IV, L-L = Ph₂PCH₂CH₂PPh₂

Detailed electrochemical and structural studies are underway on these systems together with an investigation of the ligand constraints leading to semibridging carbonyl coordination, but the feasibility of controlled sequential coordination of a polydentate ligand has been demonstrated. Obviously, these observations are relevant to the in situ production of labile species with catalytic potential.

Registry No. I, 87828-96-4; II, 87828-97-5; III, 87828-98-6; IV, 87828-99-7; (CF₃)₂C₂O₂(CO)₆, 37685-63-5; PhCCO₃(CO)₉, 13682-03-6; Co, 7440-48-4.

Supplementary Material Available: Tables of crystal data (Table S1), positional and thermal parameters for non-hydrogen atoms (Table S2), positional and thermal parameters of calculated hydrogen atoms (Table S3), bond lengths and angles (Table S4), and observed and calculated structure factors (Table S5) (16 pages). Ordering information is given on any current masthead page.

(23) IV undergoes an electrochemically irreversible two-electron reduction at -0.71 V vs. Ag/Ag Cl.

Oxidative-Addition Processes in the Reactions of (OC)₄Fe⁻ with XCY₃ Molecules

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Summary: The major or exclusive product channel in the gas-phase reactions of (OC)₄Fe⁻ with ICF₃, BrCF₃, BrCCl₃, and CCl₄ was halogen atom transfer, but minor amounts of product ions of oxidative addition with loss of one and two CO ligands were observed with the first two neutrals. Rate constants were determined, and mechanisms are discussed.

Although the preparation and reactions of (OC)₄Fe²⁻ (Collman's reagent) are well documented,¹ the chemistry of the oxidized species (OC)₄Fe⁻ has remained a mystery since, in the condensed phase, this 17-electron anion radical has only been observed in a matrix.² However, various transition-metal carbonyl anion radicals ((OC)_{x-1}M⁻) are available in the gas phase by dissociative electron attach-

(1) Collman, J. P. *Acc. Chem. Res.* 1975, 8, 342-347.

(2) Burdett, J. K. *J. Chem. Soc., Chem. Commun.* 1973, 763-764. Breeze, P. A.; Burdett, J. K.; Turner, J. J. *Inorg. Chem.* 1981, 20, 3369-3378 and references therein.

Table I. Summary of Kinetic and Product Studies of the Reactions of (OC)₄Fe⁻ with Halogenated Methanes

rxn	ion + neutral reactant (Y ₃ CX)	products [assumed neutral]	fractn of product ion signal	k _{total} ^a , cm ³ molecule ⁻¹ s ⁻¹	D ⁰ (Y ₃ C-X), ^b kcal/mol	EA(Y ₃ CX), ^c kcal/mol
1	(OC) ₄ Fe ⁻ + CH ₃ I →	no reaction		≤ 10 ⁻¹³	56.1	5 ± 2
2a	(OC) ₄ Fe ⁻ + ICF ₃ →	(OC) ₄ FeI ⁻ [+ ·CF ₃]	0.88	4.6 × 10 ⁻¹⁰	53.6	36 ± 5
2b	(OC) ₄ Fe ⁻ + ICF ₃ →	(OC) ₃ Fe(I)CF ₃ ⁻ [+ CO] + (OC) ₂ Fe(I)CF ₃ ⁻ [+ 2CO] ^d	0.12			
3a	(OC) ₄ Fe ⁻ + BrCF ₃ →	(OC) ₄ FeBr ⁻ [+ ·CF ₃]	0.73	1.7 × 10 ⁻¹²	69.2	21 ± 5
3b	(OC) ₄ Fe ⁻ + BrCF ₃ →	(OC) ₃ Fe(Br)CF ₃ ⁻ [+ CO] + (OC) ₂ Fe(Br)CF ₃ ⁻ [+ 2CO] ^d	0.27			
4	(OC) ₄ Fe ⁻ + ClCF ₃ →	no reaction		≤ 10 ⁻¹³	85.5	
5	(OC) ₄ Fe ⁻ + CCl ₄ →	(OC) ₄ FeCl ⁻ [+ ·CCl ₃]	1.00	7.7 × 10 ⁻¹²	72.9	
6	(OC) ₄ Fe ⁻ + BrCCl ₃ →	(OC) ₄ FeBr ⁻ [+ ·CCl ₃]	1.00	2.3 × 10 ⁻¹⁰	54.7	

^a k_{total}'s are estimated to be accurate to ±30%. ^b Reference 7. ^c Janousek, B. K.; Brauman, J. I. In "Gas Phase Ion Chemistry", Bowers, M. T., Ed.; Academic Press: New York 1979; Vol. 2, Chapter 10. ^d The structure assignment for the anion radical is discussed in the text.

ment (DEA) with $M(\text{CO})_x$ including $(\text{OC})_4\text{Fe}^-$.³ We have used this method to produce $(\text{OC})_4\text{Fe}^-$, and we wish to report data that bear on the mechanism of oxidative addition reactions between $(\text{OC})_4\text{Fe}^-$ and XCY_3 molecules ($\text{X} = \text{I}, \text{Br}, \text{Cl}; \text{Y} = \text{F}, \text{Cl}$) involving one- (halogen atom transfer) and two-electron changes at Fe.

Our gas-phase studies are carried out in a previously described flowing afterglow apparatus using a fast flow of helium ($P_{\text{He}} = 0.5$ torr, $\bar{v} = 80$ m s⁻¹, 298 K) as the buffer gas.^{4a,b} $(\text{OC})_4\text{Fe}^-$ was generated from $\text{Fe}(\text{CO})_5$ by DEA in the upstream end of the flow tube.^{4c} The neutral halogenated methanes were added to the flow via a gas inlet located 35 cm downstream of the ion generation region, and the ion-molecule reaction occurred in the final 65 cm of the flow tube. The flow is maintained by a fast pumping system and is sampled into a compartment containing a quadrupole mass spectrometer that monitors the ion composition of the flow as a function of added reactant. Bimolecular rate constants of the ion-molecule reactions are determined under pseudo-first-order conditions with the neutral reactant in large excess.

No reaction was observed between $(\text{OC})_4\text{Fe}^-$ and CH_3I (Table I). However, a fast reaction occurred between $(\text{OC})_4\text{Fe}^-$ and ICF_3 giving mainly $(\text{OC})_4\text{FeI}^-$ (m/z 295)⁵ with minor formation of the ions m/z 308 and 336; all three ions are primary product ions. The two minor product ions contain the reactant ICF_3 based on isotope peak ratios with the adduct having lost two and one CO ligands, respectively. The reaction of $(\text{OC})_4\text{Fe}^-$ with BrCF_3 (reaction 3, Table I) occurred by the same processes observed for the reaction with ICF_3 , but the rate constant was 270 times slower. No reaction was observed between $(\text{OC})_4\text{Fe}^-$ and ClCF_3 , but $(\text{OC})_4\text{FeCl}^-$ and $(\text{OC})_4\text{FeBr}^-$ were the exclusive products from the reactions of $(\text{OC})_4\text{Fe}^-$ with CCl_4 and BrCCl_3 , respectively (reactions 5 and 6, Table I).

The structures of the major product anions from the halogen atom transfer in the above reactions are assumed to be the 18-electron species $(\text{OC})_4\text{FeX}^-$ by analogy with the observed $(\text{OC})_5\text{MoX}^-$ anions produced in the electrochemical reduction of $\text{Mo}(\text{CO})_6$ in the presence of RX^6 and the formation of stable salts of $(\text{OC})_4\text{Fe}^-$ with C_{3v} symmetry.⁵ The small difference in $D^0(\text{H}_3\text{C}-\text{I})$ and $D^0(\text{F}_3\text{C}-\text{I})^7$ (reactions 1 and 2, Table I) cannot account for the large kinetic effect ($k_2/k_1 \geq 4600$) in these two reactions. We suggest that this kinetic effect is the result of a contribution of electron transfer in the reaction of $(\text{OC})_4\text{Fe}^-$ with ICF_3 .⁸

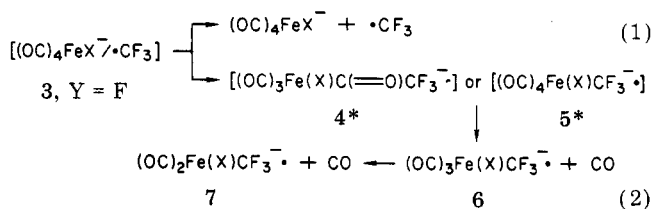
Formation of the minor product anion radicals m/z 308 and 336 and m/z 260 and 288 from the reactions of $(\text{OC})_4\text{Fe}^-$ with ICF_3 and BrCF_3 , respectively, is intriguing since they incorporate the CF_3 group and appear to be the products of oxidative addition with a two-electron change^{9a} and loss of $n\text{CO}$ ligands ($n = 1, 2$). Their structures can reasonably be $(\text{OC})_{x-1}\text{Fe}(\text{X})(\text{C}=\text{O})\text{CF}_3^-$ (1) or $(\text{OC})_x\text{Fe}(\text{X})(\text{CF}_3)^-$ (2). We note that (a) the relative amounts of

these product channels in the two reactions are similar while their total rate constants are very different and (b) the reactions of $(\text{OC})_4\text{Fe}^-$ with CCl_4 and BrCCl_3 fail to yield such products.

In the gas phase, the halogen atom transfer step would produce a loose complex $[(\text{OC})_4\text{FeX}^-/\cdot\text{CY}_3]$ (3, $\text{Y} = \text{F}, \text{Cl}$) involving attractive ion dipole and ion-induced dipole forces which can then separate giving the observed major ion product $(\text{OC})_4\text{FeX}^-$ and the radical $\cdot\text{CY}_3$. Once separated, the ion and neutral radical will not find a partner to reform complex 3 during the experiment. Thus, formation of these minor product anion radicals must proceed from complex 3 or a previously formed species, either another collision complex or a bound anion radical. That the relative amounts of these minor products are similar in reactions 2 and 3 independent of the total rate constant strongly suggests that these products result from a species formed after the halogen atom transfer step, that is, from complex 3.

The more exothermic halogen atom transfers involving the same halogen atom occurred with the larger rate constants (compare reactions 3 and 6 and reactions 4 and 5, Table I). This is expected for the radical displacement (abstraction) mechanism. One possible pathway to produce the minor oxidative-addition products 1 or 2 could involve decarbonylation of $(\text{OC})_4\text{FeX}^-$ in 3 to give $(\text{OC})_3\text{FeX}^-$. This coordinatively unsaturated anion might then combine with the neutral radical $\cdot\text{CY}_3$ present in the complex $[(\text{OC})_3\text{FeX}^-/\cdot\text{CY}_3]$ to yield $(\text{OC})_3\text{Fe}(\text{X})\text{CY}_3^-$, a portion of which fragments ($-\text{CO}$) giving $(\text{OC})_2\text{Fe}(\text{X})\text{CY}_3^-$. However, this pathway must be most favorable in the more exothermic Br atom transfer in reaction 6 than in reaction 3 and lead to observation of $(\text{OC})_x\text{Fe}(\text{Br})\text{CCl}_3^-$ ($x = 1, 2$) or $(\text{OC})_3\text{FeBr}^-$. That these product ions were not observed in reaction 6 rules out this predissociation pathway as the source of the minor anion radical products in reactions 2 and 3.

Irrespective of whether 1 or 2 represent the structures of these minor radical products, we account for their formation by a mechanism involving addition of $\text{F}_3\text{C}\cdot$ to a CO ligand or Fe of $(\text{OC})_4\text{FeX}^-$ in complex 3 yielding the vibrationally excited Fe acylate 4* or the six-coordinate species 5*,¹⁰ respectively, which is competitive with separation of 3 into the anion and radical fragments (eq 1).



The excited intermediates 4* or 5* would be expected to fragment yielding 6 and CO, the process from 4* involving retromigratory insertion.^{9b} If formation of the Fe-CF₃ bond was sufficiently exothermic, fragmentation of a second CO ligand (6 → 7) would be competitive with collisional stabilization of 6. Cl₃C-C bond energies are considerably smaller (~11 kcal mol⁻¹) than F₃C-C bond energies. A similar difference in bond energies probably exists in Cl₃C-Fe and F₃C-Fe bonds which would account for the absence of related anion radical products in the

(3) For example, see: (a) Winters, R. E.; Kiser, R. N. *J. Chem. Phys.* 1966, 44, 1964-1966. (b) Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* 1971, 93, 4924-4926. (c) *Ibid.* 1975, 97, 4808-4814.

(4) (a) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* 1983, 105, 2194-2203. (b) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *Ibid.* 1980, 102, 6491-6498. (c) Removal of all electrons and metastable He(2³S) atoms was complete within 15 cm of the electron gun since no signal for SF₆⁻ was observed when SF₆ was added at this point.

(5) Salts of $(\text{OC})_4\text{FeI}^-$ has been prepared in the condensed phase by the reaction of $\text{R}_4\text{N}^+\text{I}^-$ with $\text{Fe}(\text{CO})_5$ and assigned C_{3v} symmetry: Abel, E. W.; Butler, I. S.; Jenkin, C. R. *J. Organomet. Chem.* 1967, 8, 382-384.

(6) Pickett, S. J.; Pletcher, D. *J. Chem. Soc., Dalton Trans.* 1976, 749-752.

(7) Egger, K. W.; Cocks, A. T. *Helv. Chim. Acta* 1973, 56, 1516-1535.

(8) EA($(\text{OC})_4\text{Fe}$) = 55 ± 7 kcal mol⁻¹: Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* 1979, 101, 5569-5573.

(9) (a) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; pp 177-228. (b) *Ibid.* pp 273-274.

(10) Petz, W. *Organometallics* 1983, 2, 1044-1046 recently reported evidence for a neutral six-coordinate Fe species.

reactions of $(OC)_4Fe^-$ with CCl_4 and $BrCCl_3$ (reactions 5 and 6, Table I).

The thermochemical data available from these studies are $D^0((OC)_4Fe^-I) > 53.6 \text{ kcal mol}^{-1}$, $D^0((OC)_4Fe^-Br) > 69.2 \text{ kcal mol}^{-1}$, and $85.5 > D^0((OC)_4Fe^-Cl) > 72.9 \text{ kcal mol}^{-1}$ based on the $D^0(Y_3C-X)$ values given in ref 7, and $EA((OC)_4FeX) > 42 \pm 1.5 \text{ kcal mol}^{-1}$ ($= EA(F_3C^-)$).¹¹ Further studies with additional halogenated alkanes are expected to tighten the bracketed $D^0((OC)_4Fe^-X)$ values and, ultimately, yield $\Delta H_f^\circ((OC)_4Fe^-)$.

Acknowledgment. We gratefully acknowledge support of this research by the U.S. Army Research Office and the National Science Foundation (equipment grant) and discussions with Professors Eric Maatta, David Macomber, and Donald Setser.

(11) Bartmess, J. E.; McIver, R. T. In "Gas Phase Ion Chemistry"; Bowers M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 11.

Book Reviews

Advances in Inorganic Chemistry and Radiochemistry. Vol. 25. H. J. Emeléus and A. G. Sharpe, editors. Academic Press, New York, 1982. vii + 355 pages. \$56.00.

Volume 25 continues the high level of quality of this long-established series. There is much here for the organometallic chemist: an updating of silicon-transition-metal chemistry (133 pages) by B. J. Aylett, a 28-page review of compounds of gold in unusual oxidation states, including the very interesting gold cluster complexes, by H. Schmidbaur, and a discussion in 74 pages by G. E. Toogood and M. G. H. Wallbridge of hydride complexes of the titanium and vanadium group elements. All three are subjects that currently are receiving much attention in various laboratories throughout the world and their inclusion in this volume is timely. All three are up-to-date and well written and will make worthwhile reading for inorganic and organometallic chemists alike.

There are two other reviews in this book: one on the electronic properties of metal solutions in liquid ammonia and related solvents by P. P. Edwards and the other on metal borates by J. B. Farmer.

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Gmelin Handbook of Inorganic Chemistry. 8th Edition. Sn. Organotin Compounds. Part 10. Mono- and Diorganotin-Sulfur Compounds. Organotin-Selenium and Organotin-Tellurium Compounds. H. Schumann and I. Schumann, volume authors. H. Bitterer, volume editor. Gmelin Institut für Anorganische

Chemie der Max-Planck-Gesellschaft zur Förderung der Wissenschaften and Springer-Verlag, Berlin/Heidelberg/New York, 1983. xi + 352 pages. DM 993, \$397.20.

Certain organotin compounds that contain organosulfur substituents linked to tin by the sulfur atom are very effective stabilizers for poly(vinyl chloride). As a result, there has been much interest in and research activity devoted to organotin sulfur compounds, particularly those of type $R_2Sn(SR')_2$ and $RSn(SR')_3$. The present Gmelin volume, the second which deals with organotin sulfur compounds, covers both of these classes of compounds as well as some others: $R_2SnX(SR')$ ($X = \text{halogen}$), $RSnX(SR')_2$, and $RSnX_2(SR')$ as well as organotin-selenium and -tellurium compounds. It covers them in the usual thorough, well-nigh exhaustive Gmelin fashion, citing all original research papers, reviews, monographs, patents, theses, and conference reports that have been abstracted in "Chemical Abstracts". All available preparative, physical, spectroscopic, and reactivity data are reported here, as well as information about applications and biological activity when this has been studied. All this material is brought either in the text or by means of extensive, well-organized tables. Access to this material is provided by an empirical formula index (whose usefulness to the reader is enhanced by a listing of all the substituents on tin for a given compound) and by the detailed table of contents.

This book is a welcome addition to the Schumanns' Gmelin Handbook organotin series which now numbers 10 volumes, with more to come.

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