Quadrupole−Dipole Effects in Solid-State Phosphorus-31, CP-MAS NMR Spectra of Tertiary Phosphine Substituted Alkyl- and Acyltetracarbonylmanganese(I) Complexes

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A series of tertiary phosphine substituted alkyl- and acyltetracarbonylmanganese(I) complexes has been studied by cross-polarization and magic-angle-spinning (CP-MAS), ^{31}P solid-state NMR spectroscopy. All the spectra show an asymmetric sextet due to one-bond ^{31}P−^{55}Mn spin−spin coupling and second-order quadrupolar effects, transmitted by dipolar coupling between the ^{55}Mn and ^{31}P nuclei, which are not suppressed by magic-angle spinning. The chemical shift tensors, spin−spin coupling constants, dipolar coupling constants, quadrupolar coupling constants, and anisotropies in the spin−spin coupling have been determined. The shielding anisotropies of the alkyl complexes are larger than are those for the acyl complexes. The solid-state $^{1}J_{\mathrm{Mn-P}}$ spin−spin coupling constants range from 196 to 204 Hz for the alkyl compounds and from 216 to 233 Hz for the acyl complexes. The $^{1}J_{\mathrm{Mn-P}}$ values obtained from the solution ^{55}Mn NMR spectra for the alkyl complexes are ~50 Hz larger than are those obtained from the ^{31}P solid-state NMR studies. The nuclear quadrupole coupling constants range from 23 to 25 MHz.

Introduction

The wide chemical shift range, 100% natural abundance, high sensitivity, and large spin−spin interactions make the ^{31}P nucleus an ideal NMR probe for the study of chemical structures, bonding interactions, and molecular dynamics. When a phosphorus ligand is coordinated to a metal center, the ^{31}P chemical shift is influenced by such factors as the metal atom, the bonding interaction between the phosphorus and metal atoms, and the oxidation state and coordination number of the metal. The influence of the *cis* and *trans* ligands and the position of the phosphorus ligand within the coordination sphere can also have a large effect on the chemical shifts. Most of the theoretical and experimental work on transition metal−tertiary phosphine complexes has involved studies of isotropic chemical shifts in solution.[1−3] A change in the molecular structure may lead to small changes in the isotropic shift and spin−spin coupling but to significant differences in their tensor components. Therefore, the anisotropy of these shifts can be more informative than are the isotropic values, and this information can be obtained from solid-state ^{31}P NMR spectra.

We report here the results of an analysis of the solid-state, CP-MAS ^{31}P NMR spectra of the following series of manganese(I) complexes: *cis*-$PhCH_2C(O)Mn(CO)_4(PPh_3)$ (**I**), *cis*-$MesCH_2C(O)Mn(CO)_4(PPh_3)$ (**II**), *cis*-$PhCH_2C(O)Mn(CO)_4[P(C_6H_{11})_3]$ (**III**), *cis*-Mes-$CH_2C(O)Mn(CO)_4[P(C_6H_{11})_3]$ (**IV**), *cis*-$PhCH_2Mn(CO)_4(PPh_3)$ (**V**), *cis*-$PhCH_2Mn(CO)_4$-[P(*p*-tolyl)$_3$] (**VI**), and *cis*-$PhCH_2Mn(CO)_4$[P(*p*-$FC_6H_4)_3$] (**VII**), where $PhCH_2$ and $MesCH_2$ are benzyl ($C_6H_5CH_2$) and 2,4,6-trimethylbenzyl [2,4,6-$(CH_3)C_6H_2CH_2$], respectively. These types of complexes have received considerable attention for the past 20 years due to their mechanistic importance in homogeneous hydroformylation reactions and other catalytic processes that involve alkyl migration, carbonyl insertion, or carbonyl elimination reactions.[4−6]

The first alkyl- and acylmanganese(I) phosphine complexes were prepared in the early 1960s by Kraihanzel and Maples[7] by the reaction of pentacarbonylmethylmanganese(I) with triphenylphosphine, and the *cis* and *trans* isomers of $CH_3Mn(CO)_4(PPh_3)$ and $CH_3C(O)Mn(CO)_4(PPh_3)$ were identified. Subsequent X-ray structural analysis for these complexes[8,9] revealed that the crystal structures are disordered and confirmed the presence of the *cis* and *trans* isomers. These results led to speculation that both the methyl and/or the carbonyl groups can migrate. It was 10 years later that Flood *et al.*,[10] by using ^{13}CO, and Cotton *et al.*,[11−13] by using large alkyl groups, established that the alkyl group migrates onto a carbonyl group and that the carbonyl group does not insert into the metal−alkyl bond. The crystal structures of benzyltetracarbonyl(triarylphosphine)manganese(I) and benzyltetracarbonyl(tricyclohexylphosphine)manganese(I) were determined by Markwell and co-workers[14]

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and it was shown that only the *cis* isomer was present in the solid-state. Single crystals of the acyl product suitable for X-ray structure determination could not be obtained. Therefore, we decided to study these complexes by solution and solid-state NMR spectroscopy to test for the presence of *cis-trans* isomers and to detect the differences in the magnetic properties of the alkyl and acyl complexes.

When a spin-$^1/_2$ nucleus is bonded to a quadrupolar nucleus, the resulting solid-state spectrum is more complicated than is the solution spectrum. The latter often shows only a single line without spin−spin coupling, but in the solid-state CP-MAS spectrum, multiplets with uneven spacings are observed. Recently, these splittings have been explained by a first-order perturbation treatment for high-field cases leading to the expression in eq 1,[15] where m is the component of the spin S

$$\Delta\nu_{\mathrm{m}} = -mJ + ({}^{3}/_{20}\,\chi D'/\nu_S)\{S(S+1) - 3m^2\}/\{\mathrm{S}(2\mathrm{S}-1)\} \tag{1}$$

along the magnetic field $\boldsymbol{B}_{\mathbf{o}}$ ($m = S, S - 1, ..., -S$), J is the isotropic $I - S$ indirect coupling constant, ν_{S} is the resonance frequency of the quadrupolar nucleus, χ is the quadrupolar coupling constant (e^2qQ/h), and D' is the effective dipolar coupling constant, including the anisotropy in the spin−spin coupling (ΔJ) (eq 2). The angular terms α^D ,β^D ,α^J, and β^J

$$D' = 3(D\cos^2\beta^D - (\Delta J/3)\cos^2\beta^J) - (D - \Delta J/3) + \eta(D\sin^2\beta^D\cos 2\alpha^D - (\Delta J/3)\,D\sin^2\beta^J\cos 2\alpha^J) \tag{2}$$

describe the orientation of the internuclear dipole vector and the indirect coupling tensor in the principal-axis system of the electric field gradient $\mathbf{q}$. The term η is the asymmetry in $\mathbf{q}$. The angular terms are difficult to determine and it is often assumed that the $\mathbf{J}$ tensors are colinear with the internuclear vector r_{I-S}. This assumption results in a simplified expression for D' (eq 3).

$$D' = (D - \Delta J/3)\,(3\cos^2\beta - 1 + \eta\sin^2\beta\cos 2\alpha) \tag{3}$$

The effective dipolar coupling can be obtained from an analysis of the spinning-sideband manifolds. The intensities of the spinning-sidebands arise from interaction of the three tensors $\boldsymbol{\sigma}$, $\mathbf{D}$, and $\mathbf{J}$, and the difference in the chemical shift anisotropies between successive eigenstates should be a constant, equal to D'. The effective anisotropy for the coupling between two different spins I, S, was shown by Gobetto *et al.*[16] to be given by eq 4, where Ω_I is the shielding anisotropy of the I

$$\Omega_{mI} = \Omega_I - (2(D - \Delta J/3)/\upsilon_{\mathrm{I}})\,m_S \tag{4}$$

nucleus, Ω_{mI} is the shielding anisotropy of the I spin for the m eigenstate of the S nucleus, and υ_I is the Larmor frequency of the I spin. Thus, it is possible, in principle, to obtain the anisotropy in the chemical shift, the anisotropy in J_{I-S}, and the nuclear quadrupole coupling constant from these solid-state NMR experiments.

The electric quadrupole moment of ^{55}Mn is large but direct nuclear quadrupole resonance measurements have been reported for only a few manganese carbonyl compounds. If quadrupolar relaxation is dominant then the NMR line widths, i.e. $1/T_1$, of the ^{55}Mn resonances in solution are proportional to the square of the NQR coupling constant. Brown *et al.*[17] have shown that such a relationship exists for several manganese complexes in tetrahydrofuran solution. Thus, the NQR coupling constants can be estimated from ^{55}Mn solution NMR line widths, and such data are also reported in this paper.

Experimental Section

The solution ^{1}H, ^{13}C, ^{31}P, and ^{55}Mn NMR spectra were recorded at room temperature for concentrated solutions in $CDCl_3$ on a Varian XL-300 spectrometer operating at a field strength of 7.05 T. The ^{1}H and ^{13}C chemical shifts are referenced to an external sample of TMS. The ^{31}P chemical shifts are referenced to an external sample of 85% H_3PO_4, and the ^{55}Mn chemical shifts, to an external sample of $KMnO_4$ in D_2O. The solid-state, CP-MAS ^{31}P NMR spectra were recorded on a Chemagnetics CMX-300 spectrometer operating at 121.279 MHz, with high-power proton decoupling, using a recycle time of 6 s and a contact time of 2 ms. No line broadening was applied, and the FIDs were zero-filled to 8K points before transformation. The CP-MAS spectra were obtained for approximately 250−300 mg samples packed into bullet-type zirconia rotors (7.5 mm diameter). Different spinning rates, ranging from 2.0 to 4.5 kHz, were used to identify the isotropic peaks. Deconvolutions were performed on the center and spinning sidebands by using the program Peakfit (Jandel Scientific). Calculation of the shielding tensors was achieved with the aid of a computational package developed by Kentgens *et al.*[18] Infrared spectra were recorded on a Bruker IFS-48 FT-IR spectrometer for Nujol mulls on KBr plates at a resolution of 4 cm^{-1}. Raman spectra were measured on a Bruker IFS-88 FT-IR spectrometer equipped with a FRA-106 FT-Raman module and a liquid nitrogen-cooled proprietary detector. The 1064.1-nm line of an air-cooled, Nd^{3+}:YAG near-IR laser was used to excite the spectra at 4 cm^{-1} resolution. The samples were packed into a 2-mm diameter sampling cup, and the maximum laser power (230 mW) was employed.

The solid organomanganese(I) complexes were synthesized by methods based on those described previously by Cotton *et al.*[12] Benzyl- and (2,4,6-trimethylbenzyl)pentacarbonylmanganese(I) were prepared by reductive cleavage of $Mn_2(CO)_{10}$ with sodium amalgam in tetrahydrofuran, yielding $Na[Mn(CO)_5]$, which in turn was treated with benzyl chloride or 2,4,6-trimethylbenzyl chloride to form the alkyl product. Reaction of benzyl- and (2,4,6-trimethylbenzyl)pentacarbonylmanganese(I) with triphenylphosphine and tricyclohexylphosphine in acetonitrile yielded the solid acyl complexes, **I**−**IV**, respectively. Attempts to synthesize acyl complexes of tris(*p*-fluorophenyl)phosphine and tris(*p*-tolyl)phosphine resulted in dark brown oils, which decomposed into black solids, presumably MnO_2. The benzyl(tetracarbonyl)(triarylphosphine)manganese(I) complexes **V**−**VII** were prepared by thermal decarbonylation at 65 °C of the respective acyl complexes in acetonitrile. Attempts to synthesize the 2,4,6-trimethylbenzyl analogs were unsuccessful. Compounds **I**−**VIII** were characterized by their FT-IR, FT-Raman, and solution ^{1}H, ^{13}C, ^{31}P, and ^{55}Mn NMR spectra and the similarity of some of these spectra to those in the literature.

Characterization of Complexes. ***cis*-BzC(O)Mn(CO)$_4$(PPh$_3$).** The yellow compound was precipitated out of the reaction mixture and was washed with acetonitrile at 10 ºC. ^{1}H NMR ($CDCl_3$) δ (ppm): 4.0 (s, 2H, CH_2), 7.0 (m, 5H, phenyl), 7.5 (m, 15H, phenylphosphine). ^{13}C NMR δ (ppm): 71.2 (s, CH_2), 130 (m, phenyl), 213.4 (d, $^2J_{\mathrm{PC}}$ 12.1 Hz, CO *trans* to P), 214.1 (d, $^2J_{\mathrm{PC}}$ 20.1 Hz, CO *trans* to CO), 216.7 (d, $^2J_{\mathrm{PC}}$ 6.0 Hz, CO *trans* to CH_2) 267.9 (d, $^2J_{\mathrm{PC}}$ 16.3 Hz, C═O). ^{31}P NMR δ (ppm): 50.6 (s). ^{55}Mn NMR δ (ppm): −1682.5 (s, $\Delta\nu_{1/2}$ 2146 Hz). IR (Nujol mull on KBr plates): [ν(CO) region, $a_1{}^1$, b_1, $a_1{}^2$, b_2, acyl] 2059, 1992, 1965, 1953, 1622 cm^{-1}. Raman (powder in sample cup): [ν(CO) region, $a_1{}^1$, b_1, $a_1{}^2$, b_2, acyl] 2060, 1995, 1954, 1935, 1626 cm^{-1}.

***cis*-MesCH$_2$C(O)Mn(CO)$_4$(PPh$_3$).** A yellow powder was precipitated out of the reaction mixture and was washed with acetonitrile at 25 °C. ^{1}H NMR ($CDCl_3$) δ (ppm): 2.0 (s, , 6H *o*-CH_3), 2.2 (s, 3H, *p*-CH_3), 4.0 (s, 2H, CH_2), 6.8 (s, 2H, phenyl), 7.5 (m, 15H, phenylphosphine). ^{13}C NMR δ (ppm): 20.2 (s, *o*-CH_3), 20.8 (s, *p*-CH_3), 67.2 (s, CH_2), 130 (m, phenyl), 213.1 (d, $^2J_{\mathrm{PC}}$ 12.3 Hz, CO *trans* to P), 215.0

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(d, $^2J_{PC}$ 21.3 Hz, CO *trans* to CO), 217.7 (d, $^2J_{PC}$ 5.2 Hz, CO *trans* to CH_2), 264.3 (d, $^2J_{PC}$ 14.3 Hz, C=O). ^{31}P NMR δ (ppm): 51.2 (s). ^{55}Mn NMR δ (ppm): −1693.5 (s, $\Delta\nu_{1/2}$ 2960 Hz). IR (Nujol mull on KBr plates): [ν(CO) region, a_1^1, b_1, a_1^2, b_2, acyl] 2058, 1992,1965, 1946, 1634 cm^{-1}. Raman (powder in sample cup): [ν(CO) region, a_1^1, b_1, a_1^2, b_2, acyl] 2059, 1986, 1943, 1918, 1636 cm^{-1}.

***cis*-BzC(O)Mn(CO)$_4$[P(C$_6$H$_{11}$)$_3$].** The yellow compound was first dissolved in dichloromethane and was then precipitated out by the slow addition of acetonitrile at 10 °C. ^1H NMR ($CDCl_3$) δ (ppm): 1.7 (m, 33H, tricyclohexylphosphine), 4.26 (s, 2H, CH_2), 7.1 (m, 5H, phenyl). ^{13}C NMR δ (ppm): 28.7 (m, tricyclohexyl), 71.1 (s, CH_2), 128 (m, phenyl), 214.2 (d, $^2J_{PC}$ 14.9 Hz, CO *trans* to P), 216.6 (d, $^2J_{PC}$ 19.4 Hz, CO *trans* to CO), 217.2 (d, $^2J_{PC}$ 5.1 Hz, CO *trans* to CH_2), 267.3 (d, $^2J_{PC}$ 13.1 Hz, C=O). ^{31}P NMR δ (ppm): 53.4. ^{55}Mn NMR δ (ppm): −1802 (s, $\Delta\nu_{1/2}$ 3330 Hz). IR (Nujol mull on KBr) plates: [ν(CO) region, a_1^1, b_1, a_1^2, b_2, acyl] 2048, 1989, 1980, 1944, 1629 cm^{-1}. Raman (powder in sample cup): [ν(CO) region, a_1^1, b_1, a_1^2, b_2, acyl] 2050, 1970, 1955, 1927, 1632 cm^{-1}.

***cis*-MesCH$_2$C(O)Mn(CO)$_4$[P(C$_6$H$_{11}$)$_3$].** The yellow compound was first dissolved in dichloromethane and was then precipitated out by the slow addition of acetonitrile at 20 °C. ^1H NMR ($CDCl_3$) δ (ppm): 1.7 (m, 33H, tricyclohexylphosphine), 2.1 (s, 6H, *o*-CH_3), 2.2 (s, 3H, *p*-CH_3), 4.4 (s, 2H, CH_2), 6.8 (m, 2H, phenyl). ^{13}C NMR δ (ppm): 28.7 (m, tricyclohexyl), 66.7 (s, CH_2), 130 (m, phenyl), 214.3 (d, $^2J_{PC}$ 16.7 Hz, CO *trans* to P), 217.6 (d, $^2J_{PC}$ 19.7 Hz, CO *trans* to CO), 218.1 (d, $^2J_{PC}$ 3.1 Hz, CO *trans* to CH_2), 267.3 (d, $^2J_{PC}$ 11.5 Hz, C=O). ^{31}P NMR δ (ppm): 54.7 (s). ^{55}Mn NMR δ (ppm): −1774 (s, $\Delta\nu_{1/2}$ 3404 Hz). IR (Nujol mull on KBr plates): [ν(CO) region, a_1^1, b_1, a_1^2, b_2, acyl] 2045, 1961, 1946, 1930, 1643 cm^{-1}. Raman (powder in sample cup): [ν(CO) region, a_1^1, b_1, a_1^2, b_2, acyl] 2045, 1968, 1957, 1930, 1644 cm^{-1}.

***cis*-BzMn(CO)$_4$(PPh$_3$).** The crude sample was recrystallized from a hexane−ethanol mixture and then washed with 95% ethanol. Yellow crystals were obtained by slow evaporation from a 1:1 mixture of benzene and cyclohexane. ^1H NMR ($CDCl_3$) δ (ppm): 1.7 (d, 2H, $^3J_{PH}$ 6.0 Hz, CH_2), 7.0 (m, 5H, phenyl), 7.6 (m, 15H, phenylphosphine). ^{13}C NMR δ (ppm): 17.1 (d, $^2J_{PC}$ 8.4 Hz, CH_2), 128 (m, phenyl), 216.1 (d $^2J_{PC}$ 21.1 Hz, CO *trans* to P), 217.1 (d, $^2J_{PC}$ 10.1 Hz, CO *trans* to CH_2), 219.8 (d, $^2J_{PC}$ 20.3 Hz, CO *trans* to CO). ^{31}P NMR δ (ppm): 61.4 (s). ^{55}Mn NMR δ (ppm): −1819.3 (d, $^1J_{Mn-P}$ 256.9 Hz, peak width at half-height ($\Delta\nu_{1/2}$) 178 Hz). IR (Nujol mull on KBr plates) : [ν(CO) region, a_1^1, b_1, a_1^2, b_2] 2048, 1987, 1962, 1931 cm^{-1}. Raman (powder in sample cup): [ν(CO) region, a_1^1, b_1, a_1^2, b_2] 2050, 1973, 1961, 1917 cm^{-1}.

***cis*-BzMn(CO)$_4$[P(Tolyl)$_3$].** The sample was recrystallized from a hexane−ethanol mixture and then washed with 95% ethanol. Yellow crystals were obtained by slow evaporation from a 2:1 mixture of benzene and ethanol over a period of 2 days. ^1H NMR ($CDCl_3$) δ (ppm): 1.7 (d, 2H, $^3J_{PH}$ 6.3 Hz, CH_2), 2.41 (s, CH_3), 7.0 (m, 5H, phenyl), 7.4 (m, 12H, phenylphosphine). ^{13}C NMR δ (ppm): 17.4 (d, $^2J_{PC}$ 8.5 Hz, CH_2), 21.3 (s, CH_3), 133 (m, phenyl), 215.8(d, $^2J_{PC}$ 21.4 Hz, CO *trans* to P), 216.4 (d, $^2J_{PC}$ 9.3 Hz, CO *trans* to CH_2), 219.6 (d $^2J_{PC}$ 22.7 Hz, CO *trans* to CO). ^{31}P NMR δ (ppm): 69.0 (s). ^{55}Mn NMR δ (ppm): −1819.2 (d, $^1J_{Mn-P}$ 252.2 Hz, $\Delta\nu_{1/2}$ 148 Hz). IR (Nujol mull on KBr plates): [ν(CO) region, a_1^1, b_1, a_1^2, b_2] 2049, 1976, 1971, 1917 cm^{-1}. Raman (powder in sample cup): [ν(CO) region, a_1^1, b_1, a_1^2, b_2] 2046, 1775,1971, 1919 cm^{-1}.

***cis*-BzMn(CO)$_4$[P(p-fluorophenyl)$_3$].** The sample was recrystallized from a dichloromethane−ethanol mixture and then washed with 95% ethanol. Golden yellow crystals were obtained by slow evaporation from a 2:1 mixture of dichloromethane and ethanol over a period of 16 h. ^1H NMR ($CDCl_3$) δ (ppm): 1.7 (d, 2H, $^3J_{PH}$ 5.3 Hz, CH_2), 7.2 (m, 17H, phenyl). ^{13}C NMR δ (ppm): 17.4 (d, $^2J_{PC}$ 8.1 Hz, CH_2), 138 (m, phenyl), 216.4 (d, $^2J_{PC}$ 19.7 Hz, CO *trans* to P), 217.3 (d, $^2J_{PC}$ 8.3 Hz, CO *trans* to CH_2), 220.1 (d, $^2J_{PC}$ 21.3 Hz, CO *trans* to CO). ^{31}P NMR δ (ppm): 61.1 (s). ^{55}Mn NMR δ (ppm): −1822.5 (d, $^1J_{Mn-P}$ 254.8 Hz, $\Delta\nu_{1/2}$ 222 Hz). IR (Nujol mull on KBr plates): [ν(CO) region, a_1^1, b_1, a_1^2, *b_2*] 2050, 1977, 1967, 1929 cm^{-1}. Raman (powder in sample cup): [ν(CO) region, a_1^1, b_1, a_1^2, b_2] 2050, 1982, 1963, 1918 cm^{-1}.

Table 1. $^2J_{PC}$ Coupling Constants for Compounds **I−VII**[a]

compound	C[b] (Hz)	$^{\alpha}$CO[c] (Hz)	$^{\beta}$CO[d] (Hz)	$^{\gamma}$CO[e] (Hz)
$PhCH_2C(O)Mn(CO)_4(PPh_3)$ (**I**)	16.3	12.3	6.0	20.1
$MesCH_2C(O)Mn(CO)_4(PPh_3)$ (**II**)	14.3	12.3	5.2	21.3
$PhCH_2C(O)Mn(CO)_4[P(C_6H_{11})_3]$ (**III**)	13.1	14.9	5.1	19.4
$MesCH_2C(O)Mn(CO)_4[P(C_6H_{11})_3]$ (**IV**)	11.5	16.7	3.1	19.7
$PhCH_2Mn(CO)_4(PPh_3)$ (**V**)	8.4	21.1	10.1	20.3
$PhCH_2Mn(CO)_4[P(Tolyl)_3]$ (**VI**)	8.5	21.4	9.3	22.7
$PhCH_2Mn(CO)_4[P(PhF)_3]$ (**VII**)	8.1	19.7	8.4	21.3

[a] Data from solution ^{13}C NMR spectra with an uncertainty of ±0.5 Hz. [b] Acyl or alkyl group. [c] CO *trans* to tertiary phosphine. [d] CO *trans* to alkyl or acyl group. [e] CO *trans* to CO.

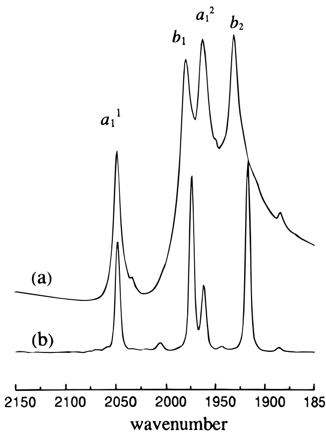

Figure 1. (a) FT-IR and (b) FT-Raman spectra of *cis*-Bz(CO)$_4$MnPPh$_3$ in the carbonyl region showing the four vibrational modes, a_1^1, b_1, a_1^2 and b_2 in decreasing wavenumber.

Results and Discussion

The solution ^{31}P NMR spectra of all the alkyl- and acylmanganese(I) complexes exhibited only sharp singlets in the 50−62 ppm range, indicating the presence of a single isomer. The ^{13}C NMR solution spectra in the carbonyl region contained three sets of doublets confirming the presence of three different carbons each coupled to phosphorus. The two-bond carbon−phosphorus spin−spin coupling constants, $^2J_{CP}$, for the acyl, alkyl, and carbonyl groups are given in Table 1. The $^2J_{CP}$ values for the carbonyl groups *trans* to another carbonyl ligand lie in the range 19−23 Hz and showed little or no variation for the series of complexes studied. The values are about 10 Hz larger for the carbonyl group *trans* to an acyl or alkyl group, and similar values were obtained for the CO ligand *trans* to the tertiary phosphine substituent in the alkyl complexes. It was observed that the $^2J_{CP}$ values for the acyl groups are larger than are those of the alkyl compounds, and the $^2J_{CP}$ values for the CO group *trans* to the acyl groups are about 3 Hz smaller compared to those for the alkyl complexes. These effects can be attributed to a Fermi contact mechanism because acyl carbons are sp^2 hybridized while those of alkyl groups are sp^3 hybridized.

The FT-IR and FT-Raman spectra exhibited four vibrational modes in the 2250−1850 cm^{-1} carbonyl region (Figure 1). Group theory for an octahedral $RMn(CO)_4L$ species predicts one IR-active (e_u) and two Raman-active ($a_{1g} + b_{1g}$) vibrational modes for the *trans* isomer, but four IR-active and four Raman-active ($2a_1 + b_1 + b_2$) vibrational modes for the *cis* isomer. The solution ^{31}P NMR, FT-IR, and FT-Raman spectra indicate *cis* geometry for all the alkyl and acyl complexes studied, which is in agreement with previous reports for *cis*-R′Mn(CO)$_4$(PR$_3$) complexes.[10−13] From these results, the possible mechanistic pathways are alkyl or carbonyl group migration but not a combination of both processes. The latter would result in a mixture of *cis* and *trans* isomers for the alkyl and acyl

Table 2. Solution and Solid-State ^{31}P NMR Isotropic Chemical Shifts and Coupling Constants of Compounds **I**−**VII**^{a,b}

compound	δ_{iso}(soln)^c	δ_{iso}(solid)^c	J_{Mn-P} (solid) (Hz)	d^e (Hz)
$PhCH_2C(O)Mn(CO)_4(PPh_3)$ (**I**)	50.6	54.1	216(4)	109(1)
$MesCH_2C(O)Mn(CO)_4(PPh_3)$ (**II**)	51.2	53.2	233(2)	112(1)
$PhCH_2C(O)Mn(CO)_4[P(C_6H_{11})_3]$ (**III**)	53.2	55.4	220(2)	108(3)
$MesCH_2C(O)Mn(CO)_4[P(C_6H_{11})_3]$ (**IV**)	54.7	54.4	232(2)	97(3)
$PhCH_2Mn(CO)_4(PPh_3)$ (**V**)	61.4	68.0	202(2)	110(2)
$PhCH_2Mn(CO)_4[P(Tolyl)_3]$ (**VI**)	59.0	65.6	196(3)	103(2)
$PhCH_2Mn(CO)_4[P(PhF)_3[$ (**VII**)	61.1	66.1	204(1)	114(3)

^{a} Values of isotropic shifts are in ppm, relative to external 85% H_3PO_4. ^{b} Abbreviations: Mes = 2,4,6-trimethylbenzyl, Ph = phenyl, Tolyl = *p*-tolyl and PhF = *p*-fluorophenyl. ^{c} Uncertainties are ±0.2 and ±0.5 ppm for the solution and solid-state ^{31}P NMR spectra, respectively. ^{e} $d = 3\chi D'/10\nu_s$.

complexes, and this was not observed. Introduction of a bulky group, 2,4,6-trimethylbenzyl, did not lead to carbonyl elimination for the acyl complexes. This may due to the steric crowding of the methyl groups on the phenyl ring which hinder the alkyl group from remigrating. If the reactions proceeded by carbonyl migration, it should then be possible for the acyl CO group located between the metal and the alkyl group to be eliminated, affording a metal−alkyl bond. But this was not observed, and it was concluded that the reactions proceeded by alkyl migration and not by carbonyl migration, in agreement with earlier studies.[10−13]

The measured ^{31}P chemical shifts of compounds **I**−**VII** in solution and the solid-state are given in Table 2. The isotropic chemical shifts, δ_{iso}, in the solid-state are close to the values obtained for the solutions, indicating that the structures are the same in the solid state and in solution. The chemical shifts for the alkyl complexes are more deshielded than are those for the acyl compounds. This may be due to the greater shielding effects of the acyl group *cis* to the tertiary phosphine ligand. The spin−spin coupling between phosphorus and manganese, $^1J_{Mn-P}$, cannot be determined from the solution ^{31}P NMR spectra because of fast quadrupolar relaxation processes. However, it could be observed in the solution ^{55}Mn NMR spectra for the alkyl complexes, **V**−**VII**, and in the solid-state ^{31}P NMR spectra for both the acyl and alkyl compounds. The $^1J_{Mn-P}$ values obtained from the solution ^{55}Mn spectra were ~50 Hz larger than those obtained from the ^{31}P solid-state spectra for the alkyl complexes. This may be due to changes in torsion angle of the aryl rings, which, in this case, are found to increase the $^1J_{Mn-P}$ coupling. The ^{55}Mn NMR chemical shift for compound **V** was determined previously by Cotton *et al.*,[13] DeShong *et al.*[19] and Rehder[20] to be −1819 ppm with a $^1J_{Mn-P}$ of 260 ± 8 Hz. These values are in excellent agreement with those we obtained, −1819 ppm and $^1J_{Mn-P}$ of 257 Hz. The structure of this complex has been characterized by X-ray diffraction and exists only in the *cis* conformation.[14] The value, δ_{Mn} −1939 ppm ($\Delta v_{1/2}$ = 22 000 Hz), reported by Torocheshniknov *et al.*[21] appears to belong to the *trans* isomer with no $^1J_{Mn-P}$ coupling. The solution ^{55}Mn spectra NMR for the acyl compounds are very broad with $\Delta v_{1/2}$ = 2100−3400 Hz, and no $^1J_{Mn-P}$ splitting is observed.

The solid-state ^{31}P spectra are complicated (Figure 2) and second-order effects are evident due to the presence of the quadrupolar ^{55}Mn nucleus ($S = {}^5/_2$). Peak fitting **(**Figure 3) and centerband analyses were feasible for all the compounds, by using eq 1, which resulted in the determination of J_{Mn-P}, the quadrupolar−dipolar constants, *d*, and the isotropic chemical shifts. The $^1J_{Mn-P}$ couplings for the acyl compounds lie in the 216−233 Hz range, about 10 Hz larger than those for the alkyl complexes. The values for the substituted phenylacyl com-

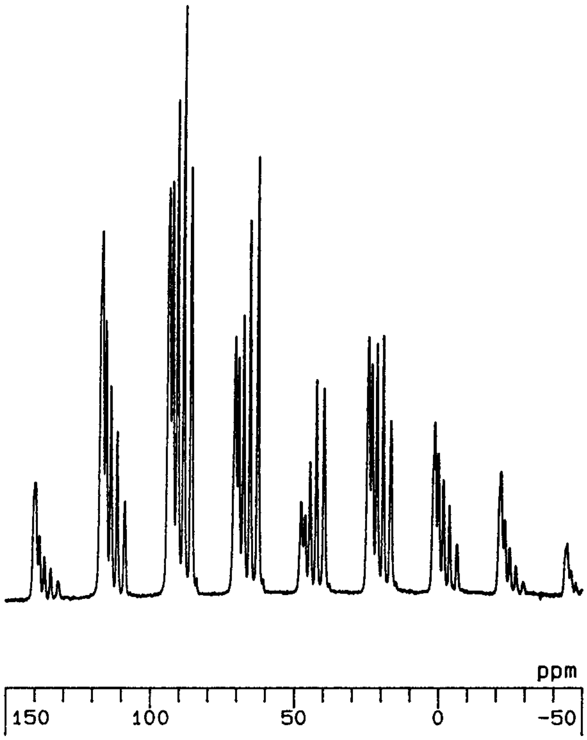

Figure 2. Solid-state ^{31}P CP-MAS NMR spectra of *cis*-$PhCH_2(CO)_4MnPPh_3$, including spinning sidebands (rotor frequency = 2800 Hz, 508 scans), obtained at 121.279 MHz with proton dipolar decoupling.

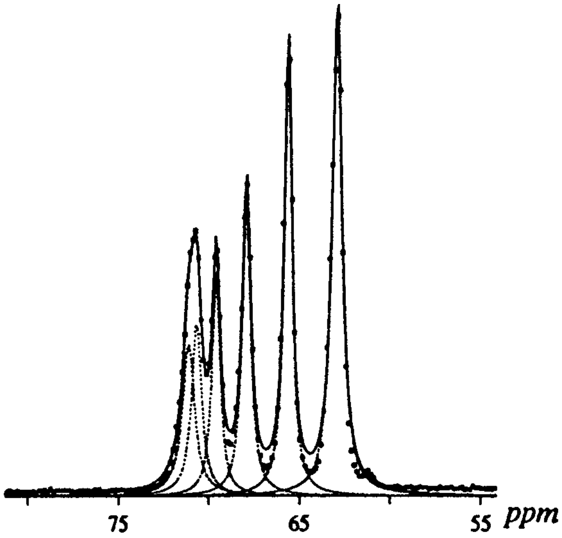

Figure 3. Experimental solid-state ^{31}P CP-MAS NMR centerband of *cis*-$PhCH_2(CO)_4MnPPh_3$ (upper trace) and simulated peak fit (bottom).

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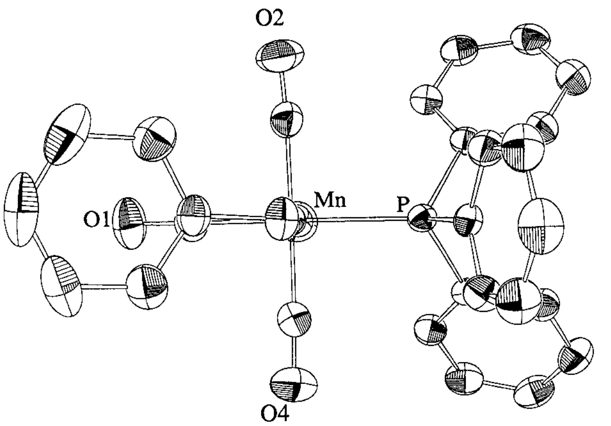

Figure 4. X-ray structure of *cis*-Bz(CO)$_4$MnPPh$_3$ showing the mirror plane.

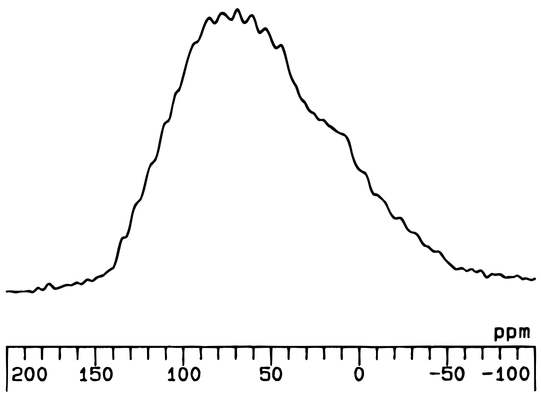

Figure 5. Solid-state ^{31}P CP-NMR power pattern for *cis*- Mes-CH$_2$C(O)(CO)$_4$MnPPh$_3$.

Table 3. Effective Dipolar and Chemical Shift Tensor Data for *cis*-PhCH$_2$Mn(CO)$_4$(PPh$_3$) from Spinning Sidebands Analysis^{a,b}

m	centerband δ (±0.2 ppm)	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)	$\Omega_{Im}{}^c$ (ppm)	$D''^{d,e}$ (Hz)
$^5/_2$	62.9	111.4	82.2	−4.8	−101.6	1097
$^3/_2$	65.7	120.4	90.6	−14.0	−119.5	1105
$^1/_2$	67.9	127.0	100.3	−23.6	−137.3	1163
$-^1/_2$	69.6	134.8	108.9	−34.8	−156.6	1190
$-^3/_2$	70.7	141.3	122.1	−51.3	−183.0	1460^f
$-^5/_2$	71.7	157.0	107.3	−50.9	−183.1	880^f

[a] Assuming $\eta = 0$. [b] Uncertainty is ±2 ppm for tensor quantities obtained from the MAS spectra at three different spinning speeds. [c] Anisotropy parameter $\Omega_{Im} = \delta_{33m} - {}^1/_2(\delta_{11m} + \delta_{22m})$, where $|\delta_{33m} - \delta_{\rm isom}| > |\delta_{11m} - \delta_{\rm isom}| > |\delta_{22m} - \delta_{\rm isom}|$. [d] $D'' = (D - \Delta J/3)$. [e] Average $D'' = 1139 \pm 39$ Hz, neglecting $m = -^5/_2$ and $-^3/_2$. [f] Reduced accuracy because of overlapping peaks.

plexes, **II** and **IV**, are about 12 Hz greater than are those for the unsubstituted phenylacyl compounds, **I** and **III**. The $^1J_{\rm Mn-P}$ values obtained by Lindner *et al.*[22] for a series of bromo complexes lie in the range 197−210 Hz and are of similar magnitude to those obtained for the alkyl complexes. The values reported by Gobetto *et al.*[16] for Mn$_2$(CO)$_9$PPh$_3$ and Mn$_2$(CO)$_8$(PPh$_3$)$_2$ are 70 and 105 Hz larger, chiefly because of *trans* effects. The ^{31}P chemical shifts of the alkyl complexes, both in solution and the solid state, are about 10 ppm less shielded than are those for the acyl complexes (Table 2). These differences may due to the steric and shielding effects of the oxygen atoms of the acyl groups on the tertiary phosphine ligand. The effective dipolar-quadrupolar term, *d*, shows little or no variation throughout the series of compounds investigated and lies in the 97−114 Hz range.

X-ray diffraction studies have shown that these types of alkyl complexes possess a plane of symmetry,[14] which results in the angle α in eq 3 being equal to 0 or 90° (Figure 4). In turn, this leads to a simplified expression for D', with only three unknowns (eq 5). It is notoriously difficult to determine the angular term,

$$D' = (D - \Delta J/3)\,(3\cos^2\beta - 1 \pm \eta\sin^2\beta) \tag{5}$$

β, and the asymmetry parameter, η. Using model calculations for bromopentacarbonylmanganese(I), Lindner *et al.*[22] have estimated that η is in the range 0−0.12. Later, on the basis of symmetry arguments, Gobetto *et al.*[16] assumed η values of 0 for [Mn(CO)$_4$(PPh$_3$)]$_2$ and Mn$_2$(CO)$_9$(PPh$_3$).

Crystal structures of the alkyl complexes have been determined by Markwell *et al.*[14] and the *cis*-C−Mn−C angles were found to be within 5° of 90°, suggesting that η should be close to 0. It is known that trialkyl- and triarylphosphines are strong σ-donor and good π-acceptor ligands compared to alkyl groups. Therefore, the principal component of the electric field gradient, q_{ZZ}, is assumed to lie along the Mn−P bond direction. From the centerband analysis, it was shown that the effective dipolar−quadrupolar term, $(3/20)\chi D'/\nu_S$, is positive; i.e., bunching of the peaks occurs to lower field (Figure 3). Gobetto *et al.*,[16] Lindner *et al.*,[22] and Brown *et al.*[17] have demonstrated that the χ values for similar types of compound are always positive. Therefore, D' is also positive, which indicates further that the angle β is close to 0°. In principle, confirmation can be obtained from the spectrum of a second nucleus bonded to the manganese atom since the quadrupole coupling constant is unchanged but the angles α and β are different. The anisotropy of the spin−spin coupling, the quadrupole coupling, and the asymmetry in the field gradient remain unknown. We have examined the solid-state ^{13}C signals of the benzyl methylene group in compound **V** at 2.5 and 7.5 T. The angle β is close to 90° in this case. Second-order effects were observed, with a bunching of the peaks to low frequency, but the spectra were difficult to analyze due to overlapping peaks, even at low field. We attempted to fit the envelope of the methylene resonance with values for the spin−spin coupling, $^2J_{\rm PC}$, of 8.4 Hz from the ^{13}C solution spectrum and $^1J_{\rm Mn-C}$ of 23.1 Hz estimated by Torochesnikov *et al.*[21] from the line broadening of the resonance line. Using the χ value from the ^{31}P spectrum, the difference between the inner and outer line positions was calculated to be 143 Hz, compared with the experimental value of 203 Hz. We believe that the value of $^1J_{\rm Mn-C}$ reported by Torochesnikov *et al.*[21] is incorrect and in fact belongs to the *trans* isomer. The value of $^1J_{\rm Mn-C}$ obtained for the methylene carbon of compound **V** is 38 Hz with the assumption that $\Delta J_{\rm Mn-C}$ and η are zero, and $\beta^D = 90°$ for the ^{13}C spectra. On the basis of solid-state ^{13}C and ^{31}P NMR data and the crystal structures, we feel confident in assuming that the angular term $\beta = 0$ for the ^{31}P analysis. This leads to an even greater simplification of the expression for D' (eq 6).

$$D' = 2(D - \Delta J/3) \tag{6}$$

In principle, the chemical shift tensors for each of the $m - I$ transitions can be obtained from the nonspinning spectra, but these were very difficult to analyze for the compounds studied, because of the overlapping of six powder patterns (Figure 5). However, band fitting of the spinning sidebands and using a modified Herzfeld and Berger program[18] afforded the chemical shift tensors (Table 3). The differences between successive values of Ω_{Im} (eq 4) are constant and equal to D'. Values of D' were obtained from a regression plot of m *vs* Ω_{Im}, where

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Table 4. Calculated Effective Dipolar Coupling Constants Quadrupolar Coupling Constants, and Spin−Spin Anisotropy for Compounds **I**−**VII**

compound	D''^{a} (Hz)	χ (MHz)	χ^{b} (MHz)	ΔJ (Hz)
$PhCH_2C(O)Mn(CO)_4(PPh_3)$ (**I**)	1162(31)	23.3(0.7)	29.3	678(42)
$MesCH_2C(O)Mn(CO)_4(PPh_3)$ (**II**)	1132(46)	24.5(1.0)	34.5	589(24)
$PhCH_2C(O)Mn(CO)_4[P(C_6H_{11})_3]$ (**III**)	1079(73)	24.8(1.6)	37.6	639(41)
$MesCH_2C(O)Mn(CO)_4[P(C_6H_{11})_3]$ (**IV**)	1031(19)	23.3(0.4)	38.7	495(10)
$PhCH_2Mn(CO)_4(PPh_3)$ (**V**)	1073(35)	25.4(0.8)	8.44	412(13)
$PhCH_2Mn(CO)_4[P(Tolyl)_3]$ (**VI**)	1105(50)	23.1(1.0)	7.71	508(22)
$PhCH_2Mn(CO)_4[P(PhF)_3]$ (**VII**)	1115(54)	25.4(1.2)	9.43	538(30)

[a] $D'' = (D - \Delta J/3)$. [b] Calculated from line width dependence according to ref 19.

Table 5. ^{31}P-NMR Chemical Shift Tensors for Alkyl- and Acylmanganese(I) Complexes **I**−**VII** Calculated from CP-MAS and Spinning Sideband Analysis[a]

compound	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)	Ω_I^{b} (ppm)	no. of spinning rate
$PhCH_2C(O)Mn(CO)_4(PPh_3)$ (**I**)	117.5	67.6	−23.2	−115.8	3
$MesCH_2C(O)Mn(CO)_4(PPh_3)$ (**II**)	120.3	58.6	−18.4	−107.9	3
$PhCH_2C(O)Mn(CO)_4[P(C_6H_{11})_3]$ (**III**)	110.6	71.0	−1.0	−91.6	2
$MesCH_2C(O)Mn(CO)_4[P(C_6H_{11})_3]$ (**IV**)	98.6	67.2	−2.6	−86.2	3
$PhCH_2Mn(CO)_4(PPh_3)$ (**V**)	132.1	101.5	−27.7	−144.5	3
$PhCH_2Mn(CO)_4[P(Tolyl)_3]$ (**VI**)	125.1	99.0	−25.5	−137.5	3
$PhCH_2Mn(CO)_4[P(PhF)_3]$ (**VIII**)	130.2	100.7	−32.2	−147.6	2

[a] Uncertainties are ±1.5 and ±2.5 ppm for chemical shifts tensors and $\Delta\delta$, respectively. [b] Anisotropy parameter $\Omega_I = \delta_{33} - {}^1/_2\,(\delta_{11} + \delta_{22})$, where $|\delta_{33} - \delta_{\rm iso}| > |\delta_{11} - \delta_{\rm iso}| > |\delta_{22} - \delta_{\rm iso}|$.

the slope of the graph is equal to $-2D'/\upsilon_I$ and the intercept equals Ω_I (eq 4). The average values of $(D - \Delta J/3)$ were found to lie in the 1030−1135 Hz range and χ, using eq 1, is about 23−26 MHz for the compounds studied (Table 4).

Brown and co-workers[17] have shown that the line widths in the solution spectra of the quadrupolar nucleus are proportional to the square of the nuclear quadrupole coupling constant, provided that the molecules have the same correlation time for molecular rotation, which in turn depends upon the molecular volume and solvent viscosity. Quadrupolar relaxation must be dominant, and since $^1J_{\rm Mn-P}$ was observed in the ^{55}Mn spectra of the alkyl compounds, this mechanism does not apply in these cases. The molecular volumes of the alkyl and acyl complexes are much larger than are the volumes of the compounds examined by Brown *et al.*,[17] and thus the line width dependence on the quadrupole moment should reflect this. Only a poor correlation was obtained for the acyl complexes due to the narrow range covered by the data.

The χ values obtained from our solid-state ^{31}P NMR experiments can be compared with the value of 16.9 MHz obtained by Lindner *et al.*[22] for the bromo substituted manganese−phosphine complex, but where the anisotropy in the spin−spin coupling was neglected, and the 17.5 MHz value obtained by Brown *et al.*[17] for $BrMn(CO)_5$. The value calculated by Gobetto *et al.*[16] for $Mn_2(CO)_9PPh_3$ was 41.6 MHz, which is nearly twice the value observed for the compounds studied in the present work. This discrepancy is due to an error in the calculation of D' by Gobetto *et al.*[16] and recalculation of D' using the values given in Table 4 of ref 19, affords $D' = 1033 \pm 21$ Hz and $\chi = 29.5 \pm 0.6$ MHz, which are closer to the values we obtained for compounds **I**−**VII**. From the crystal structural data and spinning sidebands analysis, the dipolar coupling constants and the spin−spin anisotropies were determined to be in the range of 869−945 Hz and 400−640 Hz, respectively. The values of D and ΔJ for the acyl complexes were calculated with the assumption that $r_{\rm Mn-P}$ is the same as those of the respective alkyl−phosphine complexes. This assumption was based on the fact that the $r_{\rm Mn-P}$ values for $CH_3C(O)Mn(CO)_4(PPh_3)$ and $CH_3Mn(CO)_4(PPh_3)$, of 2.315 and 2.311 ± 0.018 Å, respectively, show little change on going from the acetyl to the methyl complex.

The magnitude and principal components of the phosphorus chemical shifts tensors are given in Table 5. There is very little change in the ^{31}P isotropic chemical shifts for the alkyl complexes containing *para*-substituted triarylphosphines. This was also observed for the phenylacyl and substituted phenylacyl complexes with triphenylphosphine and tricyclohexylphosphine (Table 2). However, there are major differences in the anisotropy parameter, $\Delta\delta$, and the span of the chemical shifts tensors, $\delta_{33} - \delta_{11}$, both of which are larger for the benzyl complexes than for the phenylacyl derivatives. The δ_{33} value shows little variation for the triarylphosphine complexes, ranging from −18.4 to −32.2 ppm. These values are in the same range as those obtained by Lindner *et al.*,[22] −16 to −32 ppm, for a series of alkyl(diaryl)phosphine complexes. From these results, the orientation of δ_{33} at the phosphorus atom was assigned as lying close to, or along, the Mn−P bond, and the remaining two components, δ_{11} and δ_{22}, must therefore lie perpendicular to this axis. It was observed that δ_{22} is more shielded, >28 ppm, for the acyl complexes than for the alkyl compounds investigated. From these observations, we assign δ_{22} to be parallel to the Mn−C bond of the acyl and the alkyl groups.

Since the chemical shift tensor at the phosphorus atom is not axially symmertic, the electric field gradient at manganese is possibly not symmetric. However, since η and the angle β are both small, their combined effect is such that eq 6 is applicable.

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