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EPR Spectra of KrMn(CO)$_5$ and KrFe(CO)$_5$$^+$ in a Krypton Matrix[†]

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The EPR spectra of two species identified as KrMn(CO)$_5$ and KrFe(CO)$_5$$^+$ have been detected following γ irradiation of HMn(CO)$_5$ and Fe(CO)$_5$ in krypton matrices at low temperature. The spectra of both radicals exhibit hyperfine interactions with one ^{83}Kr nucleus. Data from ^{13}C and ^{57}Fe labeled species are used to derive information on the spin population distribution.

Introduction

There has been a flurry of activity in the last few years in the quest for the free radical Mn(CO)$_5$. After two false starts, it was identified with an optical absorption at 830 nm by pulse radiolysis of Mn$_2$(CO)$_{10}$ and Mn(CO)$_5$Br.[1] This was followed by the almost simultaneous detection of its EPR[2] and IR[3] spectra and by its detection during flash photolysis of Mn$_2$(CO)$_{10}$ solutions.[4] A common conclusion of the latter studies was that Mn(CO)$_5$ is a square-pyramidal molecule possessing a $^2A_1$ ground state in C_{4v} symmetry. The detailed composition of the semi-occupied orbital of Mn(CO)$_5$ remains of interest. Estimates[2,5] from atomic one-electron parameters indicate a spin population in Mn 3d$_{z^2}$ ($z \equiv C_4$ axis) of 0.51 and 0.60, the remaining spin population residing on the five carbonyl ligands. By analogy with the isoelectronic Fe(CO)$_5$$^+$ studied by EPR in a Cr(CO)$_6$ single crystal,[6] there appear to be two possibilities: in the first, spin population is essentially confined to Mn 3d$_{z^2}$ and C(1)(unique) 2p$_z$ in roughly equal proportions, with little or no spin population in C(2–5) 2p orbitals. The second possibility is the reverse of this, the spin population being shared between Mn 3d$_{z^2}$ and C(2–5) 2p orbitals with very little in C(1) 2p$_z$. The evidence from ^{13}C-enriched Fe(CO)$_5$$^+$ was somewhat ambiguous, but the first choice was slightly preferred.

It was with a view to resolving this ambiguity regarding the SOMO of Mn(CO)$_5$ and Fe(CO)$_5$$^+$ that we decided to investigate their EPR spectra, using the ^{13}C nucleus as a probe of the spin population in ligand orbitals. A krypton matrix was chosen since, in our experience, it is a good solvent for transition metal carbonyls and usually gives rise to extremely sharp EPR spectra. In contrast, EPR spectra in Ar[5] and Xe are usually poorly resolved.

Results

The EPR spectrum at 77 K of a γ-irradiated sample of Mn(CO)$_5$H in krypton (ca. 0.1%) is shown in Figure 1a. As can be seen, the individual lines are extremely sharp, and the spectral parameters (g, a_{Mn}) can be extracted with great precision (Table I). A simulation[7] based on the best-fit values of g and a_{Mn} is shown in Figure 1b and serves to confirm the analysis indicated. The spectrum of Figure 1a is of much higher intensity and resolution than EPR spectra previously associated with Mn(CO)$_5$ in benzene,[2] argon,[5] and xenon, and we were prompted thereby to search for ^{13}C satellites in natural abundance. This search revealed first, not ^{13}C satellites, but the characteristic decet due to hyperfine interaction between

Table I. EPR Parameters of Mn(CO)$_5$Kr in Krypton at 77 K

parameter	zz	xx, yy
g	2.0003 ± 0.0002	2.0340 ± 0.0002
a_{Mn}[a]	65.4 ± 0.1	34.8 ± 0.1
a_{Kr}	6.4 ± 0.1	4.0 ± 0.1
$a_{C(1)}$	3.3 ± 0.1	<2
$a_{C(2,4)}$	6.9 ± 0.1	4.6 ± 0.1
$a_{C(3,5)}$	6.9 ± 0.1	9.1 ± 0.1
$a_{C(2-5)}$	6.9 ± 0.1	7.5 ± 0.1

[a] a values given in gauss.

the unpaired spin and an ^{83}Kr nucleus ($I = ^9/_2$). In order to show the krypton satellites with improved signal/noise, a sample was prepared (Figure 2) containing krypton enriched to 42% in the isotope ^{83}Kr. This spectrum establishes a hyperfine interaction with one and only one ^{83}Kr nucleus (Table I). Because of the unexpected presence of ^{83}Kr satellites, the ^{13}C hyperfine interactions were obtained from samples enriched in this isotope to various percentages. For example, in Figure 3a we show the lowest field transition (H_0 parallel to z, $m_I = ^5/_2$) for a sample enriched to 30% in the isotope ^{13}C. From this spectrum, and similar ones at other ^{13}C concentrations, it was concluded that for H_0 parallel to z (the C_4 axis) the unique or apical carbon atom C(1) had a 3.3-G hyperfine interaction, and the four basal carbon atoms C(2–5) each had 6.9-G hyperfine interactions. The simulation in Figure 3b confirmed this analysis. For H_0 parallel to x or y, using 30% ^{13}C enrichment, three pairs of ^{13}C hyperfine satellites were observed, indicating hyperfine interactions of 4.6, 9.1, and 7.5 G.

Irradiated samples of Fe(CO)$_5$ in krypton showed no EPR signals at 77 K, but at 20 K a strong signal at g = 2.0686 was observed and attributed to g_{yy} (Table I). A very much weaker signal at 2.0022 was attributed to g_{zz}. The signal at 2.0686 showed a hyperfine interaction of 6.8 G with a ^{57}Fe nucleus, when a sample enriched to 30% in this isotope was used. In addition, the 2.0686 signal showed ^{83}Kr hyperfine structure, the hyperfine interaction being

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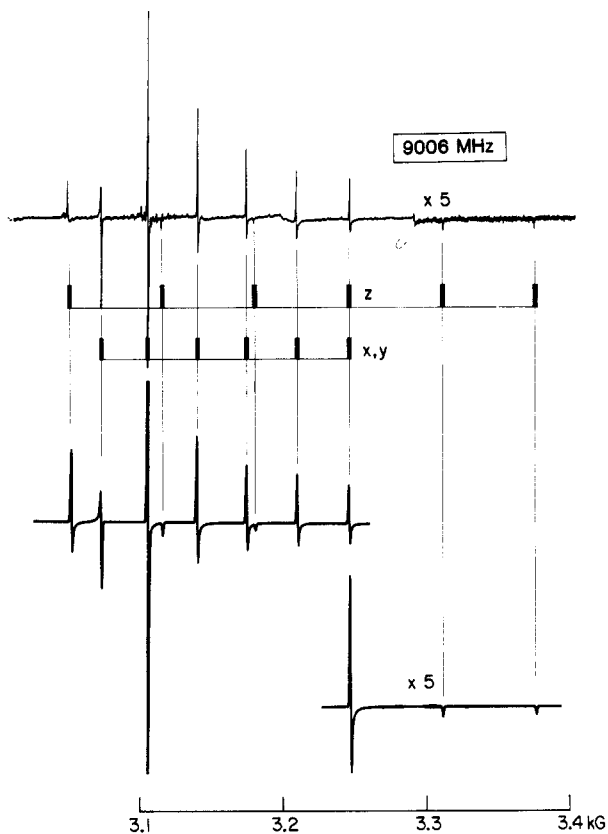[‡] Visiting scientist; present address: Department of Chemistry, York University, England.

Figure 1. (a) EPR spectrum of $KrMn(CO)_5$ in a Kr matrix at 77 K. (b) Computer simulation using parameters given in Table I.

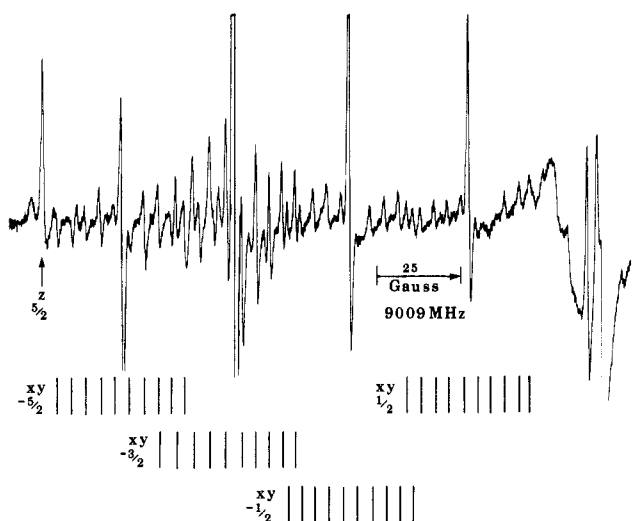**Figure 2.** Part of the EPR spectrum of $KrMn(CO)_5$, obtained in a matrix of krypton enriched to 42% in the isotope ^{83}Kr ($I = {}^9/_2$).

3.4 G. Using 10% enriched ^{13}C $Fe(CO)_5$, satellites of the line at 2.0686 were observed, corresponding to ^{13}C hyperfine interactions of 5.0, 8.3, and 12.5 G.

Discussion

(1) $KrMn(CO)_5$. There can be no doubt that the present radicals are closely related to species identified previously as $Mn(CO)_5$ and $Fe(CO)_5^+$. For example, compare the data in Table I with those for $Mn(CO)_5$ in benzene:[2] $g_{xx} = g_{yy} = 2.038$ with $a_{Mn} = 30$ G and $g_{zz} = 2.000$ with $a_{Mn} = 66$ G.

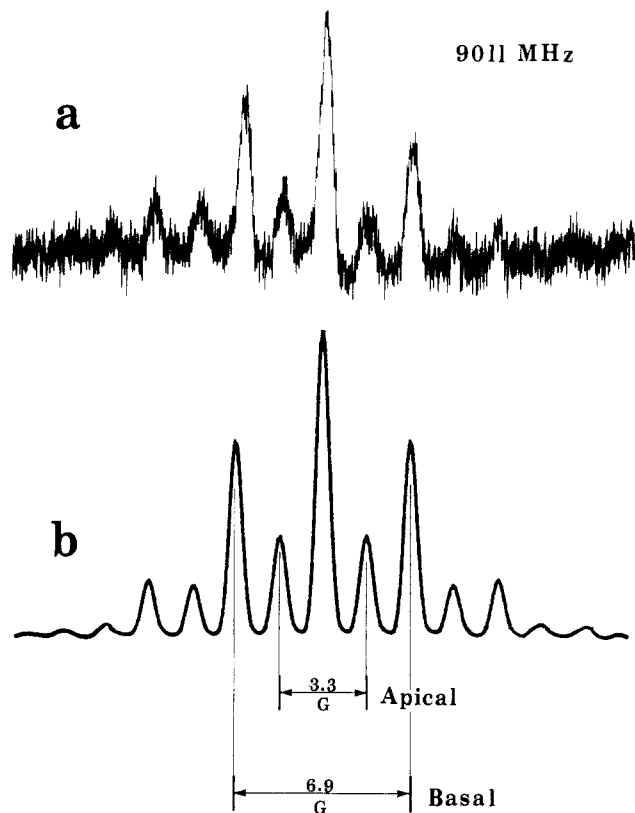Whether a krypton atom can bind to a metal carbonyl fragment is a moot point, and one debated at length by

Figure 3. (a) The $m_I = {}^5/_2$ transition (H_0 parallel to z) of $KrMn(CO)_5$ obtained using a sample of $HMn(CO)_5$ enriched to 30% in the isotope ^{13}C ($I = {}^1/_2$). (b) Composite simulation of a.

Perutz and Turner in their study[8] of the visible spectra of $LCr(CO)_5$, $LMo(CO)_5$, and $LW(CO)_5$, where $L = Ne$, SF_6, CF_4, Ar, Kr, Xe, and CH_4. Their conclusion was that the L–metal interaction may reasonably be described as a weak chemical bond, even when L is a rare-gas atom. We concur with this view and identify our radicals as $KrMn(CO)_5$ and $KrFe(CO)_5^+$, respectively, with the following rationale. There is unquestionably unpaired spin on the krypton nucleus; the ^{83}Kr interaction is far too large to be attributable to the electron–nucleus dipole–dipole interaction. The magnitude of the estimated spin population on ^{83}Kr depends on the relative signs of the principal values of the hyperfine interaction, as indeed it does for the other nuclei. If we assume the signs are opposite, spin population in Kr 4p can be estimated by the usual method[9] as 0.06; same signs, 0.01. Compare this to the hyperfine interaction of the unique carbon C(1) in Table I. Taking a_{xx} and a_{yy} as 2 G (a maximum value), opposite signs yield a spin population in C(1) 2p of 0.05, same signs 0.01. In other words, the spin populations in Kr $4p_z$ and C(1) $2p_z$ are very similar, 0.05–0.06 if we can make the assumption of opposite signs in both cases. We are thus drawn inescapably to the conclusion that the Kr atom is bound to the $Mn(CO)_5$ moiety.

In considering the other carbon nuclei (Table I), we note that they are all equivalent at 6.9 G for g_{zz}. For H_0 in the xy plane, three hyperfine interactions are apparent, one of which (7.5 G) is the root-mean-square of the other two (4.6 G, 9.1 G), within experimental error. We conclude that the latter values correspond to H_0 along x or y (Figure 4), for which directions the basal carbon nuclei are equivalent in pairs, and that the former value (7.5 G) corresponds to H_0 along the bisectors of x and y, for which directions all

(8) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791–4800.
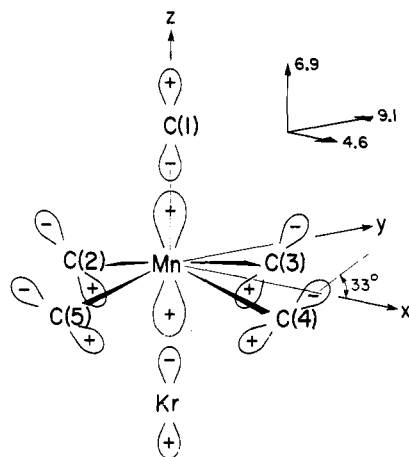(9) Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1978**, *30*, 577–582.

Figure 4. The semioccupied molecular orbital of KrMn(CO)₅.

Table II.   EPR Parameters of
KrFe(CO)₅⁺ in Krypton at 20 K

parameter	zz	xx, yy
g	2.0022 ± 0.0002	2.0686 ± 0.0002
a_{Fe}[a]		6.8 ± 0.1
a_{Kr}		3.4 ± 0.1
$a_{C(1)}$		12.5
$a_{C(2,4)}$		4.9
$a_{C(3,5)}$		8.2

[a] a values given in gauss.

four basal ¹³C nuclei are equivalent. It may further be concluded that the 2p functions of the four basal carbon atoms are not parallel to any of the molecular axes x, y, and z, since neither a_{xx} nor a_{yy} is equal to a_{zz} (6.9 G). Furthermore, although the xy elements of these tensors must be zero, we know nothing about the xz or yz elements that would enable us to estimate the tilt out of the xy plane. However, if we *assume* an xz (C(2,4)) or yz (C(3,5)) off-diagonal element large enough to generate an axial tensor upon diagonalization we obtain, for the four basal carbon atoms: (a) principal values 10.4, 4.6, and 4.6 G; (b) angle with xy plane 33°.

If we further assume that the angle between apical and basal bonds is 96°, as in Mn(CO)₅,[3] the angle between the basal 2p function and the corresponding Mn–C bond is approximately 40°. Thus, a SOMO such as that illustrated in Figure 4 results, in which the basal 2p orbitals point toward the Kr atom rather than toward the unique carbon atom C(1).[10] Spin population in C(2–5) 2p orbitals can be estimated from (a) as (⁵/₆)(10.4 − 4.6)/96 or 0.05 each, assuming the principal values are all positive.

(2) KrFe(CO)₅⁺. The EPR parameters obtained from Fe(CO)₅ in krypton are closely related to those of Fe(CO)₅⁺ in a single crystal of Cr(CO)₆,[6] as well as those of the isoelectronic KrMn(CO)₅. It was unfortunate that the transition at g_{zz} of Fe(CO)₅:Kr was so weak that hyperfine satellites could not be observed, even in enriched samples. In Cr(CO)₆, Fe(CO)₅⁺ had g_{xx} = 2.0797 and g_{yy} = 2.0833, compared to g_{yy} = 2.0686 in the present case.

The species observed in Fe(CO)₅:Kr samples also showed ⁸³Kr hyperfine structure, although the hyperfine interaction was slightly lower than in KrMn(CO)₅. We identify the species in Fe(CO)₅:Kr samples as KrFe(CO)₅⁺.

In the absence of ¹³C hyperfine satellites for g_{zz} we cannot estimate spin population in carbon 2p orbitals with the same degree of confidence as was possible with KrMn(CO)₅. Assuming that (+) 4.9 G are principal values of the basal carbon hyperfine tensors, we note that this corresponds to spin population in each C 2p orbital of 0.03, a value which must be regarded as a minimum estimate. Thus the situation with respect to the basal carbon contribution to the SOMO is very similar to that for KrMn(CO)₅.

The hyperfine interaction of the unique carbon atom C(1) in KrFe(CO)₅⁺ is somewhat less than that of Fe(CO)₅⁺ in Cr(CO)₆ (principal values 21, 18, and 18 G),[6] presumably as a result of a slight difference in geometry. However, it would appear that the spin population in C(1) 2s is dramatically lower in KrMn(CO)₅ than in KrFe(CO)₅⁺. It could be argued that this is a consequence of decreased 4s, 4p$_z$, 3d$_{z^2}$ mixing in the SOMO of the charged species.[11]

In Cr(CO)₆ single crystals Fe(CO)₅⁺ is effectively "naked"; i.e., there is no possibility of a sixth ligand being present, even one held only by van der Waals forces. Addition of a krypton atom (forming KrFe(CO)₅⁺) causes a marked reduction in g_{xx} and g_{yy}. In the case of Mn(CO)₅, however, there is no significant difference between g_{xx}, g_{yy} in benzene[2] and g_{xx}, g_{yy} in krypton. From this result we conclude that "naked" Mn(CO)₅ has still not been detected and that in benzene we are dealing with the complex Mn(CO)₅(C₆H₆). Some evidence for this lies in the fact that the spectrum of the latter is considerably sharper in C₆D₆ than in C₆H₆. To date, all our efforts to implant Mn(CO)₅ in crystals of Cr(CO)₆ have failed.

Experimental Section

HMn(CO)₅ was obtained by reacting the dimer Mn₂(CO)₁₀ (Strem Chemical Corp.) with sodium amalgam and converting the NaMn(CO)₅ to HMn(CO)₅ with phosphoric acid.[12] Enrichment of HMn(CO)₅ with ¹³C was carried out by photolyzing it in the vapor phase with a low-pressure Hg lamp in the presence of excess ¹³CO. Enriched Fe(CO)₅ was prepared in a similar way; Fe(CO)₅ enriched in ⁵⁷Fe was prepared by reacting ⁵⁷Fe₂O₃ with excess CO in an autoclave (300 °C, 300 atm). Oak Ridge National Laboratory provided enriched Fe₂O₃, and krypton enriched to 42% in ⁸³Kr was obtained from Monsanto Research Laboratories, Miamisberg, OH.

The samples were prepared by mixing either HMn(CO)₅ or Fe(CO)₅ with krypton in a 100-mL quartz bulb (partial pressures 1:1000) and condensing the gaseous mixture at 77 K into a 4-mm o.d. Suprasil tube. After the sample tube was sealed off, the contents were homogenized by placing it in a bath of melting n-pentane for 30 min. The refrozen samples were then γ irradiated at 77 K for 10–15 min in a 19 000 Ci ⁶⁰Co γ cell.

The irradiated samples were examined with a Varian E12 EPR spectrometer equipped with the usual field and frequency-measuring devices. An Oxford Instruments ESR 9 cryostat permitted variation of the sample temperature down to 4 K.

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