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ESR and Molecular Orbital Study of Acyltetracarbonyliron Radicals

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A major new development in organometallic chemistry has been the recent discovery of redox or electron-transfer catalysis of ligand substitution[1] and of alkyl-to-acyl migratory insertion reactions[2] of metal carbonyl complexes. The basis of this catalysis is that a one-electron change in oxidation state can bring about dramatic enhancements in substitutional lability[3] as well as in the rate of alkyl migration from the metal to coordinated carbon monoxide (eq 1). The latter is a reaction step that is essential for the success

$$\mathrm{L}_x\mathrm{M(R)CO} \xrightarrow{\mathrm{CO}} \mathrm{L}_x\mathrm{M(CO)C({=}O)R} \qquad (1)$$

of many carbonylation reactions of industrial importance. The catalysis is initiated either by electrochemical means or by the addition of chemical oxidation or reduction agents, and the chain-propagating species are organometallic radicals[4] which are usually short-lived and often inadequately characterized. Especially scarce is information on paramagnetic acyl complexes.[5] We present now an ESR study of novel acyltetracarbonyliron radical species with trigonal-bipyramidal (TBP) structures and further evidence for easy alkyl migration in 17-electron metal alkyls.

The thermally labile $\mathrm{(CO)_4FeCOR}$ radicals **I** can be obtained by one-electron oxidation of acyltetracarbonylferrates[6] in THF (0.01 M) at −80 °C by equimolar ferrocenium tetrafluoroborate. The ESR spectrum at −80 °C is a single resonance, 5 G wide, with $g = 2.0491$. The spectrum in 2-methyltetrahydrofuran at −170 °C reveals three g tensor components: 2.1020, 2.0305, 2.0154. The acyl anion can also be generated directly in the ESR tube by microsyringe addition of an alkyllithium to a THF solution of $\mathrm{Fe(CO)_5}$. Starting with 93% ^{13}C-enriched $\mathrm{Fe(CO)_5}$[7] and phenyllithium, a quartet of 11.0 G is obtained after oxidation. These ESR data establish a TBP structure having an axial acyl group in which the unpaired electron interacts appreciably with three equivalent equatorial ^{13}C atoms. Similar low-temperature oxidations of alkyl tetracarbonylferrates[6] $\mathrm{RFe(CO)_4^-}$ yield no ESR spectra. The $g = 2.0491$ line does appear, however, after brief warming at room temperature. We conclude that the $\mathrm{RFe(CO)_4}$ radicals necessarily formed by oxidation couple to diamagnetic dimers.[8] These dimers, on warming, dissociate back into $\mathrm{RFe(CO)_4}$ radicals, which undergo rapid alkyl migration to the more stable acyliron radicals **I**.

Table I. EH Unpaired Electron Populations for $\mathrm{(formyl)Fe(CO)_4}$ and $\mathrm{HFe(CO)_4}$ Radicals[a]

		$\mathrm{Fe}(sxy)$	$\mathrm{Fe}(z)$	$\mathrm{CO_{eq}}$	$\mathrm{CO_{ax}}$	CHO or H
$\mathrm{(CO)_4Fe(CHO)_{ax}}$[b]	TBP	52	4	41 (1.7)	2 (0.01)	1 (0)
$\mathrm{(CO)_4Fe(CHO)_{ax}}$[c]	SP	1	20[d]	63 (0.08)		16 (0.7)
$\mathrm{(CO)_4FeH_{ax}}$	TBP	51	3	42 (1.6)	3 (0.3)	0.5
$\mathrm{(CO)_4FeH_{ax}}$	SP	4	30[e]	60 (0.2)		6.6

[a] The numbers in the Table are sums of the squares of the EH coefficients (×100) of the valence atomic orbitals which make up the SOMO divided into several groups: (1) Fe(sxy), Fe s orbital and all Fe orbitals in the equatorial plane; (2) Fe(z), Fe orbitals outside the equatorial plane; (3) $\mathrm{CO_{eq}}$, $\mathrm{CO_{ax}}$, CHO, and H, atomic orbitals of equatorial CO's and of the axial ligand. When the numbers did not add up exactly to 100, they were normalized to do so but the change was always small. The values in parentheses are the squares of the EH coefficient for the s orbital of an equatorial or axial C atom. The average value is given when the C atoms are not strictly equivalent or in case of orbital degeneracy. The following geometric assumptions and parameters were used: 120° angles for CHO, 1.15 Å for all CO bonds, and 1.59 Å for FeH bonds. [b] Formyl CO eclipses equatorial CO. [c] The projection of formyl CO on the equatorial plane bisects the CFeC angle. [d] 13 (d_{z^2}), 7 (p_z). [e] 23 (d_{z^2}), 7 (p_z).

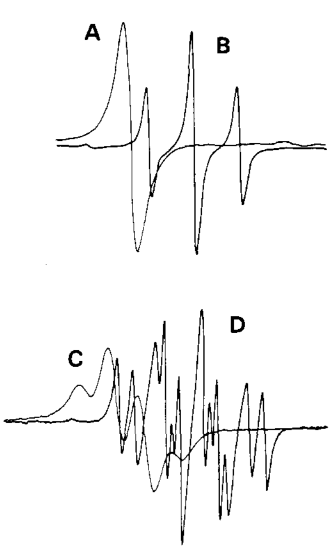

Figure 1. ESR spectra of (A) $\mathrm{(benzoyl)Fe(CO)_4}$, (B) $\mathrm{(benzoyl)Fe(CO)_2[P(OCH_3)_3]_2}$, (C) $\mathrm{(benzoyl)Fe(^{13}CO)_4}$, and (D) $\mathrm{(benzoyl)Fe(^{13}CO)_2[P(OCH_3)_3]_2}$ at −90 °C in pentane.

The $\mathrm{(CO)_4FeCOR}$ radicals can be generated also by low-temperature photochemical reactions of $\mathrm{Fe(CO)_5}$ in pentane with

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several organic substances.[9] An intense spectrum of I (R = C_9H_{19}, $g = 2.0496$) is obtained by photolysis at −40 °C in the presence of decanoyl peroxide. The 11.0-G quartet is obtained by using $Fe(^{13}CO)_5$. $^{57}Fe(CO)_5$[7] ($I(^{57}Fe) = ^1/_2$) gives a doublet of 6.5 G confirming the mononuclearity of I. Some of the reactions that take place are shown below. The addition of an alkyl radical

$$RCO_2\text{—}O_2CR \xrightarrow{h\nu} 2R\cdot + 2CO_2 \tag{2}$$

$$R\cdot + Fe(CO)_5 \rightarrow \underset{\mathbf{I}}{RC(=O)Fe(CO)_4\cdot} \tag{3}$$

$$Fe(CO)_5 \xrightarrow{h\nu} Fe(CO)_4 + CO \tag{4}$$

$$Fe(CO)_4 + R\cdot \rightarrow RFe(CO)_4\cdot \rightarrow {}^1/_2[RFe(CO)_4]_2 \tag{5}$$

to coordinated CO (eq 3) is unprecedented but may well occur in many homogeneously catalyzed carbonylation reactions.

The low-temperature photolysis of alkyl and acyl chlorides and bromides in pentane (generally at −130 °C) in the presence of $Fe(CO)_5$ also leads, after brief warm-up, to clean spectra of I. Initially, the predominant species are thermally unstable $(CO)_4FeX$ radicals[10] which disappear on warming. We suppose that the oxidative addition of the CX bond to the photochemically generated $Fe(CO)_4$ fragments is followed by loss of the halogen atom from the diamagnetic $R(X)Fe(CO)_4$ intermediates. The resulting $RFe(CO)_4$ radicals dimerize at the low temperatures used. On warming, the dimers dissociate, and the $RFe(CO)_4$ radicals are converted to I by facile alkyl migration.

Another source of I is the low-temperature photolysis in pentane of $Fe(CO)_5$ in the presence of aldehydes. In this case, radicals I result most likely by loss of a hydrogen atom from the initially formed $(CO)_4Fe(H)COR$ diamagnetic intermediates.[11] Benzaldehyde gives a particularly robust benzoyliron radical (Figure 1A). If 0.5 μL of $(CH_3O)_3P$ is added by microsyringe to the ESR tube at −80 °C, the spectrum of I is replaced, after a quick shake, by a triplet (17.5 G, $\Delta H = 2$ G, $g = 2.0351$) for 2 equiv ^{31}P atoms (Figure 1B). If the phosphite is added to a solution of I prepared with $Fe(^{13}CO)_5$, the 11 G quartet (Figure 1C) is replaced by the same triplet (17.5 G) split into two doublets (14.6, 5.8 G; Figure 1D). The spectrum of I obtained with benzaldehyde-α-^{13}C is identical with that of unlabeled I. This spectrum is replaced, however, by a triplet of doublets (17.6, 5.9 G) on addition of the phosphite. Finally, the same procedure with benzaldehyde-α-^{13}C and $Fe(^{13}CO)_5$ gives a triplet of doublets of triplets (17.5, 14.5, 5.8 G). There is thus no doubt that two phosphorus ligands have entered the coordination sphere of I in the *equatorial positions* of a TBP. The distortion after substitution and/or electronic effects make now visible the two axial ^{13}C atoms (5.8 G), which were invisible in the unsubstituted TBP, while the single equatorial ^{13}C atom (14.5 G) remains approximately unchanged.

We have carried out EHMO calculations[12] for the hypothetical (formyl)$Fe(CO)_4$ and $HFe(CO)_4$ radicals in TBP and square-pyramidal (SP) structures as models for I and $RFe(CO)_4$ radicals, respectively. We have grouped the *squares* of the atomic orbital coefficients (×100) of the SOMO as shown in Table I to visualize the MO containing the unpaired electron. In the radicals of TBP geometry the unpaired electron resides mostly in the Fe atomic orbitals in the equatorial plane (~50%) and in the atomic orbitals of the equatorial CO ligands (~40%).[13] There is very little unpaired-electron population outside of the equatorial plane. This orbital, smeared over seven equatorial atoms, gives little incentive to the TBP radicals to dimerize as was observed for I. The large s-orbital population for the equatorial C atoms (1.7% and 1.6%) is also consistent with the 11-G splitting for three equivalent ^{13}C atoms in I. For the SP radicals, on the other hand, the unpaired electron is substantially localized (20% and 30%) in Fe d_{z^2} and p_z orbitals, which form a lobe directed along the z axis ready to form an Fe–Fe bond.[14] Our hypothesis that $RFe(CO)_4$ radicals were not observed because of dimerization is then justified assuming that they have SP geometry.

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[9] Typical procedure: An ESR quartz tube is filled under nitrogen with 0.4 mL of olefin-free pentane, 1 μL of $Fe(CO)_5$, and 2–5 μL of an organic compound. The low-temperature irradiation is carried out in a standard quartz Dewar for variable-temperature ESR surrounded by the coils of a low-pressure Hg discharge tube (mostly 2500-Å UV) in the shape of a tight spiral. The cooling is provided by a flow of cold nitrogen. After irradiation, the tube is plunged into liquid nitrogen and is transferred to the ESR cavity kept at the desired low temperature.

[10] Krusic, P. J., unpublished results.

[11] If the photolysis is carried out below −100 °C, $HFe_2(CO)_8$ radicals (Krusic, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 2131) are also observed.

[12] Extended Hückel Calculations, Quantum Chemistry Program Exchange, No. 358, Indiana University.

[13] The d orbital splitting scheme for a TBP is well-known. See, e.g.: Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

[14] For the d-orbital splitting scheme for 17-electron SP species, see: Elian, M.; Hoffmann, R. Inorg. *Chem.* **1975**, *14*, 1058.

Monensin 26-Pyromellitate Forms Lithium Channels in Monolayer Lipid Membranes

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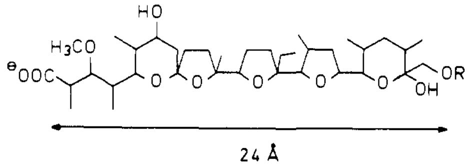
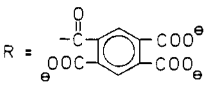
We recently reported preparations of extremely thin (~20 Å) monolayered vesicle membranes made from α,ω-bifunctional amphiphiles ("bolaamphiphiles").[1,2] In this communication we describe an α,ω-bifunctional amphiphile with a polar chain in a hydrophobic skeleton of equal length. It functions as a channel for lithium ions in the 20-Å monolayer membrane but not in a 40-Å bilayer lipid membrane. The 20-Å channel former is easily accessible from commercial monensin.

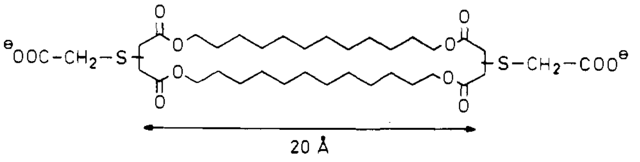
Monensin **1a** is a well-known ionophore with a hydrophobic and a hydrophilic side. It predominantly exists in a cyclic con-



1a R = H

1b R =





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