studies concerning the main-group organometallic chemistry of these ligands. The interaction of aluminum species with multidentate ligands containing phosphorus and sulfur represents an important extension of organoaluminum chemistry. While organoaluminum compounds containing Al–S bonds, characterized by X-ray diffraction techniques, are relatively rare, the title compound is unique, inter alia, in that it contains an S_2Al_4 moiety.

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Supplementary Material Available: Tables of crystal data, bond distances and angles, final fractional coordinates, thermal parameters, and a summary of data collection and refinement (14 pages); a listing of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

Electrochemical Reduction of $Fe(CO)_5$ Revisited

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Summary: The electrochemical reduction of $Fe(CO)_5$ in THF has been studied by cyclic voltammetry with microelectrodes. The electron stoichiometry of the reduction varies with potential scan rates because the initial two-electron reduction leading to $Fe(CO)_4^{2-}$ is followed rapidly by the reaction of the latter with $Fe(CO)_5$ to yield $Fe_2(CO)_8^{2-}$, the major product of electrolysis. An analysis of the cyclic voltammograms yields the rate of this reaction (6×10^6 M^{-1} s^{-1}). The anodic waves following reduction of $Fe(CO)_5$ have been assigned to specific electrode processes by comparison with the cyclic voltammograms of several iron carbonylate anions.

The electrochemical reduction of $Fe(CO)_5$ has attracted considerable attention.[1-6] There is general agreement that this reduction is chemically irreversible and that it is followed by fast chemical reactions. Several anodic peaks for the oxidation of reaction products have been observed after reduction in cyclic voltammetry which have not been positively assigned to specific electrode processes. In aprotic media, the electrolytic process was shown to involve an overall *one-electron* consumption and the major product was the $Fe_2(CO)_8^{2-}$ carbonylate anion.[3,6] It has been implicitly assumed that this product arises from the dimerization of the transient 17-electron $Fe(CO)_4^{\bullet-}$ radical anion intermediates formed by CO loss from the initial 19-electron $Fe(CO)_5^{\bullet-}$ radical anion. During its fleeting life, the latter behaves as an organic acyl radical[7] which can be intercepted by adding $(n\text{-Bu})_3SnH$ from which it abstracts a hydrogen atom affording the formyl anion $(CO)_4FeCOH^-$.[8] An apparently conflicting result was obtained when the cyclic voltammetry was performed in acetone at a Hg drop electrode[4] or in the presence of protic impurities:[6] in these cases the reduction was shown to be an overall *two-electron* process.[9] Furthermore, in synthetic work using Na naphthalenide as a one-electron carrier, it was found that the reduction of $Fe(CO)_5$ using 2 equiv of this reagent afforded Collman's reagent $Fe(CO)_4^{2-}$ whereas 1 equiv yielded $Fe_2(CO)_8^{2-}$.[10] The discrepancies concerning the observed electron stoichiometries could be related to the fate of the initially formed radical intermediates. Since we have recently studied by ESR the transient $Fe(CO)_4^{\bullet-}$ radical anion and we did not find it to be exceedingly short-lived under the photochemical conditions used for its generation (photolysis of $Fe_2(CO)_8^{2-}$ in THF),[11] we decided to reexamine the cyclic voltammetry of $Fe(CO)_5$ at faster potential scan rates than have been used so far in hopes of observing it directly by electrochemical techniques. We also felt that a complete understanding of the chemistry following reduction demands the positive identification of the associated anodic peaks. For this purpose we examined by cyclic voltammetry several iron carbonylate anions which could be involved in this chemistry (Table I). In this communication we report that the electron stoichiometry of the electrochemical reduction of $Fe(CO)_5$ in THF is dependent on the potential scan rates and that the $Fe(CO)_4^{\bullet-}$ radical anion, contrary to accepted views, is not a significant intermediate in this reduction at conventional scan rates.

Table I. Standard Potentials of Iron Carbonylate Anions[a]

electrochemical couple	$E°$ (V)
$Fe(CO)_4^{2-}/Fe(CO)_4^{\bullet-}$	−1.95[b]
$Fe_2(CO)_8^{2-}/Fe_2(CO)_8^{\bullet-}$	−1.68
$Fe_2(CO)_8^{\bullet-}/Fe_2(CO)_8$	−0.53[c]
$Fe_3(CO)_{11}^{2-}/Fe_3(CO)_{11}^{\bullet-}$	−1.55[d]
$Fe_4(CO)_{13}^{2-}/Fe_4(CO)_{13}^{\bullet-}$	−0.96[d]

[a] In THF with 0.3 M $(n\text{-Bu})_4N^+BF_4^-$ (except $Fe(CO)_4^{2-}/Fe(CO)_4^{\bullet-}$, cf. footnote *b*). $E°$ are given vs $Ag/AgBF_4$, 0.02 M in THF. In this medium and with this reference electrode, $E°$ for ferrocene/ferrocenium(1+) is −0.226 V. [b] In THF/HMPA (95:5 v/v) without supporting electrolyte and with Au electrode of 0.1-mm diameter. [c] Irreversible one-electron oxidation. Peak potential value at 5 V s^{-1}. [d] Additional oxidation waves are observed at more positive potentials.

Two cyclic voltammograms for the reduction of $Fe(CO)_5$ in THF are shown in parts A and B of Figure 1. The

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† Du Pont Contribution No. 4800.

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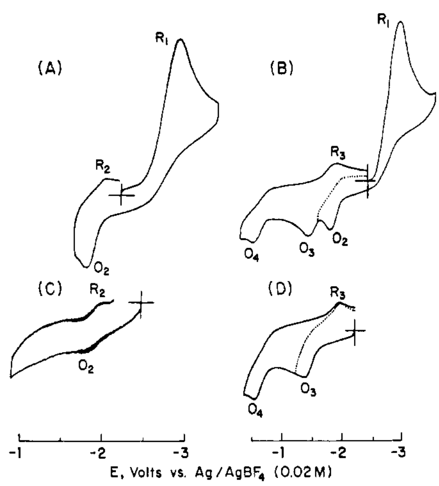

Figure 1. Cyclic voltammograms for (A) 1 mM $Fe(CO)_5$ in THF (0.3 M $(n\text{-}Bu)_4N^+BF_4^-$) at 20 V s^{-1} ($n_{ap} = 1.3$), (B) same at 5 V s^{-1} ($n_{ap} = 1.1$), (C) 2 mM $Na_2Fe(CO)_4$ in THF/HMPA (95/5 v/v) at 20 V s^{-1} without supporting electrolyte, and (D) 1 mM $Na_2Fe_2(CO)_8$ in THF (0.3 M $(n\text{-}Bu)_4N^+BF_4^-$) at 5 V s^{-1}. Different current scales apply to each voltammogram.

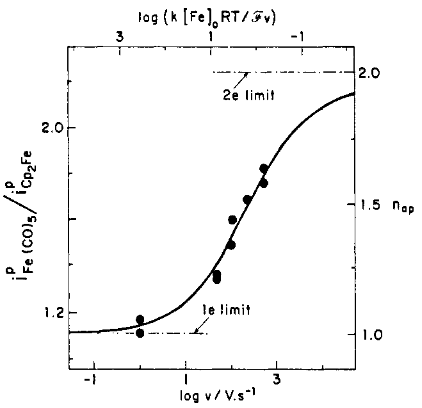

Figure 2. Electron stoichiometry of the reduction of $Fe(CO)_5$ as a function of potential scan rates (see text for calculated curve[22]).

behavior of $Fe(CO)_5$ at 5 V s^{-1} as shown in Figure 1B is essentially equivalent to that reported before[6] with one irreversible reduction wave R_1 followed by three associated anodic processes O_2, O_3, and O_4. At faster scan rates the O_2 wave increases at the expense of O_3 and O_4 and starts showing chemical reversibility at 20 V s^{-1} (Figure 1A). Concomitantly, the number of electrons exchanged at R_1 per mole of $Fe(CO)_5$ *increases* from 1.1 (Figure 1B) to 1.3 (Figure 1A) by comparison with ferrocene under the same conditions (see below). This trend continues as the potential scan rate increases, as shown in Figure 2, approaching the two-electron limit.

The O_2/R_2 couple (Figure 1A) pertains to the one-electron oxidation of Collman's reagent $Fe(CO)_4^{2-}$ to the transient $Fe(CO)_4^{\bullet-}$ radical anion as is demonstrated by the cyclic voltammogram of Figure 1C obtained with authentic $Na_2Fe(CO)_4$ in the absence of supporting electrolyte in 95:5 v/v THF/HMPA.[12,13] Similarly, the O_3/R_3 couple and the chemically irreversible wave O_4 are associated with the electrochemical oxidation of $Fe_2(CO)_8^{2-}$ as shown in Figure 1D obtained with an authentic sample of $Na_2Fe_2(CO)_8$. Although ESR studies have shown that the $Fe_2(CO)_8^{\bullet-}$ radical anion is stable on this time scale at room temperature in THF,[14] the large peak-to-peak separation ($\Delta E_p = 0.53$ V) for the one-electron oxidation of $Fe_2(CO)_8^{2-}$ to the $Fe_2(CO)_8^{\bullet-}$ radical anion is expected because of a considerable structural reorganization occurring upon electron transfer. IR[15] and X-ray structural studies[16] have shown that $Fe_2(CO)_8^{2-}$ has an unbridged metal–metal bond whereas a recent single-crystal ESR study[17] has established that the most stable structure of the $Fe_2(CO)_8^{\bullet-}$ radical has two bridging CO ligands. The chemically irreversible wave O_4 is then associated with the one-electron oxidation of $Fe_2(CO)_8^{\bullet-}$ to the neutral, coordinatively unsaturated $Fe_2(CO)_8$ fragment which undergoes further rapid reactions. No additional simple polynuclear iron carbonylate anions are formed on the time scale of our cyclic voltammograms as judged by a comparison with the chemically reversible cyclic voltammograms obtained with authentic samples of $Fe_3(CO)_{11}^{2-}$ and $Fe_4(CO)_{13}^{2-}$ (Table I). The chemical reversibility of these waves is in good agreement with previous ESR studies of the radical anions $Fe_3(CO)_{11}^{\bullet-}$ and $Fe_4(CO)_{13}^{\bullet-}$ and further confirms the ESR assignments.[14,18]

The above results indicate that at sufficiently fast potential scan rates the electrochemical reduction of $Fe(CO)_5$ in THF is, in fact, a *two-electron* ECE process leading to the formation of $Fe(CO)_4^{2-}$ (eq 1–3). This is a direct

$$Fe(CO)_5 \xrightarrow{+e} Fe(CO)_5^{\bullet-} \tag{1}$$

$$Fe(CO)_5^{\bullet-} \xrightarrow{\text{fast}} Fe(CO)_4^{\bullet-} + CO \tag{2}$$

$$Fe(CO)_4^{\bullet-} \xrightarrow{+e} Fe(CO)_4^{2-} \tag{3}$$

consequence of the fact that the reduction potential of $Fe(CO)_5$ is much more negative than the standard potential for the couple $Fe(CO)_4^{2-}/Fe(CO)_4^{\bullet-}$ (−3.02 V vs −1.95 V). In other words, any $Fe(CO)_4^{\bullet-}$ formed when $Fe(CO)_5$ accepts an electron and loses a CO, finding itself at a potential which is much more negative than that at which it is reversibly formed from $Fe(CO)_4^{2-}$, must of necessity be immediately further reduced to $Fe(CO)_4^{2-}$. As a consequence, under these reductive conditions, *$Fe_2(CO)_8^{2-}$ cannot result by dimerization of two $Fe(CO)_4^{\bullet-}$ radicals* even if the dimerization were diffusion limited.[19] The apparent one-electron consumption at slower potential scan rates must therefore result from further chemical reactions of $Fe(CO)_4^{2-}$. The only plausible reaction leading to $Fe_2(CO)_8^{2-}$ is that with unreduced $Fe(CO)_5$ (eq 4) which

$$Fe(CO)_4^{2-} + Fe(CO)_5 \xrightarrow{k} Fe_2(CO)_8^{2-} + CO \tag{4}$$

is indeed also a convenient synthetic route to the $Fe_2(CO)_8^{2-}$ dianion.[20] A quantitative analysis based on eq 1–4 leads to the working curve shown in Figure 2 from which

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[12] Cf. Amatore, C.; Deakin, M. R.; Wightman, R. M. *J. Electroanal. Chem.* **1987**, *220*, 49.

[13] Exclusion of supporting electrolyte was necessary because of the reactivity of Collman's reagent. HMPA increases the solubility of sparingly soluble $Na_2Fe(CO)_4$ and dissociates the tight ion pairing. Cf. Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 2515.

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[19] Amatore, C.; Savéant, J. M. *J. Electroanal. Chem.* **1981**, *125*, 1.

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a rate constant of (6.0 ± 2) × 10^6 M^{-1} s^{-1} can be extracted for this reaction.[21,22]

In conclusion, the observation by several authors[1,4,6] of an overall two-electron process in the reduction of $Fe(CO)_5$ at slow potential scan rates indicates reactions of $Fe(CO)_4^{2-}$ which are faster than the reaction of $Fe(CO)_4^{2-}$ with $Fe(CO)_5$. Cyclic voltammetry with $Fe(CO)_5$ at fast potential scan rates is thus a convenient method for the in situ generation of the $Fe(CO)_4^{2-}$ anion. The kinetics of any reaction of $Fe(CO)_4^{2-}$ that can compete with eq 4 can thus be studied electrochemically provided there is no fast reaction between $Fe(CO)_5$ and the reactant before commencing cyclic voltammetry. We are exploring the scope of such kinetic studies, and we are applying the same methodology to group VI carbonyls (Cr, Mo, and W).

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(21) Cf. Andrieux, C. P.; Nadjo, L.; Savéant, J. M. *J. Electroanal. Chem.* **1970**, *26*, 147.

(22) Note the two vertical scales in Figure 2. Ferrocene was not used as a reference for a one-electron wave but only as an internal standard to which the height of the $Fe(CO)_5$ wave was normalized. In the 1e limit, the system is essentially equivalent to a simple EC system for which it can be shown that $i^{p}_{Fe(CO)_5}/i^{p}_{Cp_2Fe} = 1.11$, assuming equal diffusion coefficients for $Fe(CO)_5$ and Cp_2Fe and a pure diffusion wave for the latter.[23a,b] In the 2e limit, the bimolecular reaction of eq 4 is suppressed because of the short time scale, and the system is then a classical ECE system (eq 1–3) for which, with the same assumptions, $i^{p}_{Fe(CO)_5}/i^{p}_{Cp_2Fe} = 2.22$.[23b]

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Book Reviews

Comprehensive Carbanion Chemistry. Part C. Ground and Excited State Reactivity. E. Buncel and T. Durst, Editors. Elsevier, Amsterdam. 1987. x + 372 pages. Dfl. 250.00.

The generic term, "carbanions", applies not only to negatively charged organic species but even more widely to polar organometallic compounds. Both Grignard reagents and organolithium compounds, for example, have a large degree of ion pair character. As implied by the title, the emphasis of most of the book is on the carbanion moiety rather than on the metal.

Grovenstein's chapter on the "Structures of Organodialkalimetal Compounds ("Dianions")" is the significant exception. In the gas phase, polyanions are unstable toward electron loss. The situation is quite different in solution, where interactions with the alkali-metal counterions predominate. The structures of such ion aggregates are quite different from their covalent counterparts. Representative examples taken from the X-ray crystallographic and from the theoretical literature are interpreted. The ability of calculations to predict structures which were later confirmed experimentally emphasizes the ever increasing importance of theory as an adjunct to the experimental tools available to the organometallic chemist.

Indeed, the longest chapter (by Nobes, Poppinger, Li, and Radom) deals with the "Molecular Orbital Theory of Carbanions". The subtitle of the book is somewhat misleading, as this chapter also is concerned with structure rather than with "reactivity". Surprisingly, calculations on carbanions have "come of age" only recently. As isolated entities, most carbanions have quite low electron affinities. Many simple species, such as the ethyl, isopropyl, and *tert*-butyl anions, cannot exist in the gas phase, as electron loss would occur spontaneously. This means that the standard "black box" theoretical treatments which work well for neutral and positively charged species often give poor results for anions. While theoreticians have known for a long time how to overcome this problem (by including diffuse functions which allow the electron density to extend far from the nucleus), appropriate basis sets for all the first- and second-row atom-based anions were not introduced until 1981. Since then, calculations on carbanions have become routine, as Radom's authoritative review documents. This chapter, written from a chemist's rather than from a theoretician's view point, is highly recommended to the general reader.

The redox reactions of carbanion species, e.g. as observed in solution by cyclic voltammetry, have a longer history but also a rapidly increasing current literature. Marye Anne Fox's "Electrochemistry of Carbanions" provides an overview, not only of the methodology and the electrochemical characterization of carbanions but also of the many types reactions which can be carried out. Tolbert's chapter "The Photochemistry of Resonance-Stabilized Anions" also is in keeping with the general theme of the volume. The examples chosen for discussion are relatively simple and are illustrative rather than comprehensive (natural product syntheses are not covered). Another short chapter, by H. F. Koch on the "Reactions of Hydrogen-Bonded Carbanion Intermediates", is more limited in scope than the title implies. The mechanistic evidence dealing with selected reactions, principally involving proton transfers and isotope effects, is described. The role of the metal is not developed.

This is less the case in the "Fluoro-carbanions" chapter by a leading investigator in this area, R. D. Chambers, and his colleague, M. R. Bryce. The peculiarities of polyfluoroorganic molecules have intrigued many chemists. The presence of carbanions or carbanion–alkali-metal ion pairs in the such molecules results in unusual chemistry. The highly electronegative fluorines stabilize carbanions inductively and even more effectively by negative hyperconjugation. This "loosening" of C–F bonds leads not only to elimination but also to rearrangements, both of the halogens and of the carbon skeletons.

Although aimed at the physical organic chemists, this volume will be a useful reference for the polar organometallic specialist. The topics in this relatively small book are not treated exhaustively but are written by recognized researchers who inform the general reader well. Although "reactivity" is hardly addressed at all, this volume is a good addition to a high quality and useful series.

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