Halide-Induced Disproportionation of $Fe_3(CO)_{12}$ To Form the Radical Anion $[Fe_3(CO)_{11}]^{\bullet-}$ and Its Characterization by Single-Crystal X-ray Diffraction

Fabio Ragaini,† David L. Ramage, Jeong-Sup Song, and
Gregory L. Geoffroy*

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

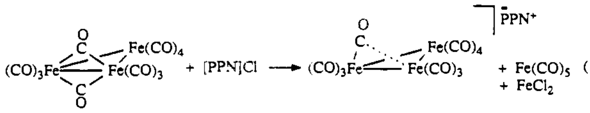
Arnold L. Rheingold

Department of Chemistry
University of Delaware
Newark, Delaware 19716

Received August 16, 1993

Numerous studies in recent years have demonstrated the importance of free-radical processes in organometallic chemistry, including a number of catalytic reactions known or proposed to involve radical intermediates.[1] However, few of these intermediates have been definitely characterized, and because of their elusive nature it has seldom proven possible to conduct detailed investigations of their chemical behavior. One of the radical anions that has been invoked in a number of reactions is $[Fe_3(CO)_{11}]^{\bullet-}$. This cluster radical anion has been observed during the reaction of $Fe_3(CO)_{12}$ with nitro- and nitrosoparaffins, under conditions similar to those used for $Fe_3(CO)_{12}$-catalyzed carbonylation of these reagents.[2] The anion $[Fe_3(CO)_{11}]^{\bullet-}$ has also been invoked as a key intermediate in the electron-transfer-catalyzed substitution reactions of $Fe_3(CO)_{12}$.[3,4] This anion has been claimed to form in a number of ways, including reduction of $Fe(CO)_5$ and $Fe_3(CO)_{12}$,[5,6] oxidation of the anion $[Fe_3(CO)_{11}]^{2-}$,[5] electron transfer between $Fe_3(CO)_{12}$ and $[Fe_3(CO)_{11}]^{2-}$,[7] disproportionation of $Fe_3(CO)_{12}$ induced by strong bases and basic solvents such as DMF,[8-10] and ^{60}Co radiolysis of $Fe_3(CO)_{12}$ and $[HFe_3(CO)_{11}]^-$.[5c,11] Although the $[Fe_3(CO)_{11}]^{\bullet-}$ anion appears to have been isolated on two occasions,[7] it has only been characterized by its EPR data,[5] and even that has been disputed.[6] We report herein the facile formation of this radical anion via the halide-induced disproportionation of $Fe_3(CO)_{12}$, its isolation as $[PPN]^+$ $\{[PPN]^+ = [(Ph_3P)_2N]^+\}$ and $[Ph_4P]^+$ salts, and its definitive characterization by X-ray diffraction studies of those salts. The isolation and characterization of $[Fe_3(CO)_{11}]^{\bullet-}$ should now make possible detailed explorations of the mechanistic and reaction chemistry of this important species.

Although the reactions of halides with $Ru_3(CO)_{12}$ are now well understood,[12,13] the corresponding reactivity of $Fe_3(CO)_{12}$ with halides has not been well developed.[14] We have found that $[Ph_4P]Cl$ and the $[PPN]^+$ salts of Cl^-, Br^-, I^-, and NCO^- react with $Fe_3(CO)_{12}$ to induce a disproportionation reaction to form the radical anion $[Fe_3(CO)_{11}]^{\bullet-}$, $Fe(CO)_5$, and FeX_n salts as principal products, *e.g.*, eq 1. Trace amounts of other anionic clusters have also been observed, among which the most abundant was $[PPN]_2[Fe_4(CO)_{13}]$.[15] These disproportionation reactions occur in thoroughly dried THF, CH_2Cl_2, and Et_2O solvents, with the latter found to be best for isolation of the product, since all other byproducts are insoluble in this solvent except for $Fe(CO)_5$, which is easily removed by evaporation. In a typical experiment, *methanol-free*[16] $Fe_3(CO)_{12}$ (200 mg, 0.40 mmol) and [PPN]Cl (230 mg, 0.40 mmol) were placed in a 50-mL Schlenk flask under N_2, and Et_2O (20 mL) was added. The solution was stirred until the IR spectrum showed complete disappearance of the 2049-cm^{-1} absorption of $Fe_3(CO)_{12}$ (~1.5 h). The solution was then filtered through a pad of Celite and evaporated under vacuum to yield $[PPN][Fe_3(CO)_{11}]$ as a purple solid (200 mg, 50% yield). The $Fe(CO)_5$, which formed in ~20% yield, was identified by its characteristic IR spectrum $\{\nu_{CO}$ (Et_2O) = 2020 (s), 2000 (vs) $cm^{-1}\}$. The residue from the reaction of $Fe_3(CO)_{12}$ with [PPN]NCO, after extraction with THF, was shown to contain the $[PPN]^+$ salt of the known[17] anion $[Fe(NCO)_4]^-$ by comparison of its IR spectra (Nujol mull, ν_{NCO} = 2189 cm^{-1}; $MeNO_2$, ν_{NCO} = 2195 cm^{-1}) to those reported[17] and by the presence of a molecular ion for the anion at M^- = 224 in its negative ionization FAB mass spectrum. The identification of $FeCl_2$ in the residue from the reaction of $Fe_3(CO)_{12}$ with [PPN]Cl was less certain, but the presence of a shoulder at 494 cm^{-1} on the 499-cm^{-1} $[PPN]^+$ peak in the KBr IR spectrum of the tan residue compares to the 493.2-cm^{-1} band reported for $FeCl_2$.[18] This shoulder is not observed in the KBr IR spectrum of pure [PPN]Cl.



(1)

The $[PPN]^+$ and $[PPh_4]^+$ salts of radical anion $[Fe_3(CO)_{11}]^{\bullet-}$ are stable in the crystalline state under N_2 for several days, but

---

* Author to whom correspondence should be addressed.

† On leave from Dipartimento di Chimica Inorganica, Metallorganica e Analitica, Milano, Italy.

(1) (a) Chanon, M.; Julliard, M.; Poite, J. C., Eds. *Paramagnetic Organometallic Species in Activation/Selectivity, Catalysis*, Nato ASI Series C257; Kluwer Academic Publishers: Dordrecht, 1989. (b) Trogler, W. C., Ed. *Organometallic Radical Processes*, Journal of Organometallic Chemistry Library 22; Elsevier: Amsterdam, 1990. (c) Chanon, M. *Acc. Chem. Res.* **1987**, *20*, 214–221. (d) Julliard, M.; Chanon, M. *Chem. Rev.* **1983**, *83*, 425–506.

(2) Belousov, Yu. A.; Kolosova, T. A. *Polyhedron* **1987**, *6*, 1959–1970.

(3) Bruce, M. I.; Hambley, T. W.; Nicholson, B. K. *J. Chem. Soc., Dalton Trans.* **1983**, 2385–2390.

(4) Luo, F.; Yang, S.; Li, C.; Duan, J.; Cheng, C. *J. Chem. Soc., Dalton Trans.* **1991**, 2435–2439.

(5) (a) Krusic, P. *Int. Conf. EPR Spectrosc.* **1978**. (b) Krusic, P. J.; San Filippo, J., Jr.; Hutchinson, B.; Hance, R. L.; Daniels, L. M. *J. Am. Chem. Soc.* **1981**, *103*, 2129–2131. (c) Morton, J. R.; Preston, K. F.; Charland, J.-P.; Krusic, P. J. *J. Mol. Struct.* **1990**, *223*, 115–122.

(6) Dawson, P. A.; Peake, B. M.; Robinson, B. H.; Simpson, J. *Inorg. Chem.* **1980**, *19*, 465–472.

(7) (a) Chini, P. *J. Organomet. Chem.* **1980**, *200*, 37–61. (b) Furuya, F. R.; Gladfelter, W. L. *J. Chem. Soc., Chem. Commun.* **1986**, 129–130.

(8) Babain, V. N.; Belousov, Yu. A.; Gumenyuk, V. V.; Salimov, R. M.; Materikova, R. B.; Kochetkova, N. S. *J. Organomet. Chem.* **1983**, *241*, C41–C44.

(9) Yang, S. L.; Li, C. S.; Cheng, C. H. *J. Chem. Soc., Chem. Commun.* **1987**, 1872–1874.

(10) Other studies in these laboratories have shown that phosphinimines, $R_3P{=}NR'$, efficiently induce disproportionation of $Fe_3(CO)_{12}$ to form $[Fe_3(CO)_{11}]^{\bullet-}$ as the $[R_3P{-}NHR']^+$ salt: Nguyen, S. T.; Mirkin, C. A.; Ragaini, F.; Geoffroy, G. L., unpublished results.

(11) Peake, B. M.; Symons, M. C. R.; Wyatt, J. L. *J. Chem. Soc., Dalton Trans.* **1983**, 1171–1174.

(12) (a) Han, S. H.; Geoffroy, G. L.; Dombeck, B. D.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 4355–4361. (b) Lavigne, G.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 4647–4648. (c) Lavigne, G.; Lugan, N.; Bonnet, J.-J. *Inorg. Chem.* **1987**, *26*, 2345–2347. (d) Rivomanana, S.; Lavigne, G.; Lugan, N.; Bonnet, J.-J. *Organometallics* **1991**, *10*, 2285–2297. (e) Lavigne, G.; Lugan, N.; Kalck, P.; Soulié, J. M.; Lerouge, O.; Saillard, J. Y.; Halet, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 10669–10670. (f) Cenini, S.; Pizzotti, M.; Crotti, C.; Ragaini, F.; Porta, F. *J. Mol. Catal.* **1988**, *49*, 59–69. (g) Chin-Choy, T.; Harrison, W. T. A.; Stucky, G. D.; Keder, N.; Ford, P. C. *Inorg. Chem.* **1989**, *28*, 2028–2029.

(13) For recent reviews, see: (a) Ford, P. C.; Rokicki, A. *Adv. Organomet. Chem.* **1988**, *28*, 139–209. (b) Lavigne, G.; Kaesz, H. D. In *Metal Clusters in Catalysis*; Gates, B., Guczi, L., Knözinger, H., Eds.; Elsevier: Amsterdam, 1986; Chapter 4, pp 43–88. (c) Lavigne, G. In *The Chemistry of Metal Cluster Complexes*; Shriver, D., Adams, R. D., Kaesz, H. D., Eds.; VCH: New York, 1990; Chapter 5, pp 201–303.

(14) (a) In ref 12a, it was noted that $Fe_3(CO)_{12}$ reacted with [PPN]I in refluxing THF to form $[PPN][HFe_3(CO)_{11}]$ and $[PPN][Fe(CO)_4I]$, but the presence of 5–10% MeOH in commercial $Fe_3(CO)_{12}$ is likely responsible for those results, which differ from those reported herein.

(15) Whitmire, K.; Ross, J.; Cooper, C. B., III; Schriver, D. F. *Inorg. Synth.* **1982**, *21*, 66–69.

(16) McFarlane, W.; Wilkinson, G. *Inorg. Synth.* **1965**, *8*, 181–183.

(17) Forster, D.; Goodgame, D. M. L. *J. Chem. Soc.* **1965**, 262–267.

(18) Jacox, M. E.; Milligan, D. E. *J. Chem. Phys.* **1969**, *51*, 4143–4155.

0002-7863/93/1515-12183$04.00/0

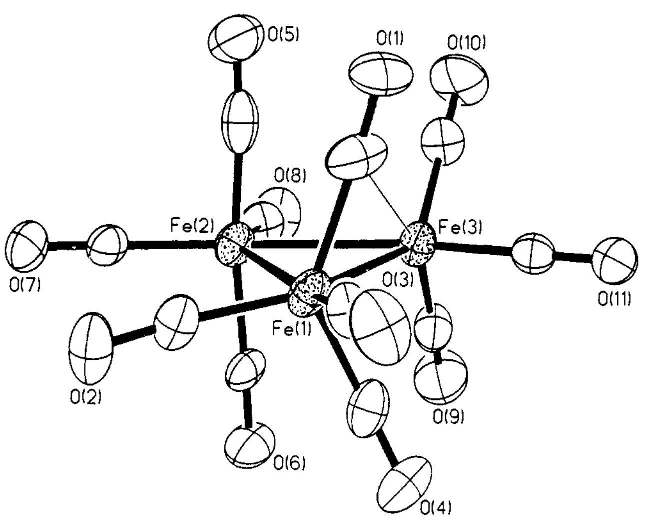


Figure 1. ORTEP drawing of $[Ph_4P][Fe_3(CO)_{11}]$ with thermal ellipsoids drawn at the 35% probability level. Important bond distances (Å) and angles (deg): Fe(1)–Fe(3), 2.503(2); Fe(1)–Fe(2), 2.685(2); Fe(2)–Fe(3), 2.630(2); Fe(1)–C(1), 1.885(12); Fe(3)–C(1), 2.488(11); Fe(1)–C(1)–O(1), 168.1(10); Fe(3)–Fe(1)–C(1), 67.4(4).

THF solutions decompose over the course of 1–2 days to yield $[PPN][HFe_3(CO)_{11}]$,[19] $Fe(CO)_5$, and $[PPN]_2[Fe_4(CO)_{13}]$.[15,20] The anion $[HFe_3(CO)_{11}]^-$ likely forms via hydrogen atom abstraction from THF, a conclusion supported by the observation that its formation was completely suppressed when $[Fe_3(CO)_{11}]^{\bullet -}$ was allowed to decompose in benzene solution, whereas the two other products still formed. Addition of CO (1 atm) to solutions of $[Fe_3(CO)_{11}]^{\bullet -}$ induced its immediate disproportionation to form mainly $Fe(CO)_5$ and $[Fe_3(CO)_{11}]^{2-}$.[21] The same two products were also obtained when $Fe_3(CO)_{12}$ was allowed to react with halides under a CO atmosphere, although the intermediate formation of $[Fe_3(CO)_{11}]^{\bullet -}$ was not directly observed in this latter reaction. The disappearance of $Fe_3(CO)_{12}$ was ~3 times faster when the halide reactions were performed under a CO atmosphere. This rate acceleration suggests an autocatalytic reaction in which the initially formed radical anion $[Fe_3(CO)_{11}]^{\bullet -}$ reacts with CO to yield radical species of lower nuclearity which readily transfer an electron to $Fe_3(CO)_{12}$, regenerating $[Fe_3(CO)_{11}]^{\bullet -}$.[22]

The EPR signal obtained for $[PPN][Fe_3(CO)_{11}]$ {g(THF, −78 °C) = 2.0489] compares well with data previously reported in the literature for the radical anion $[Fe_3(CO)_{11}]^{\bullet -}$.[5] In the IR, the compound shows only terminal carbonyl bands [ν_{CO} (THF) = 2057 (vw), 2017 (w), 1984 (vs), 1966 (ms), 1933 (mw), 1922 (w, sh) cm^{-1}], and the spectrum is identical to the spectra produced upon reacting together equimolar amounts of $[PPN]_2[Fe_3(CO)_{11}]$ and $Fe_3(CO)_{12}$ and upon oxidation of $[Fe_3(CO)_{11}]^{2-}$, routes which have been used previously to prepare $[Fe_3(CO)_{11}]^{\bullet -}$.[5,7] The absence of an IR band in the region characteristic of bridging COs is in accord with the solid-state structure which shows 10 terminal carbonyls and a weakly semibridging CO (see Figure 1).

Despite the high reactivity of $[Fe_3(CO)_{11}]^{\bullet -}$, X-ray quality crystals of its $[PPN]^+$ and $[PPh_4]^+$ salts were obtained by slow diffusion of pentane into −70 °C Et_2O solutions of the salts. Both salts were characterized by X-ray diffraction studies, although the $[PPN]^+$ salt was disordered and produced a lower quality structure (see supplementary material). An ORTEP drawing of the $[Fe_3(CO)_{11}]^{\bullet -}$ anion in the $[Ph_4P]^+$ salt is shown in Figure 1.[23] Unlike the related Fe_3 carbonyl clusters $Fe_3(CO)_{12}$,[24] $[Fe_3(CO)_{11}]^{2-}$,[21] and $[HFe_3(CO)_{11}]^-$,[19] which display 2-fold symmetry and have bridging COs, $[Fe_3(CO)_{11}]^{\bullet -}$ is without symmetry and possesses only a very weakly semibridging CO. The semibridged Fe(1)–Fe(3) bond distance of 2.503(2) Å is significantly shorter than the Fe(1)–Fe(2) and Fe(2)–Fe(3) distances, which are more typical of Fe–Fe single-bond values.[24] The CO groups at Fe(2) are arranged in the expected axial (5, 6) and equatorial (7, 8) arrangement. However, the presence of the unsymmetrical bridge has caused the tilting of CO(1) away from an axial position toward Fe(3), while the nearly equatorial plane for CO(2) and CO(3) is twisted so as to bring CO(1) closer and CO(4) further from Fe(3). The geometry of Fe(3) is roughly trigonal bipyramidal.

Overall, the determined structure is in remarkable agreement with that proposed on the basis of a single-crystal EPR study of $[PPN][Fe_3(CO)_{11}]$ doped into crystals of $[PPN][HFe_3(CO)_{11}]$,[5c] which, along with EPR studies of ^{57}Fe-enriched $[Fe_3(CO)_{11}]^{\bullet -}$, led to the conclusion that the unpaired electron was localized on a single iron atom.[5] The crystallographic results presented herein combined with these EPR data[5] indicate that the electron is likely delocalized on the unique trigonal-bipyramidal-coordinated $Fe(CO)_3$ center {Fe(3) in Figure 1}.

The radical anion $[Fe_3(CO)_{11}]^{\bullet -}$ is an interesting and highly reactive compound. As noted previously, it is likely involved in the electron-transfer-catalyzed reaction of $Fe_3(CO)_{12}$ with $CNBu^t$ and PPh_3 to afford $Fe_3(CO)_{11}(CNBu^t)$ and $Fe_3(CO)_{11}(PPh_3)$,[3,4] and its presence has been observed during the reaction of various carbonyl ferrate anions with Bu^tNO and Bu^tNO_2.[2] In preliminary work in these laboratories, it has also been shown to reduce nitro- and nitrosobenzene to yield, after workup, azo- and azoxybenzene as the main organic products.[25] The latter reactions are much faster then the corresponding reactions of $Fe_3(CO)_{12}$. Further studies of this species are in progress.

Acknowledgment. We thank the U.S. Department of Energy, Office of Basic Energy Sciences, for support of this work, and F.R. acknowledges the Italian Consiglio Nazionale delle Ricerche for a fellowship which permitted his stay in Pennsylvania.

Supplementary Material Available: Lists of atomic positional parameters, bond lengths, and bond angles for $[PPh_4][Fe_3(CO)_{11}]$ and $[PPN][Fe_3(CO)_{11}]$; ORTEP drawing for $[PPN][Fe_3(CO)_{11}]$ (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(19) Dahl, L. F.; Blount, J. F. *Inorg. Chem.* **1965**, *4*, 1373–1375.

(20) Although no other product was observed by IR, some non-carbonyl compound is probably formed, since additional CO is necessary to complete the disproporationation of $[Fe_3(CO)_{11}]^{\bullet -}$ into $Fe(CO)_5$ and $[Fe_4(CO)_{13}]^{2-}$.

(21) Lo, F. Y.; Longoni, G.; Chini, P.; Lower, L. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1980**, *102*, 7691–7701.

(22) (a) For related reactions, see refs 3, 4, and 9. In ref 9, reaction of $Fe_3(CO)_{12}$ with CO to yield $Fe(CO)_5$ was reported to be catalyzed by an electron-transfer path and $[Fe_3(CO)_{11}]^{\bullet -}$ was detected by EPR, along with $[Fe_3(CO)_{12}]^{\bullet -}$ and $[Fe_2(CO)_8]^{\bullet -}$. (b) $[Fe_3(CO)_{11}]^{\bullet -}$ can be produced upon reduction of $Fe_3(CO)_{12}$ *in the absence of CO* since under these conditions insufficient CO is released in the transformation of $[Fe_3(CO)_{12}]^{\bullet -}$ into $[Fe_3(CO)_{11}]^{\bullet -}$ to induce further fragmentation of the latter species.

(23) Crystal data: $[PPh_4][Fe_3(CO)_{11}]$, $C_{35}H_{20}Fe_3O_{11}P$, monoclinic, $P2_1/n$, $a = 11.313(2)$, $b = 12.966(3)$, and $c = 23.682(5)$ Å, $\beta = 91.380(9)°$, $V = 3472.8(9)$ Å^3, $Z = 4$, $T = 213$ K. Of 8537 data collected (Siemens P4, $2\theta_{max} = 55°$, Mo Kα), 7974 were independent and 3410 were observed at $5\sigma F_o$. At convergence, with all non-hydrogen atoms idealized and the phenyl rings constrained to rigid, planar hexagons, $R(F) = 6.73\%$ and $R(wF) = 8.05\%$. In the structure of the $[PPN]^+$ salt, the anion is structurally identical to that found for the $[PPh_4]^+$ salt, but the iron triangle shows a minor contribution of a "Star-of-David" disorder: monoclinic, $I2/a$, $a = 17.868(4)$, $b = 14.066(3)$, and $c = 36.610(7)$ Å, $\beta = 93.82(3)°$, $Z = 8$, $R(F) = 10.33\%$.

(24) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4155–4159.

(25) (a) Song, J. S. Ph.D. Thesis, The Pennsylvania State University, 1990. (b) Ramage, D. L.; Ph.D. Thesis, The Pennsylvania State University, 1992.