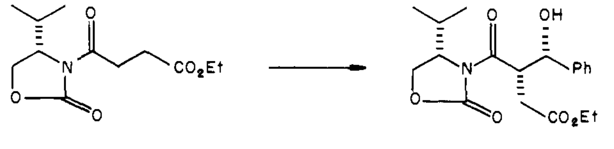
Table II. Aldol Condensations of 1c and 1d with Representative Aldehydes (Scheme II)[9]

imide	R_1CHO	ratio 11a:12a[a]	$[\alpha]^{25}_D$ 13	optical purity 13:14[c]
1d	Me_2CHCHO	98.4:1.6	−42.1° (1.8)[d]	97.8:2.2
1d	n-C_3H_7CHO	98.9:1.1	−27.3° (2.1)[e]	99.4:0.6
1d	CH_3CHO	99.6:0.4	−45.8° (1.7)[f]	>99.9:<0.1
1d	C_6H_5CHO	92.4:7.6	−17.1° (4.1)[g]	92.4:7.6[h]

[a] Determined by GLC (ref 13). [b] All rotations were carried out in $CHCl_3$ except for the C_6H_5CHO case. EtOH was used instead. [c] Inferred from the ratios of 11a and 12a after chromatographic purification. [d] Literature rotation: $[\alpha]_D$ −24.7° (c 0.98, $CHCl_3$) (ref 19a); $[\alpha]_D$ −40.3° (c 4.6, $CHCl_3$) (ref 2d). [e] Literature rotation: $[\alpha]_D$ −28° (c 2.0, $CHCl_3$) (ref 19b). [f] Value is $[\alpha]_D$ of methyl ester of 13 from methanolysis of 11a and 12a. Literature rotation for methyl ester of 14: $[\alpha]_D$ +33.3° (c 1.2, $CHCl_3$) (ref 19c). [g] Literature rotation for antipode 14: $[\alpha]_D$ +18.9° (c 5.15, EtOH) (ref 2g) $[\alpha]_D$ −18.9° (c 2.3, EtOH) (ref 19d). [h] Products 11a and 12a, $R_1 = C_6H_5$, are not stable on silica gel. The crude product from desulfuriztion was hydrolyzed directly to the acid.

1b in anhydrous CH_2Cl_2 under argon (0 °C) is added 1.1 equiv of boron triflate (**7**)[4e] followed by 1.2 equiv of diisopropylethylamine. After allowing 30 min for complete enolization, the reaction is cooled (−78 °C) and 1.1 equiv of freshly distilled aldehyde is added and stirred for 0.5 h at −78 °C and 1.5 h at room temperature. The boron aldol ate complex is quenched with pH 7 phosphate buffer and oxidized with 30% hydrogen peroxide–methanol (0 °C, 1 h). The aldol adduct is then isolated by ether extraction.

It appears that these reactions will be useful for more highly functionalized substrates as well. For example, the selective enolization of **8** and its subsequent condensation with benzaldehyde afforded the diastereomerically pure adduct **9** [mp 101–102 °C, J (erythro) = 5.0 Hz] in 67% isolated yield. The absolute stereochemical assignment for **9** was carried out by a straightforward degradation to (2R)-benzylsuccinic acid (**10**), mp 162–163 °C, $[\alpha]_D$ −28.6° (c 0.9, acetone) whose optical purity was judged to be ≥98%.[18]



8 9

In view of the high levels of asymmetric induction observed in the cases cited above, it was surprising to observe that the boryl enolate derived from the N-acetyloxazolidone (**1c**)[10] afforded nearly 1:1 ratios of the aldol adducts **11a** and **12a** with the representative aldehydes illustrated in Table II. For example, the boron enolate derived from **1c** afforded a **11a**:**12a** ratio of 52:48 with isobutyraldehyde and 72:28 with acetaldehyde. It had been hoped that **1c** and **2c** might function as useful chiral acetate enolate equivalents.[2g] A practical solution to this objective was accomplished upon examination of the aldol condensations of oxazolidone **1d**[10] which were found to be highly stereoregular in nature. Desulfurization of the aldol adducts **11b** and **12b** to **11a** and **12a** proceeded in good yield with Raney nickel[20] (acetone, 60 °C, 20 min). Gas chromatographic analysis[13] (Table II) indicated that asymmetric induction in the range of 92–99% could be achieved. Chromatographic purification of **11a** followed by base hydrolysis, as previously described, afforded the β-hydroxy acids **13** in 80–90% yields. Since the absolute configurations of acids **13** (R_1 = Ph, Me, n-C_3H_7, and i-C_3H_7) have been previously established,[2g,19] it follows that the sense of asymmetric induction of both **1b** and **1d** are the same for all aldehydes examined. One important consequence of this study pertains to the *critical* role of enolate substitution in aldol asymmetric induction. In related studies we have made parallel observations that unsubstituted methyl ketone boryl enolates exhibit much lower levels of asymmetric induction than the corresponding (Z)-ketone enolates.[2d,2e]

Oxazolidones **1a** and **1b** appear to fulfill all of the design requirements for a generally useful chiral auxiliary for the aldol process. These systems confer high stereoselection on the enolization process, provide remarkable levels of erythro-diastereoface selection ($\Delta\Delta G^{\ddagger}$ at −78 °C ~ 3 kcal/mol), and are readily removed and recycled without attendant racemization of the substrate.

Acknowledgment. This research has been supported by the National Science Foundation and the National Institutes of Health.

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(18) Fredga, A. *Ark. Kemi, Mineral. Geol.* **1948**, *26B* (n-11), 1–4. The reported rotation for **10** (mp 164.5 °C) is $[\alpha]_D$ −29.0° (c 3.2, acetone).

(19) (a) Büchi, G.; Crombie, L.; Godin, P. J.; Kaltenbronn, J. S.; Siddalingaiah, K. S.; Whiting, D. A. *J. Chem. Soc.* **1961**, 2843–2860. (b) Serck-Hanssen, K. *Ark. Kemi* **1956**, *10*, 135–149. (c) Lemieux, R. U.; Giguere, J. *Can. J. Chem.* **1951**, *29*, 678–690. (d) Cohen, S. G.; Weinstein, S. Y. *J. Am. Chem. Soc.* **1964**, *86*, 725–728.

(20) Billica, H. R.; Adkins, H. *Org. Synth. Coll. Vol. III* **1955**, 176–180.

ESR Study of Iron Carbonyl Radical Anions

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The neutral carbonyl compounds of iron, $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, the related carbonylate dianions, $Fe(CO)_4^{2-}$, $Fe_2(CO)_8^{2-}$, $Fe_3(CO)_{11}^{2-}$, $Fe_4(CO)_{13}^{2-}$, and their conjugate acids, $HFe(CO)_4^-$, $HFe_2(CO)_8^-$, $HFe_3(CO)_{11}^-$, $HFe_4(CO)_{13}^-$ occupy an important position in organometallic chemistry.[1] Several of these complexes are employed as useful stoichiometric reagents or precursors to catalytically active species. They are all diamagnetic, and their very considerable chemistry has been discussed virtually exclusively in terms of even-electron mechanisms. We wish to report now our investigations on a new series of iron carbonyl species which parallel the carbonylate dianions and are related to the latter by having one less electron. The existence of these radical anions, their conjugated protonated species,[2] and other organoiron radicals[3,4] suggests an important but not yet generally recognized role for one-electron pathways in the chemistry of iron carbonyl compounds.

When dilute solutions of $Fe(CO)_5$ in rigorously dry, oxygen-free THF are stirred with excess alkali metals or alkali–metal alloys,[5] they become red brown and display ESR spectra of up to *four* paramagnetic species in variable relative concentrations. Each

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(1) For a review, see *Org. Synth. Metal Carbonyls*, **1**, 1 (1968).

(2) P. J. Krusic, *J. Am. Chem. Soc.*, following paper in this issue.

(3) P. J. Krusic and J. San Filippo, Jr., submitted for publication.

(4) E. L. Muetterties, B. A. Sosinsky, and K. I. Zamaraev, *J. Am. Chem. Soc.*, **97**, 5299 (1975); N. El Murr, M. Riveccie, and P. Dixneuf, *J. Chem. Soc., Chem. Commun.*, 552 (1978).

(5) All operations and reactions were carried out in a high-quality nitrogen glove box. Solutions employed in ESR studies ranged from 1×10^{-3} to 5×10^{-3}M. $Fe(CO)_5$ was bulb-to-bulb distilled in the dark.

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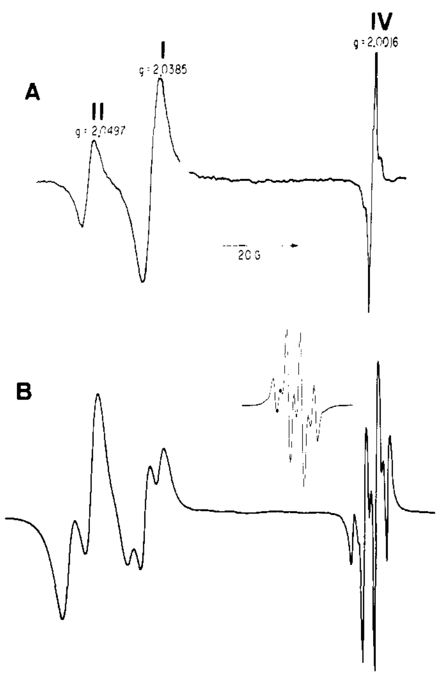

Figure 1. (A) ESR spectra of I, II, and IV in THF at -80 °C. (B) ESR spectra of the same species also at -80 °C derived from $^{57}Fe(CO)_5$ in THF. The ^{57}Fe hyperfine structure for IV is expanded in the inset.

species is characterized by a single ESR absorption and a unique *g* factor: I, 2.0385; II, 2.0497; III, 2.0134; IV, 2.0016. The spectra of I, II, and IV are shown in Figure 1A.[6] The spectrum of IV is remarkably narrow ($\Delta H \sim 1$ G) and displays distinct shoulders which suggest a ^{13}C satellite doublet ($\sim$3 G) for a species with many equivalent carbon atoms. Only I is observed in the early course of such reductions or when $Fe(CO)_5$ is reacted with an equimolar solution of sodium naphthalide in THF at ambient temperature.[7] The line width of I is strongly temperature dependent being $\sim$3 G at -80 °C and increasing up to $\sim$20 G at 25 °C. Frozen solutions of I exhibit a powder spectrum appropriate for an axially symmetric *g* tensor ($g_\perp = 2.0540$, $g_\parallel = 2.0092$). II, IV, and particularly III occur much less predictably in high concentrations. Reproducible high yields of I, II, and IV are obtained, however, in the early stages of a titration of the above red-brown reaction mixtures (filtered to remove excess alkali metals) with successive aliquots of one-electron oxidants such as $AgBF_4$ or [ferrocenium]BF_4 in THF at -80 °C. In the later stages of the titration, I and IV disappear and II and III can be reproducibly observed. The end point is marked by the loss of all paramagnetic species.[8]

The identification of I–IV was greatly aided by the use of isotopically labeled $Fe(CO)_5$. A THF solution of $^{57}Fe(CO)_5$ (92 atom % ^{57}Fe)[9] was treated with Na/K eutectic alloy. Titration at -80 °C with [ferrocenium]BF_4 led to the spectrum in Figure 1B. Since ^{57}Fe has a nuclear spin of $^1/_2$, the splitting patterns observed for I, II, and IV (triplet, 3.7 G; doublet, 5.2 G; quartet, 3.10 G; respectively)[10] show the presence of a unique Fe atom in II, two equivalent Fe atoms in I, and three equivalent Fe atoms in IV.

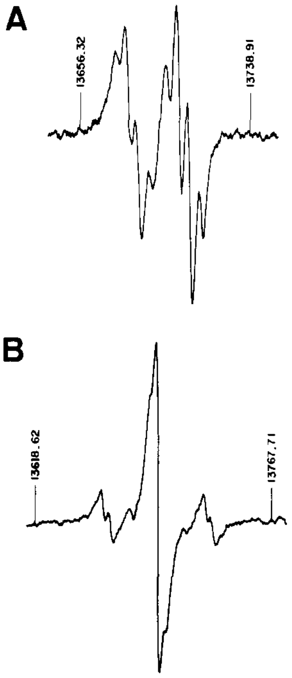

Figure 2. (A) ESR spectrum of species III in THF at -80 °C derived from $^{57}Fe(CO)_5$. (B) ESR spectrum of III in THF at -80 °C derived from $Fe(CO)_5$ $\sim$10% enriched in ^{13}C. The NMR field markers are in kHz.

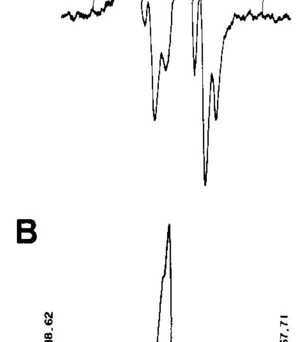

Figure 3. ESR spectrum of $Fe_3(CO)_{12}^{-}\cdot$ in THF at -50 °C derived from 92% ^{13}C enriched $Fe(CO)_5$ (left) and computer simulation. For line spectrum see ref 13.

Analogous experiments were carried out with $\sim$10% ^{13}C-enriched $Fe(CO)_5$.[11] The spectrum of III obtained in the later stages of the titration (Figure 2B) clearly shows four ^{13}C satellite doublets (16.2, 14.2, 7.9, and $\sim$2.5-G shoulders), indicating a species with four distinct sets of CO ligands. Two of these sets (doublets of equal amplitude) contain the same number of CO ligands. Figure 2A shows the spectrum of III obtained analogously from $^{57}Fe(CO)_5$. Clearly, III is a cluster containing three equivalent Fe atoms (quartet, 1.27 G) and a unique Fe atom (doublet, 5.80 G).

Similar treatment of 92% ^{13}C-enriched $Fe(CO)_5$[12] permitted an unambiguous identification of IV. The resulting spectrum of IV (Figure 3) can be most satisfactorily interpreted and computer simulated in terms of a species with *12 equivalent* carbon atoms

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[6] These ESR signals have been reported several times: (a) B. M. Peake, B. H. Robinson, J. Simpson, and D. J. Watson, *Chem. Commun.*, 945 (1974); (b) E. Z. Gildenberg, V. A. Shvets, A. L. Lapidus, V. B. Kazanskii, and Y. G. Eidus, *Kinet. Katal.*, **16**, 1077 (1975); (c) D. Miholova, J. Klima, and A. A. Vlček, *Inorg. Chim. Acta*, **27**, L67 (1978); (d) J. P. Collman, R. G. Finke, P. L. Matlock, R. Wahren, R. G. Komoto, and J. I. Brauman, *J. Am. Chem. Soc.*, **100**, 1119 (1978); (e) P. A. Dawson, B. M. Peake, B. H. Robinson, and J. Simpson, *Inorg. Chem.*, **19**, 465 (1980); (f) only IV was correctly identified in ref 6c,e.

[7] Reaction of $Fe(CO)_5$ with 1 equiv of sodium naphthalide gives good yields of $Fe_2(CO)_8^{2-}$, isolable as the PPN^+ (bistriphenyliminium) salt. ESR examination of the isolated product showed it to be contaminated with trace amounts of I. Treatment of $Fe(CO)_5$ with 2 equiv of sodium naphthalide produces $Na_2Fe(CO)_4$ in excellent yields.

[8] Just prior to the end point thermally unstable paramagnetic hydrido species can also be observed (cf. ref 2).

[9] Prepared from $^{57}Fe_2O_3$ (New England Nuclear Co.) by a recently published procedure: B Hutchinson, R. L. Hance, L. Daniels, and B. Bernard, *Synth. React. Inorg. Metal-Org. Chem.*, **10**, 1 (1980).

[10] Final splittings were obtained by computer fitting of the line shapes. These simulations took into account all significant isotopic species whose abundances were calculated by combinatorial considerations. For example, together with the quartet of IV appropriate for three ^{57}Fe atoms, there is also a triplet of the same splitting corresponding to 20.3% of IV with two ^{57}Fe and one ^{56}Fe atoms (cf. inset, Figure 1).

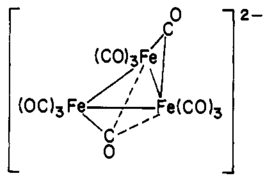
[11] K. Noack and M. Ruch, *J. Organomet. Chem.*, **17**, 309 (1969).

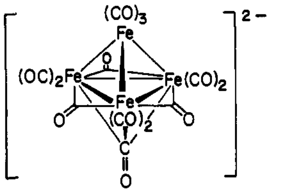
[12] Obtained from Pressure Chemical Co.

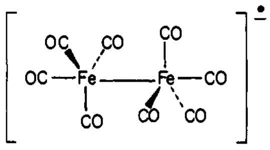
[$a(^{13}C)$ = 3.55G].[13] Taken together with the ^{57}Fe data, these results identify IV as the radical anion $[Fe_3(CO)_{12}]^{-}\cdot$[6e,14] in which all carbonyls are most probably rendered equivalent by a rapid intramolecular exchange.[15,16]

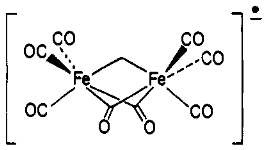
Final confirmations of the identities of I, II, and III come from the observation that each of these species can be cleanly generated by the oxidation of the dianions $Fe_2(CO)_8^{2-}$, $Fe_3(CO)_{11}^{2-}$, and $Fe_4(CO)_{13}^{2-}$, respectively, with 1 equiv of [ferrocenium]BF_4 or $AgBF_4$ in THF at -80 °C.[17] These results, together with the isotopic studies described above, leave little doubt that I, II, and III are the radical anions $Fe_2(CO)_8^{-}\cdot$, $Fe_3(CO)_{11}^{-}\cdot$, and $Fe_4(CO)_{13}^{-}\cdot$.[18] Intensive efforts have so far failed to provide the ESR spectrum of the simplest member of this family, $Fe(CO)_4^{-}\cdot$,[19] probably because it rapidly dimerizes to the diamagnetic $Fe_2(CO)_8^{2-}$ or combines with other iron carbonyl fragments. Interestingly, the oxidation of $Fe(CO)_4^{2-}$ with equimolar solutions of the above oxidants as well as of $Fe(CO)_5$ gives only the spectrum of I.

Our isotopic studies are consistent with structures for II and III which are closely related to those of the corresponding diamagnetic dianions II⁻ and III⁻ shown below.[20] Interestingly, III cannot be fluxional on the ESR time scale at -80 °C; indeed, the relative intensities of the ^{13}C satellites for III (Figure 2B) are consistent with two sets of three equivalent carbonyls (16.2 G, 14.2 G), one set of six equivalent carbonyls (2.5 G), and one unique carbonyl (7.9 G), in complete analogy with the structure of its diamagnetic analogue III⁻. The two structures shown below, possibly rapidly interconverting in solution,[21] seem likely for I.









The unbridged structure is that of $Fe_2(CO)_8^{2-}$ in the solid state[22] as well as of one of two isomers of matrix-isolated neutral $Fe_2(CO)_8$, while the bridged structure is analogous to that proposed for the second isomer of $Fe_2(CO)_8$.[23]

Acknowledgment. We express our gratitude to Messrs. B. F. Gordon, D. J. Jones, and R. O. Balback for dedicated technical assistance, Professor D. F. Shriver for essential synthetic information, and Dr. A. Stout of the Pressure Chemical Co. for the synthesis of ^{13}C-labeled $Fe(CO)_5$. Financial support to B.H. and R.L.H. was given by the R. A. Welch Foundation and to J.S.F. by the National Science Foundation and the Department of Energy.[24]

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(13) The spectrum consists of a superposition of 13 lines for IV with 12 ^{13}C atoms (36.8%), 12 lines for IV with 11 ^{13}C atoms and 1 ^{12}C (38.4%) atoms, 11 lines for IV with 10 ^{13}C and 2 ^{12}C atoms (18.3%), etc. (cf. inset, Figure 3).

(14) See also A. M. Bond, P. A. Dawson, B. M. Peake, B. H. Robinson, and J. Simpson, *Inorg. Chem.*, **16**, 2199 (1977).

(15) The neutral species $Fe_3(CO)_{12}$ is also highly fluxional: F. A. Cotton and D. L. Hunter, *Inorg. Chim. Acta*, **11**, L9 (1974).

(16) $Fe_3(CO)_{12}^{-}\cdot$ is also obtained quantitatively by treating a dilute solution of $Fe_3(CO)_{12}$ in THF with an equimolar solution of sodium naphthalide at -80 °C. This reaction can be carried out on a preparative scale at ambient temperature. Use of 2 equiv of naphthalide followed by treatment with [PPN]Cl produces analytically pure $[PPN]_2Fe_3(CO)_{11}$.

(17) $Na_2Fe_2(CO)_8$ was prepared by the method of ref 6d; $[PPN]_2Fe_3(CO)_{11}$ and $[PPN]_2Fe_4(CO)_{13}$ were prepared as described by H. A. Hodali and D. F. Shriver (*Inorg. Synth.*, **20**, 222 (1980); and to be published). Samples prepared by alternative methods gave equivalent results. All these salts, but particularly those of $Fe_2(CO)_8^{2-}$, are difficult to prepare free of the paramagnetic anions discussed in this work.

(18) (a) The powder spectrum of II reveals a nearly symmetric *g* tensor with g_1 = 2.0243, g_2 = 2.0321, and g_3 = 2.0921. (b) It should be noted that the ^{57}Fe doublet for II in Figure 1B does not preclude a trinuclear structure for this species; the splitting due to the remaining ^{57}Fe atoms is simply not resolved because of the relatively broad line width.

(19) $Fe(CO)_4^{-}$ has been detected by IR using matrix isolation techniques [J. K. Burdett, *Coord. Chem. Rev.*, **27**, 1 (1978); *Chem. Commun.*, 763 (1973)] and in the gas phase by ion cyclotron resonance [R. C. Dunbar, J. F. Ennever, and J. P. Fackler, Jr., *Inorg. Chem.*, **12**, 2734 (1973); J. H. Richardson, L. M. Stephenson, and J. I. Brauman, *J. Am. Chem. Soc.*, **96**, 3671 (1974); M. S. Foster and J. L. Beauchamp, *ibid.*, **97**, 4808 (1975)].

(20) (a) F. Y. Lo, G. Longoni, P. Chini, L. D. Lower, and L. F. Dahl, *J. Am. Chem. Soc.*, **102**, 7691 (1980); (b) R. J. Doedens and L. F. Dahl, *ibid.*, *88*, 4847 (1966).

(21) The spectrum of I derived from 92% ^{13}C-enriched $Fe(CO)_5$ at -80 °C is a single line of 7.7-G p-t-p width vs. 3.1-G width for I derived from normal $Fe(CO)_5$ under strictly comparable conditions. This is consistent with several equivalent (rapidly exchanging) ^{13}C ligands but does not prove it. Work at lower temperatures in THF, at which I might be static on the ESR time scale, was hampered by severe line broadening.

(22) H. B. Chin, M. B. Smith, R. D. Wilson, and R. Bau, *J. Am. Chem. Soc.*, **96**, 5285 (1974).

(23) M. Poliakoff and J. J. Turner, *J. Chem. Soc. A*, 2403 (1971).

(24) NSF Grant 80-17045 and DOE Contract DE-AS05-80ER-10662.

ESR Study of Paramagnetic Iron Carbonyl Hydrides

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In the preceding communication,[1] electron spin resonance (ESR) evidence was presented for a new series of iron carbonyl radical anions, I⁻·–IV⁻·, having one less electron than the corresponding well-known diamagnetic iron carbonylate dianions, I^{2-}–IV^{2-}. Iron also forms a parallel series of diamagnetic anionic

$[Fe(CO)_4]^{2-}$	$[Fe_2(CO)_8]^{2-}$	$[Fe_3(CO)_{11}]^{2-}$	$[Fe_4(CO)_{13}]^{2-}$
I^{2-}	II^{2-}	III^{2-}	IV^{2-}
$[HFe(CO)_4]^{-}$	$[HFe_2(CO)_8]^{-}$	$[HFe_3(CO)_{11}]^{-}$	$[HFe_4(CO)_{13}]^{-}$
HI⁻	HII⁻	HIII⁻	HIV⁻

carbonyl hydrides, HI⁻–HIV⁻, which have found extensive applications in organic synthesis and homogeneous catalysis,[2] as well as a series of homologous neutral dihydrides, H_2I–H_2IV, which are relatively unstable and less studied. The anionic hydrides are strong reducing agents, and it is therefore possible that the series of neutral odd-electron hydrides, HI·–HIV·, formally the conjugate acids of I⁻·–IV⁻·, may also be important as reaction intermediates. We now present evidence supporting this conjecture and an ESR characterization of $HFe_2(CO)_8\cdot$ (HII·) and $HFe_3(CO)_{11}\cdot$(HIII·). The latter provides, for the first time, ESR evidence for the very high mobility of CO ligands in a paramagnetic transition metal cluster.

UV irradiation in an ESR cavity of dilute, olefin-free pentane solutions of $Fe(CO)_5$ (~10^{-3} M) below -100 °C and under a pressure of ~30 atm of hydrogen[3] gives rise to a spectrum of two narrow lines ($\Delta H \simeq$ 1.3 G) separated by 22.2 G with a *g* factor of 2.0120. The observation of a 1:1:1 triplet with a 3.3-G splitting and the same *g* factor in a similar experiment using deuterium establishes the formation of a paramagnetic iron carbonyl hydride.[4]

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(1) P. J. Krusic, J. San Filippo, Jr., B. Hutchinson, R. L. Hance, and L. M. Daniels, *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) For a review, see *Org. Synth. Metal Carbonyls*, **1**, 1 (1968).

(3) A thick-wall quartz tube with a special Teflon-plunger valve was used.

0002-7863/81/1503-2131$01.25/0