$_2$)$_2$PCy$_2$, **2e**: {Mn}$_2\mu$-Cy$_2$P(CH$_2$)$_2$PCy$_2$ ({Mn} = Mn(Cp(CO)$_2$); d: Cp(CO)MnPR$_2$(CH$_2$)$_2$PR$_2$. Several minor signals are unassigned.

0.5 M, 7.5 mm diameter vials in 10 mm vials containing aceton-d$_6$ as external lock) were scanned at 300 (monophosphines) and 230 K (PEtPh$_2$ and bis(phosphines)). The low temperature was necessary to suppress line broadening caused by scalar interaction with the ^{55}Mn nucleus (nuclear spin = 5/2) through relaxation decoupling, and thus to provide comparatively sharp signals. $\delta(^{31}P)$ are quoted relative to 80% H$_3$PO$_4$.

Results and Discussion

Depending on the irradiation time, monodentate phosphines can replace one or two CO groups in [Mn(Cp)(CO)$_3$], provided they are not too spacious (cone angle ≦160°). Bulky phosphines such as P(tBu)$_3$ form monosubstitution products only. Ditertiary phosphines PP, and the chelating arsaphosphines Ph$_2$As(CH$_2$)$_2$PPh$_2$ (arphos) and *o*-C$_6$H$_4$-AsPh$_2$(PPh$_2$) (pab) yield mono- and di-substituted complexes. The latter are mononuclear chelates, which are also formed with bis(phosphines) of substantial steric requirement (dcpe) and with the long-chain ligand dpph, although these phosphines need longer irradiation times than, *e.g.*, dppe, and have not been isolated in a pure form. In many cases, monosubstitution with PP affords a mixture of [Mn(Cp)(CO)$_2$PP*] with one of the phosphorus functions unligated (P*), and [{Mn(Cp)(CO)$_2$}$_2\mu$-PP]. The two complexes can easily be distinguished by their ^{31}P NMR patterns, except where the two PR$_2$

TABLE II. ^{31}P NMR[a] and IR Data of Bis(phosphine) and Arsaphosphine Derivatives of $[Mn(Cp)(CO)_3]$.

PP[b] Solvent		$\delta(^{31}P)^c$	$[Mn(Cp)(CO)_2PP^*]$				$[\{Mn(Cp)(CO)_2\}_2\mu\text{-}PP]$			$[Mn(Cp)(CO)PP]$				
			$\delta(^{31}P)$	^nJ	$\delta(^{31}P)_c$	$\Delta\delta$	$\delta(^{31}P)_c$	$\Delta\delta$	$\nu(CO)^j$	$\delta(^{31}P)_c$	$\Delta\delta$	ΔR^1	ΔR^2	$\nu(CO)$
dppm		−25.0	−28.4	87	+84.6	109.6	+91.0[d]	116.0[d]	1930 1866	+59.8[e]	84.8	−15.7	−31.2	1850
THF													(−24.8)	
dppe		−14.7					+87.9[f]	102.6	1927 1857	+117.2[g]	131.9	31.4	29.3	1820
THF														
dcpe[h]		−0.6	+0.8	19	+87.8	88.4	+86.6	87.2	1828 1855	+117.0	117.6	17.1	30.4	1817
THF													(29.2)	
dtpe		−10.1					+89.3	99.4	1930 1868	+90.2	100.3	−0.2	0.9	1828
THF														
pepe[h]	PEt$_2$:	−20.7	−21.6	26	+80.7	101.4			1928 1860	+110.9[i]	131.6	31.1	(30.2)	1832
THF	PPh$_2$:	−14.4	−14.7		+87.4	101.8				+120.8[i]	135.2	34.7	(33.4)	
c-dpe		−24.2	−32.2	15	+81.3	105.5			1930 1869	+121.1[k]	145.3	44.7	(39.8)	1858
THF														
ppb[l]		−15.2	−20.6	41	+95.0	110.2			1928 1862	+112.8	128.0	27.5	(17.8)	1848
THF														
arphos		−12.0					+87.0	99.0		+122.0	134.0	33.5	35.0	
pab[l]		−14.2	−20.1[n]				+95.8	110.0	1930 1870	+119.6	133.8	33.3	23.8	1860
THF														
dppp		−17.8	−18.1	<2	+83.8	101.6	+83.3	101.1	1926 1861	+87.3[o]	105.1	4.6	4.0	1826
toluene													(3.5)	
dppb		−17.8	−18.1	<2	+83.3	101.1	+83.8	101.6	1920 1861	+87.3	105.1	4.6	3.5	1829
toluene													(4.0)	
ppx		−17.9	−13.5	<2	+83.3	101.1	+92.4	110.3	1929 1850	+91.3	109.2	8.7	−1.1	1832
THF													(8.0)	
dpppe		−18.3	p				p		1925 1864	p				1828
THF														
dpph		−18.2	q				q		1924 1860	q				1822
THF														

[a] At 230 K. $\delta(^{31}P)_c$ = coordinated P; $\Delta\delta$ (coordination shift) = $\delta(^{31}P)_c - \delta(^{31}P)$ [free PP]; ΔR = ring contribution to $\delta(^{31}P)_c$: $\Delta R^1 = \delta$[chelate] − $\delta[Mn(Cp)(CO)(PEtPh_2)_2]$. ΔR^2 = δ[chelate] − $\delta[Mn(Cp)(CO)_2PP^*]$ or (in parenthesis) δ[chelate] − $\delta[\{Mn(Cp)(CO)_2\}_2\mu\text{-}PP]$. An asterisk denotes uncoordinated P. All values in ppm. ^nJ = $^{31}P-^{31}P$ coupling constants (in Hz) via n bonds. [b] Abbreviations: Cp = η^5-C_5H_5, Cp′ = η^5-C_5H_4Me; dppm; $Ph_2PCH_2PPh_2$, dppe = $Ph_2P(CH_2)_2PPh_2$, dcpe = $Cy_2P(CH_2)_2PCy_2$, dtpe = $(p\text{-Tol})_2P(CH_2)_2P(p\text{-Tol})_2$, pepe = $Ph_2P(CH_2)_2PEt_2$, c-dpe = cis-$Ph_2PCH{=}CHPPh_2$, ppb = o-$C_6H_4(PPh_2)_2$, arphos = $Ph_2As(CH_2)_2PPh_2$, pab = o-$C_6H_4AsPh_2(PPh_2)$, dppp = $Ph_2P(CH_2)_3PPh_2$, dppb = $Ph_2P(CH_2)_4PPh_2$, ppx = o-$C_6H_4(CH_2PPh_2)_2$, dpppe = $Ph_2P(CH_2)_5PPh_2$, dpph = $Ph_2P(CH_2)_6PPh_2$. [c] For the free phosphine in the reaction mixture. [d] For $[\{Mn(Cp')(CO)_2\}_2\mu\text{-dppm}]$ from ref. 11. [e] Compares to +58.4 ppm for $[Mn(Cp')(CO)dppm]$ [11]. [f] Compares to +91.0 ppm for $[\{Mn(Cp')(CO)_2\}_2\mu\text{-dppe}]$ [11]. [g] See also +117.3 [12] and +122.0 ppm ($[Mn(Cp')(CO)dppe]$) [11]. [h] Cf. Fig. 1. [i] Three-bond $^{31}P-^{31}P$ coupling = 22 Hz. [j] For monosubstitution (mono- and dinuclear not distinguished). [k] See also +121.3 ppm [13]. [l] From ref. 13. [m] From ref. 11 for $[\{Mn(Cp')(CO)_2\}_2\mu\text{-pape}]$ and $[Mn(Cp')(CO)pape]$. [n] Coordinated via $AsPh_2$. [o] The resonance position reported in ref. 12 is +82.0 ppm and might be erroneously assigned. [p] Two resonances (+89.0 and +84.3), not assigned. [q] Two resonances (+83.6 and +82.2), not assigned; cf. text.

groups are separated by more than four CH_2. Mononuclear monosubstitution products have not been observed in the case of dppe, arphos and dtpe. On the other hand, only dinuclear species are formed with $Ph_2P(CH_2)_2PEt_2$ (pepe), *cis*-$Ph_2PCH{=}CHPPh_2$ (*c*-dpe) and *o*-$C_6H_4(PPh_2)_2$ (ppb).

In Tables I and II, ^{31}P and IR results for the compounds with monodentate (Table I) and bidentate ligands (Table II) are collated. For comparison, a few selected data from the literature have been included. In the case of the ligands $Ph_2P(CH_2)_n$-PPh_2 with n = 5 and 6, unambiguous assignment of the ^{31}P resonances cannot be carried out. The identity of mono- and disubstituted species is, however, established by the CO stretching frequencies. In Fig. 1, representative spectra are shown for the photoproducts between $[Mn(Cp)(CO)_3]$ and the phosphines pepe and dcpe.

The usual down-field (high-frequency) shift of the ^{31}P resonance is observed as the phosphorus coordinates to a metal. For monodentate alkylphosphines, the coordination shift (*i.e.* the shift difference between the coordinated and the free phosphine) $\Delta\delta$ decreases, as the cone angle of the phosphine increases. This trend is quite commonly observed with other transition metal phosphine complexes [8, 14], where shielding variations have been interpreted in terms of varying $P(p_\sigma)$ and $P(d_\pi)$ influences on the bond order density matrix, Q, of the paramagnetic deshielding contribution to the overall shielding [8, 15, 16]. Increasing π-occupation of the phosphorus-3d orbitals (or corresponding π-type MOs of PR_3) leads to a decrease of shielding, as evidenced by the low-field (high-frequency) ^{31}P shift on coordination, or by the extreme low-field position of $[Mn(Cp)(CO)_2P(OEt)_3]$ (Table I). The impact of varying electronegativities of R and the RPR angles in PR_3 and MPR_3 upon Q have been deduced from theoretical considerations [15] and recently discussed comprehensively for $[M(Cp)$-$(CO)_3PZ_3]$ systems (M = V, Nb) [8].

Monosubstituted compounds containing bis(phosphines) show quite similar $\Delta\delta$ values (+99 to +110 ppm), if steric conditions are 'normal'. The monophosphine $PEtPh_2$ ($\Delta\delta$ = 99.2) falls within this range. Steric hindrance (complexes with coordinated PCy_2 groups) gives rise to an upfield shift of the ^{31}P resonance (decrease of $\Delta\delta$) comparable to that noted for $[Mn(Cp)(CO)_2PPh_3]$. There is no apparent difference between the $\Delta\delta$ of mono- and dinuclear monosubstitution products except for dppm (and this is again due to steric crowding in the dinuclear form). For the $[Mn(Cp)(CO)_2PP^*]$, two signals are observed in the ranges for coordinated P and P* (in the case of dpph, the signal for P* coincides with the ^{31}P resonance of the free phosphine). P* may be shifted to higher field with respect to the free phosphine (as in most cases), or to lower field (dcpe and *o*-$C_6H_4(CH_2PPh_2)_2$(ppx)); *cf.* also Fig. 1. The doublet splittings due to $^nJ(^{31}P-^{31}P)$ coupling observed with dppm (87), ppb (41), pepe (26), dcpe (19) and *c*-dpe (15 Hz) are comparable to those in $[Nb(Cp)(CO)_3PP]$ (dppm: 57, *c*-dpe: 22, pepe: 24 Hz) [8].

Steric factors become still more pronounced in the chelate complexes $[Mn(Cp)(CO)PP]$. The stable, basically unrestrained chelate five-membered ring structures all show extreme ^{31}P coordination shifts of about 135 ppm. In the torsionally-strained six- (dppp) and seven-membered (dppb, ppx) rings, deshielding on coordination is less by *ca.* 20 ppm, and the four-membered ring formed with dppm, which is especially strained by angle deformations at the phosphorus, exhibits a $\Delta\delta$ of 85 ppm. Analogous trends have been noted for, *inter alia, cis*-$[V(Cp)(CO)_2PP]$ [6], *cis*-$[Nb(Cp)(CO)_2PP]$ [17], *cis*-$[M(CO)_4PP]$ (M = Cr, W) [18] and *cis*-$[PtMe_2$-$PP]$ [19, 20].

Deviation from optimum bond angles (chelate four rings) or torsional strains due to conformational fluctuation (six- and seven-membered systems) lead to decreased metal-phosphorus interaction both in the σ donor and the π acceptor domaine, and thus give rise to a diminished Q term (relative to less strained or unstrained structures). This situation may also be quantified by the so-called ring-contribution ΔR, which can be defined through the difference of the $\Delta\delta$ values between a chelate and an appropriate open structure formed with two monodentate ligands [5]. Here we employ the complex $[Mn(Cp)(CO(PEtPh_2)_2]$ ($\Delta\delta$ = 100.5 ppm) as a reference. The near-to-identical $\delta(^{31}P)$ and $\Delta\delta$ for $[Mn$-$(Cp)(CO)_2PEtPh_2]$ and $[Mn(Cp)(CO)(PEtPh_2)_2]$ demonstrate that there is practically no steric hindrance in the complex containing two of the monodentate phosphines. The values, ΔR^1, are tabulated in Table II. Alternatively, the difference of $\Delta\delta$ values for the chelate system on the one hand, and the monosubstituted compounds carrying the same ligand on the other hand, can be used [6] to give ΔR^2 (Table II). The ΔR range from a negative value for $[Mn(Cp)(CO)dppm]$ to an optimum positive value for $[Mn(Cp)(CO)c$-dpe$]$. For the complexes formed with dtpe, dppp and dppb, the ΔR values are almost negligibly small.

It is also apparent that, in the block of chelate-five rings (dppe, dcpe, dtpe, pepe, arphos, *c*-dpe, ppb and pab), there are variations which can be attributed to steric (and – usually to a lesser extent – electronic) influences imposed by the substituents R in the $\{\overline{MnR_2P(CH_2)_2P}R_2\}$ moiety. The ambidentate pepe exhibits a slightly (3.6 ppm) smaller $\Delta\delta$ for the PEt_2 than for the PPh_2 group, but in general all the bis(phosphines) which carry phenyl substituents have very similar values. An exception is *c*-dpe, which contains an unsaturated back-bone and produces an extreme low-field shift, possibly because the π orbitals associated with the C=C double bond can participate in the overall π delocalizing ability of the ligand *via* a Mn(3d) → P(3d) → π^*(C=C) mechanism. The same extreme position has been observed with [V(Cp)(CO)$_2$*c*-dpe] [6]. The smaller $\Delta\delta$ for R = Cy may be due to the steric crowding around phosphorus while the still smaller $\Delta\delta$ and ΔR for R = *p*-Tol seem to be indicative of the +I effect of the methyl group (hence, an effect primarily electronic in nature), which diminishes the acceptor power of the phosphorus function and gives rise to less pronounced or reversed P(3d)–π(phenyl) electron transfer.

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