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# EPR Spectrum of Mn($\eta$-$C_4H_6$)$_2$PMe$_3$ in a Single Crystal of Fe($\eta$-$C_4H_6$)$_2$PMe$_3$[†]

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The EPR spectrum of Mn($\eta$-$C_4H_6$)$_2$PMe$_3$ doped into a single crystal of Fe($\eta$-$C_4H_6$)$_2$PMe$_3$ is described, together with the spectra of the same species in hydrocarbon solvents and powdered Fe($\eta$-$C_4H_6$)$_2$PMe$_3$. One principal value of the $\mathbf{g}$ and $\mathbf{a}_{Mn}$ tensors is quite different in the crystal from that which had been deduced from the spectra of powdered or glassy samples. It turns out that the average of the principal values in the crystal is not equal to the isotropic value observed in soluton. This unusual result is presumably because the molecule has slightly different geometry in the crystal from that in solution. The orthorhombic nature of the $^{55}$Mn hyperfine tensor (principal values 57.0, 42.0, 164.0 G) is due to a small spin population in Mn 3d$_{x^2-y^2}$, in addition to the dominant contribution which is in Mn 3d$_{z^2}$ (where $z$ is the Mn–P direction).

## Introduction

For many years the controversial free radical Mn(CO)$_5$ eluded detection, although several investigators had identified it with EPR signals from manganese-containing peroxides and Mn$^{2+}$.[1-4] Finally it was detected and identified by applying the technique of matrix isolation to EPR[5] and IR[6] spectroscopy. As expected, Mn(CO)$_5$ turned out to be square pyramidal in shape, with the unpaired electron spending about 50% of its time in the Mn 3d$_{z^2}$ orbital directed along the fourfold $z$ axis. The tensor of the $^{55}$Mn ($I = {}^5/_2$) hyperfine interaction was axial, 66 G parallel to and (–) 30 G perpendicular to the unique ($z$) direction.

It was, therefore, with some surprise that we read recently[7] that certain analogues of Mn(CO)$_5$, notably Mn($\eta$-$C_4H_6$)$_2$CO and Mn($\eta$-$C_4H_6$)$_2$PMe$_3$, had quite different EPR parameters and chemical properties from those of Mn(CO)$_5$. For example, Mn($\eta$-$C_4H_6$)$_2$PMe$_3$ in frozen 3-methylpentane was reported to have an orthorhombic $^{55}$Mn hyperfine tensor with principal values of 68, <5, and 164 G. These results were supported by an isotropic $^{55}$Mn hyperfine interaction in liquid 3-methylpentane of 82.5 G, close to the average of the above values for the frozen matrix.

These results, consistent in themselves, were so different from those of Mn(CO)$_5$ that we decided to investigate the EPR spectrum of Mn($\eta$-$C_4H_6$)$_2$PMe$_3$ doped into single crystals of the hitherto unknown compound Fe($\eta$-$C_4H_6$)$_2$PMe$_3$.

## Experimental Section

All air-sensitive materials were manipulated in vacuo or under a nitrogen atmosphere using standard techniques.[8] Tetrahydrofuran was distilled from sodium benzophenone ketyl. Other solvents were saturated with nitrogen prior to use. Anhydrous FeCl$_2$[9] and Mn($\eta$-$C_4H_6$)$_2$PMe$_3$[7] were prepared by published procedures. Trimethylphosphine (Aldrich), 2-chloropropane (Anachemia), and 1,3-butadiene (Matheson Research Grade, 99.86%) were used as received. Infrared, $^1$H NMR, and mass spectra were recorded on Perkin-Elmer 683, Varian EM-360, and Finnigan GC/MS Model 4010 spectrometers, respectively. Microanalyses were carried out in these laboratories.

**Mg($C_4H_6$)·2THF.** The preparation of this compound followed the general method of Wreford and Whitney,[10] except that ultrasound irradiation was used in place of mechanical shaking. This change reduced the reaction time and simplified workup. A 500-mL flask with a sealed side arm and constricted center arm was charged with 6.10 g of Mg turnings and flushed with nitrogen. Dry THF (100 mL) and iodobenzene (0.3 mL, 3 mmol) were added by syringe. 1,3-Butadiene (0.15 mol) was condensed into the flask which was then sealed and warmed to room temperature. The vessel was placed in an ultrasonic cleaner (125 W, 50 kHz) and irradiated for 2 days to give a thick yellow slurry. After the mixture was cooled to –196 °C, the side arm was opened, a nitrogen line attached and the vessel warmed to room temperature.

The previously sealed center arm was then opened to enable transfer of the slurry by syringe to a Schlenk filter. Excess magnesium remaining in the vessel was washed with several small portions of THF.

After the mixture was dried in vacuo overnight, 16.9 g (75.9 mmol, 51%) of the pyrophoric pale green powder was transferred to a storage container in a nitrogen-filled glovebag.

**Fe($\eta$-$C_4H_6$)$_2$PMe$_3$.** A 200-mL flask was charged with a magnetic stirring bar, FeCl$_2$ (1.0 g, 7.9 mmol), and THF (20 mL). The degassed mixture was frozen at –196 °C, and 1,3-butadiene (9.9 mmol) and PMe$_3$ (8.0 mmol) were condensed into the vessel. Warming to 0 °C gave a brown solution. The vessel was filled with nitrogen, and a dropping funnel was attached. A slurry of Mg($C_4H_6$)·2THF (2.1 g, 9.4 mmol) in THF (20 mL) was added dropwise to the ice-cold stirred reaction mixture. Stirring was continued for 1 h at 0 °C and then overnight at room temperature. Volatile components were removed in vacuo. The residue was extracted with 8 × 25 mL aliquots of boiling hexanes, filtering through a Celite pad. The orange filtrate was concentrated in vacuo to an oily solid. About 2 mL of diethyl ether was added. Cooling to –78 °C gave fine orange needles. Further purification was effected by sublimation in vacuo at 33 °C on to a water-cooled finger to give 0.285 g (1.19 mmole, 15%) of an orange, microcrystalline sublimate: decomp pt 126 °C (sealed capillary tube under nitrogen); proton NMR (benzene-$d_6$) $\delta$ 4.33 (m, 4 H, *CH*=CH$_2$), 1.38 (d, $J$(P–H) = 7.6 Hz, 9 H, P-CH$_3$), 0.92 (m, 4 H, CH=C*H*H), –1.22 (m, 4 H, CH=CH*H*); mass spectrum (50 eV), molecular ion at $m/z$ 240 (4.5%); IR (KBr disk) 3025 (s), 2970 (s), 2905 (m), 1425 (m), 1418 (s), 1297 (m), 1275 (s), 1208 (s), 1185 (m), 1042 (m), 942 (vs), 925 (m), 900 (m), 845 (m), 838 (m), 753 (m), 710 (s), 668 (s), 648 (m), 540 (s), 465 (m), 402 (s) cm$^{-1}$. Calcd for $C_{11}H_{21}$FeP: C, 55.03; H, 8.82; P, 12.90. Found: C, 55.07; H, 8.86; P, 12.83.

Crystals of Fe($\eta$-$C_4H_6$)$_2$PMe$_3$ containing ca. 0.4% Mn($\eta$-

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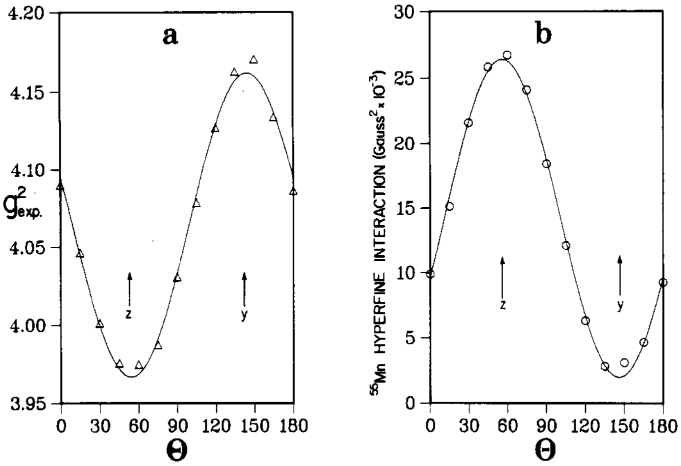

**Figure 1.** The variation with angle ($\theta$) in the $yz$ plane of (a) the value of $\mathbf{g}^2$ and (b) the $^{55}$Mn (hyperfine splitting)$^2$ for $Mn(\eta\text{-}C_4H_6)_2PMe_3$ in a single crystal of $Fe(\eta\text{-}C_4H_6)_2PMe_3$ at 100 K.

Table I. EPR Parameters for $Mn(\eta\text{-}C_4H_6)_2PMe_3$ in a Single Crystal of $Fe(\eta\text{-}C_4H_6)_2PMe_3$ at 100 K and in Liquid 2-Methylbutane at 153–223 K

| solvent | axis | $g$ | $a_{Mn}$/G | $a_P$/G |
|---|---|---|---|---|
| crystal | $x$ | 2.0301[a] | 57.0 | 27.0 |
| | $y$ | 2.0450 | 42.0 | 26.4 |
| | $z$ | 1.9908 | 164.0 | 29.3 |
| | average | 2.0220 | 87.7 | 27.6 |
| 2-MB | | 2.0186[b] | 82.4[b] | 25.0[b] |

[a] Errors are ±5 in the last digit given. [b] Invariant over temperature range 153–223 K.

$C_4H_6)_2PMe_3$ were grown by cosublimation of a mixture of the two compounds on to a cold finger held at 15 °C.

## Results and Discussion

The EPR spectrum at 100 K of $Mn(\eta\text{-}C_4H_6)_2PMe_3$ in a single crystal of $Fe(\eta\text{-}C_4H_6)_2PMe_3$ consists of a single set of six 27 G doublets. The doublet splitting is almost isotropic and is due to hyperfine interaction with a $^{31}$P ($I = {}^1/_2$) nucleus. The sextet structure, on the other hand, is highly anisotropic and due to hyperfine interaction with a $^{55}$Mn ($I = {}^5/_2$) nucleus. Although the crystal structure of $Fe(\eta\text{-}C_4H_6)_2PMe_3$ is not known, the observation of a single site for the manganese-containing impurity tends to suggest a triclinic crystal system. In any event, the procedure we have described elsewhere[11] for handling a triclinic crystal on a two-circle goniometer was followed: an arbitrary axis system was chosen in which the apparent $\mathbf{g}^2$ and first-order $^{55}$Mn and $^{31}$P hyperfine splittings (G$^2$) were determined. It was clear (Figure 1) that the principal directions of $\mathbf{g}^2$ and of $\mathbf{a}^2_{Mn}$ were parallel. Having identified these directions, the goniometer was adjusted so as to place $H_0$ along each of the principal directions ($x$, $y$, $z$) in turn. The spectra so obtained yielded, by exact diagonalization of the spin Hamiltonian, principal values of the $\mathbf{g}$ tensor and of the $^{55}$Mn and $^{31}$P hyperfine tensors (Table I).

We then took some polycrystalline $Fe(\eta\text{-}C_4H_6)_2PMe_3$ containing ca. 0.4% $Mn(\eta\text{-}C_4H_6)_2PMe_3$ impurity and obtained its spectrum at 100 K. This was compared (Figure 2a,b) with a computer-simulated EPR spectrum[12] generated from input parameters obtained in the single crystal study (Table I).

Finally, we dissolved 2 mg of $Mn(\eta\text{-}C_4H_6)_2PMe_3$ in 100 $\mu$L of 2-methylbutane and obtained its spectrum at 100 K (Figure 2c) and at various temperatures up to 223 K. The isotropic 12-line spectra obtained between 153 and 223 K were analyzed by a computer program which varied the parameters of the spin Hamiltonian ($\mathbf{g}$, $\mathbf{a}_{Mn}$, $\mathbf{a}_P$) until the sum of (residuals)$^2$ was minimized. The results of this computation are also given in Table I.

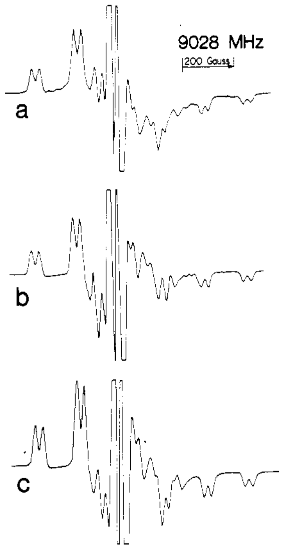

**Figure 2.** The EPR spectrum of $Mn(\eta\text{-}C_4H_6)_2PMe_3$: (a) in a $Fe(\eta\text{-}C_4H_6)_2PMe_3$ powder at 100 K; (b) simulated by using the parameters of Table I; (c) in a 2-methylbutane glass at 100 K.

If we compare our results for $Mn(\eta\text{-}C_4H_6)_2PMe_3$ in a single crystal with those of Harlow et al.[7] for the same radical in frozen 3-methylpentane, we note excellent agreement for two of the three principal axes. For the remaining direction ($y$), they reported $g = 2.0511$, $a_{Mn} < 5$ G, and $a_P = 29.2$ G, whereas it was clear from our examination of the single crystal that $\mathbf{a}_{Mn}$ never fell below 40 G. It seems that Harlow et al. relied heavily on the isotropic (193 K) $^{55}$Mn hyperfine interaction (82.5 G) to infer a small third principal value. The present results, while confirming the isotropic value, underline the dangers of placing too much reliance on the assumption that isotropic (liquid-phase) parameters are the average of the corresponding solid-phase principal values.

It will be noted (Figure 2a,b) that the simulation based on single crystal parameters is an excellent reproduction of the actual spectrum of $Mn(\eta\text{-}C_4H_6)_2PMe_3$ in powdered $Fe(\eta\text{-}C_4H_6)_2PMe_3$, bearing in mind that the simulation program carries the computation only to first order in $\mathbf{a}_{Mn}$ and assumes zero quadrupole interaction. In particular, the simulation successfully reproduces the strong central doublet, a feature which Harlow et al. erroneously assigned to the $y$ direction.

We presumed at first that the discrepancy between the average of the principal values in the crystal and the isotropic parameters obtained in solution was due to temperature dependence of the solution parameters $\mathbf{g}$, $\mathbf{a}_{Mn}$, and $\mathbf{a}_P$. This was not so: over the temperature range 153–223 K the $\mathbf{g}$ factor of $Mn(\eta\text{-}C_4H_6)_2PMe_3$ in liquid 2-methylbutane did not change by more than 0.0002, and the hyperfine interactions did not change by more than 0.2 G. We were therefore forced to the conclusion that there is a slight but measurable difference between the isotropic spectral parameters of $Mn(\eta\text{-}C_4H_6)_2PMe_3$ in liquid hydrocarbon and their average values obtained in a single crystal of $Fe(\eta\text{-}C_4H_6)_2PMe_3$. Furthermore, since the spectrum in powdered $Fe(\eta\text{-}C_4H_6)_2PMe_3$ was not significantly different from that in frozen 2-methylbutane (Figure 2a,c), it could be argued that the isotropic spectral parameters of $Mn(\eta\text{-}C_4H_6)_2PMe_3$ in liquid 2-methylbutane

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Table II. Breakdown of $^{55}$Mn Hyperfine Interaction in $Mn(\eta\text{-}C_4H_6)_2PMe_3$ into Isotropic and Anisotropic Parts

| | $^{55}$Mn hyperfine interaction, G | | |
|---|---|---|---|
| axis | exptl | isotropic (4s) | anisotropic ($3d_{z^2}$) |
| $x$ | 57.0 | 87.7 | −30.7 |
| $y$ | 42.0 | 87.7 | −45.7 |
| $z$ | 164.0 | 87.7 | 76.3 |
| spin pop. | | 0.05 | 0.59 |

differ from the average of the principal values in frozen 2-methylbutane. In other words, the EPR parameters of $Mn(\eta\text{-}C_4H_6)_2PMe_3$ change slightly at the melting point of the solvent.

Returning to $Mn(\eta\text{-}C_4H_6)_2PMe_3$ in the single crystal matrix, we note that the main differences between it and $Mn(CO)_5$ are (a) an increase in the isotropic $^{55}$Mn hyperfine interaction from near zero in $Mn(CO)_5$ to 88 G in $Mn(\eta\text{-}C_4H_6)_2PMe_3$ and (b) the lack of axial symmetry in the spectral parameters of $Mn(\eta\text{-}C_4H_6)_2PMe_3$. Both (a) and (b) are symptomatic of a slightly different wave function for the semioccupied orbital of $Mn(CO)_5$ and $Mn(\eta\text{-}C_4H_6)_2PMe_3$: (a) suggests an increase in Mn 4s spin population from negligible in $Mn(CO)_5$ to 0.05 in $Mn(\eta\text{-}C_4H_6)_2PMe_3$ and (b) indicates spin population not only in $3d_{z^2}$ but also in $3d_{x^2-y^2}$. The breakdown of the orthorhombic $^{55}$Mn tensor into isotropic and anisotropic components associated with Mn 4s and $3d_{z^2}$ spin populations[13] is given in Table II. The appreciable departure of both the **g** and $^{55}$Mn tensors from axiality is undoubtedly[14] due to configuration interaction between the $d_{z^2}$ and $d_{x^2-y^2}$ components of the $a_1$ SOMO. With use of McGarvey's expressions for the hyperfine tensor components of a $d^7$ system, we estimate that the $d_{x^2-y^2}$ contribution to the $a_1$ orbital is less than 1% of that from $d_{z^2}$.

At first we thought that free rotation, or lack of it, in the $PMe_3$ moiety of $Mn(\eta\text{-}C_4H_6)_2PMe_3$ was responsible for the differences between its (solid-) and liquid-phase parameters. Since it appears,[7] however, that the same phenomena occur in $Mn(\eta\text{-}C_4H_6)_2CO$, it must be concluded that it is the butadiene ligands which cause the problem. We surmise that in the solid phase the butadiene ligands are sterically crowded and that in soluton the molecule is free to take up its equilibrium conformation.

We end on a note of caution. The present study has illuminated the pitfalls of a facile interpretation of powder EPR spectra. In our experience, an analysis of such spectra is only reliable if the system is truly axial—$Co(CO)_4$, for example.[15] If the system has orthorhombic **g** and hyperfine tensors, it may be quite impossible (even with the aid of the isotropic spectrum of the same radical) to correctly disentangle three principal values of **g** and **a** from a powder spectrum.

**Note Added in Proof.** It has now been established that $Fe(\eta\text{-}C_4H_6)_2PMe_3$ crystallizes in the monoclinic system with space group $P2_1/c$. A further report is in progress.

**Registry No.** $Mn(\eta\text{-}C_4H_6)_2PMe_3$, 82963-75-5; $Fe(\eta\text{-}C_4H_6)_2PMe_3$, 87922-45-0; $Mg(C_4H_6)\cdot 2THF$, 87922-46-1.

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# Reactions of the Octachlorodirhenate(III) Anion with Aryl Isocyanides: Homoleptic Isocyanides of Rhenium(I) and Mixed-Ligand Complexes of Rhenium(III)

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The reactions of aryl isocyanides ArNC (Ar = phenyl, *p*-tolyl, 2,6-dimethylphenyl, and 2,4,6-trimethylphenyl) with the quadruply bonded complexes $Re_2(O_2CCH_3)_4Cl_2$ and $(n\text{-}Bu_4N)_2Re_2Cl_8$ in refluxing methanol provide an excellent high-yield synthetic route to the homoleptic rhenium(I) species $[Re(CNAr)_6]PF_6$. When the reactions between ArNC and $(n\text{-}Bu_4N)_2Re_2Cl_8$ are conducted at room temperature, then rhenium(III)-containing intermediates of the types $[Re(CNAr)_6]_2Re_2Cl_8$, $[Re(CNAr)_6][ReCl_4(CNAr)_2]$, and $ReCl_3(CNAr)_3$ can be isolated. These aryl isocyanide complexes all display well-defined electrochemistry (cyclic voltammetry) in 0.2 M TBAH–$CH_2Cl_2$, the mononuclear rhenium(III) species displaying the redox processes Re(IV) + $e^-$ ⇄ Re(III) and Re(III) + $e^-$ ⇄ Re(II). In the case of $[Re(CNAr)_6]^+$ (Ar = Ph or *p*-tol), oxidation to the dark blue 17-electron cation $[Re(CNAr)_6]^{2+}$ has been accomplished electrochemically (at ca. +1.2 V) and the resulting solutions have been characterized spectroscopically. Characterization of the salts $[Re(CNAr)_6][ReCl_4(CNAr)_2]$ has shown that freshly prepared samples contain the trans anion but the dichloromethane solutions slowly isomerize to the corresponding cis isomer. The $^1$H NMR spectra of these same salts reveal substantial Knight shifts associated with the paramagnetic $d^4$ $[ReCl_4(CNAr)_2]^-$ anions.

## Introduction

The direct reductive cleavage of multiply bonded dimetal complexes of molybdenum(II) and tungsten(II) by aryl isocyanides (ArNC) constitutes a convenient synthetic strategy for the preparation of the homoleptic isocyanide complexes $M(CNAr)_6$.[1,2] The same is true in the case of the reactions between the quadruply bonded dirhenium-

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