Reactions of complex ligands. Part 28. Nucleophilic acylation of metal carbonyls. Synthesis and structure of a tetracarbonyl(pivaloylacyl)ferrate and its reaction with electrophiles

Karl Heinz. Doetz, Ulrike. Wenicker, Gerhard. Mueller, Helmut G. Alt, and Dietmar. Seyferth

More About This Article

The permalink http://dx.doi.org/10.1021/om00143a036 provides access to:
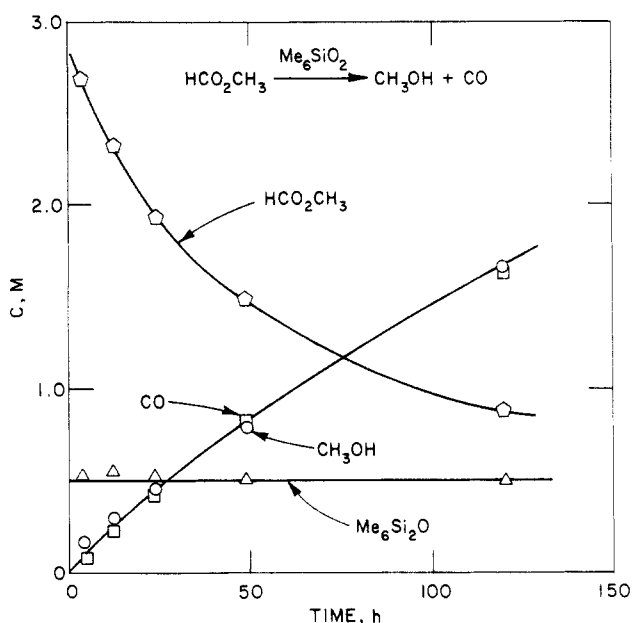
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article
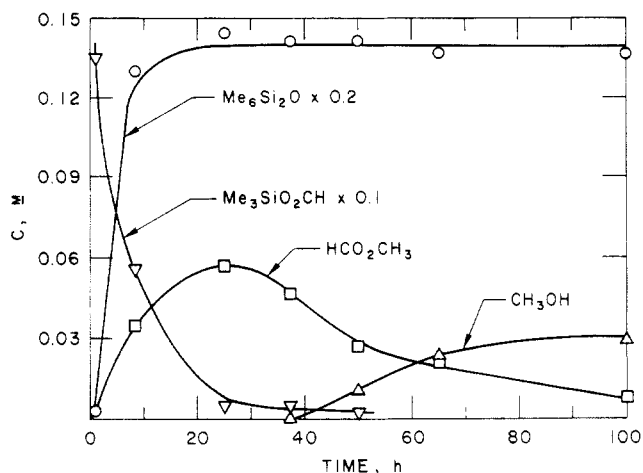
Figure 2. Time dependence of the liquid products for the disproportionation of trimethylsilyl formate at 250 °C in 1,4-dioxane.

Figure 3. Decarbonylation of methyl formate with Me_6Si_2O in dioxane at 250 °C.

isolated[13] from the thermolysis of trimethylsilyl formate-d, thereby demonstrating that the formate moiety is the source of the hydrogen in the methyl formate product. Significantly, the process described by eq 5 is experimentally reversible at 250 °C in dioxane. Thus, the same equilibrium reaction quotient is obtained in Figure 1 starting with either pure trimethylsilyl formate (pentagons) or a mixture of methyl formate and hexamethyldisiloxane (circles). Continued heating of the solution in the first row of Table I (under the gas mixture of columns 7–9) for an additional 75 h at 250 °C reveals a second slower process that results in the production of methanol, which reaches a concentration of 30 mM, at the expense of methyl formate, whose concentration declines to 8 mM as indicated in Figure 2. Indeed, it is possible to independently demonstrate that the decarbonylation of methyl formate (eq 4) under these experimental conditions (Figure 3) is slow

in comparison to the initial formate disproportionation of eq 5 (Table I). Significantly, the results in Figure 2 clearly demonstrate that methyl formate is produced prior to methanol in the homogeneous trialkylsilyl system. In contrast, previous results under heterogeneous conditions were ambiguous because they yielded mixtures consisting of methanol together with smaller quantities of methyl formate.[6]

It is hoped that further analysis of this homogeneous formate system may provide a useful comparison to the reaction chemistry of surface formate being studied on heterogeneous methanol synthesis catalysts[2] and the parallel surface formate chemistry being investigated on the heterogeneous catalyst for the oxidation of methanol to formaldehyde.[5]

Nucleophilic Acylation of Metal Carbonyls: Synthesis and Structure of a Tetracarbonyl(pivaloylacyl)ferrate and Its Reaction with Electrophiles[1]

Karl Heinz Dötz,* Ulrike Wenicker, and Gerhard Müller

Anorganisch-chemisches Institut der Technischen Universität München, D-8046 Garching, Germany

Helmut G. Alt

Laboratorium für Anorganische Chemie Universität Bayreuth D-8580 Bayreuth, Germany

Dietmar Seyferth

Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139
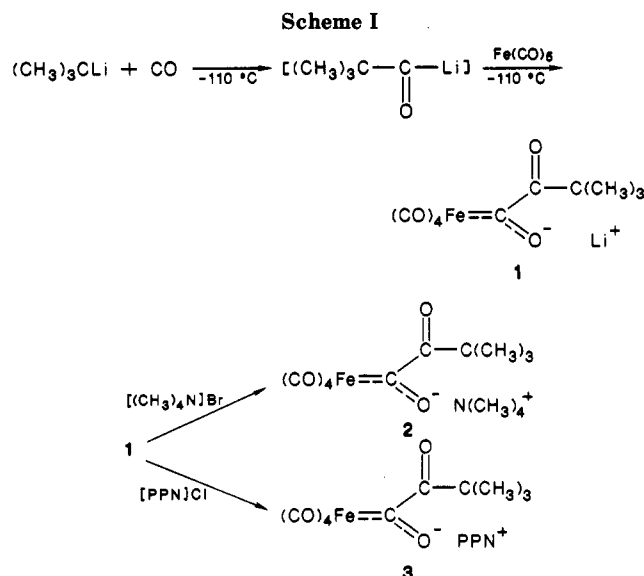
Summary: The nucleophilic acylation of pentacarbonyliron by in situ generated pivaloyllithium at low temperature affords an acylferrate complex. The structure of the $[(Ph_3P)_2N]^+$ salt is determined by X-ray analysis. The acylferrate reacts with electrophiles to give thermolabile products which are characterized as tetracarbonyl acylcarbene complexes by IR spectroscopy.

The tandem addition of a nucleophile and an electrophile across the C–O bond of metal carbonyls represents the most versatile access to transition-metal carbene complexes.[2] In general, organolithium reagents are used as

(13) Experimental details together with the ^2H and ^{13}C NMR spectrum of the isolated methyl-d_3 formate-d are given in the supplementary material. Also included are representative first-order rate plots for formate ion decay which exhibits a deuterium kinetic isotope effect of 2.0.

(1) Reactions of Complex Ligands, Part 28. For part 27, see: Dötz, K. H.; Sturm, W. *J. Organomet. Chem.*, in press.

(2) Recent review: Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, 1983.

Scheme I

$(CH_3)_3CLi + CO \xrightarrow[-110\ °C]{} [(CH_3)_3C-\overset{\displaystyle O}{\underset{\displaystyle \parallel}{C}}-Li] \xrightarrow[-110\ °C]{Fe(CO)_6}$

$(CO)_4Fe=C\begin{smallmatrix} C(CH_3)_3 \\ \\ O^- \end{smallmatrix}$ with C=O, Li$^+$

1

$1 \xrightarrow{[(CH_3)_4N]Br}$ $(CO)_4Fe=C$ ... C(CH$_3$)$_3$, O$^-$, N(CH$_3$)$_4$$^+$

2

$1 \xrightarrow{[PPN]Cl}$ $(CO)_4Fe=C$ ... C(CH$_3$)$_3$, O$^-$, PPN$^+$

3

nucleophiles. Recently, it has become apparent that acyllithium species can be generated in situ by a low-temperature carbonylation of organolithium compounds.[3] The scope of this reaction in organic synthesis has been demonstrated in the nucleophilic acylation of a series of carbonyl compounds[4-6] and heterocumulenes.[7-9] In an effort to probe the applicability of acyllithium reagents in metal carbene synthesis, we have studied the reactivity of pivaloyllithium toward pentacarbonyliron.

The addition of *tert*-butyllithium to a CO-saturated solution of Fe(CO)$_5$ at -110 °C results in the formation of the lithium acylferrate **1**.[10] The compound decomposes slowly at room temperature. Therefore, it is advantageous to store it as its tetramethylammonium salt **2** or as its iminium [bis(triphenylphosphine)nitrogen(1+)] salt **3**.[11] The addition of the pivaloyl nucleophile to a carbonyl carbon atom of pentacarbonyliron is clearly evident from the ^{13}C NMR spectrum of **2**. The resonance signal for the metal-coordinated acyl carbon atom is observed at 276.4 ppm which—in comparison with similar acylferrates containing a free anion[12,13] —exhibits a slight downfield shift

Figure 1. Molecular structure of the anion of **3** (ORTEP, thermal ellipsoids at the 35% probability level, only one alternative is shown for the disordered *tert*-butyl group). Important distances (Å) and angles (deg): Fe–C1 = 1.984 (6), Fe–C7 = 1.786 (6), Fe–C8 = 1.772 (6), Fe–C9 = 1.796 (7), Fe–C10 = 1.768 (7), C1–C2 = 1.47 (1), C2–C3 = 1.49 (1), C1–O1 = 1.255 (8), C2–O2 = 1.25 (1); Fe–C1–C2 = 122.6 (5), Fe–C1–O1 = 124.9 (6), O1–C1–C2 = 112.4 (6), C1–C2–O2 = 114.8 (7), C1–C2–C3 = 125.1 (7), O2–C2–C3 = 120.1 (7).

due to the electron-withdrawing properties of the pivaloyl group. In order to gain more insight into the bonding and the conformation of the acylmetalate, the crystal and molecular structure of **3** was established by X-ray diffraction.[14]

The molecular structure of the anion of **3** (Figure 1) shows the pivaloyl-substituted acyl ligand to be η^1-bonded to the Fe(CO)$_4$ fragment. In the resulting trigonal-bipyramidal complex, it occupies the apical position which points to poorer π-acceptor ability of the acyl ligand as compared with the CO ligands,[15] thereby rendering it somewhat carbene-like.[16,17] In accord with this description, the Fe–C1 bond length (Figure 1) is comparable to long Fe–C$_{Carbene}$ bonds in a variety of iron carbene complexes.[16] As expected, the C1–C2 bond is slightly shortened with respect to C–C single bonds. The carbonyl bond lengths C1–O1 and C2–O2 are equal and slightly longer than typical ketone carbonyl bonds. They are skewed by 101.5° about the C1–C2 axis. C1–O1 forms a torsion angle of -48.8° with the Fe–C9 bond. Both C1 and C2 have an essentially coplanar trigonal arrangement with their three bonded neighbors.

(3) Seyferth, D.; Weinstein, R. M. *J. Am. Chem. Soc.* **1982**, *104*, 5534.

(4) Seyferth, D.; Weinstein, R. M.; Wang, W.-L.; Hui, R. C. *Tetrahedron Lett.* **1983**, *24*, 4907.

(5) Seyferth, D.; Weinstein, R. M.; Wang, W.-L. *J. Org. Chem.* **1983**, *48*, 1144.

(6) Weinstein, R. M.; Wang, W.-L.; Seyferth, D. *J. Org. Chem.* **1983**, *48*, 3367.

(7) Seyferth, D.; Hui, R. C. *Tetrahedron Lett.* **1984**, *25*, 5251.

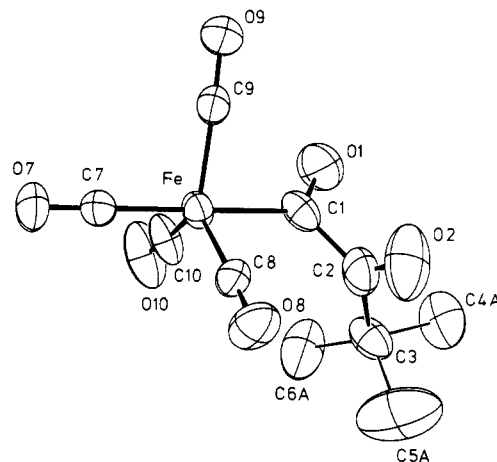(8) Seyferth, D.; Hui, R. C. *J. Org. Chem.* **1985**, *50*, 1985.

(9) Seyferth, D.; Hui, R. C. *Tetrahedron Lett.* **1984**, *25*, 2623.

(10) In a typical experiment, a solution of Fe(CO)$_5$ (3.53 g, 18 mmol) in 300 mL of THF/ether/pentane (4/4/1) is cooled to -110 °C and saturated with CO. *tert*-Butyllithium (18 mmol, dissolved in hexane) is added dropwise. After 2 h the solution is warmed slowly to -40 °C. Removal of the solvent at -40 °C yields **1** (4.73 g, 91%) as a dark brown oil. IR (ν_{CO}, CH$_2$Cl$_2$): 2025 m, 1950 s (sh), 1915 cm^{-1} vs (br).

(11) **2**: [N(CH$_3$)$_4$]Br (2.77 g, 18 mmol) dissolved in 10 mL of H$_2$O is added to a solution of **1** (4.73 g, 16.4 mmol) in 50 mL of H$_2$O. The yellow-green precipitate is recrystallized twice from CH$_2$Cl$_2$/ether to yield yellow needles (3.98 g, 62%). Anal. Calcd for C$_{14}$H$_{21}$O$_6$NFe: C, 47.34; H, 5.96; O, 27.03; N, 3.94; Fe, 15.72. Found: C, 47.07; H, 5.95; O, 27.18; N, 4.12; Fe, 16.13. IR (ν_{CO}, CH$_2$Cl$_2$): 2017 m, 1932 s (sh), 1905 cm^{-1} vs (br). IR (ν_{CO}, KBr): 1667 m, 1551 cm^{-1} m. ^{1}H NMR (CD$_3$COCD$_3$): δ 3.47 (s, 12, N(CH$_3$)$_4$), 1.21 (s, 9, C(CH$_3$)$_3$). ^{13}C NMR (CD$_2$Cl$_2$): δ 276.4 (Fe–C), 238.4 (C(O)C(CH$_3$)$_3$), 219.6 (Fe–CO); 39.9 (N(CH$_3$)$_4$), 29.3 (C(CH$_3$)$_3$, in CD$_3$COCD$_3$).

3: [PPN]Cl (2.87 g, 5 mmol) dissolved in 100 mL of acetone is added to a solution of **1** (1.44 g, 5 mmol) in 20 mL of THF. The solvent is partly removed, and ether is added in excess. Crystallization at -78 °C leads to bright yellow needles in nearly quantitative yield. IR (ν_{CO}, CH$_2$Cl$_2$): 2015 m, 1925 s (sh), 1900 cm^{-1} vs (br).

(12) Collman, J. P.; Winter, S. R. *J. Am. Chem. Soc.* **1973**, *95*, 4089.

(13) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342.

(14) Crystal structure data: C$_{46}$H$_{39}$FeNO$_6$P$_2$, M_r = 819.62, triclinic, space group P$\bar{1}$, a = 11.321 (2) Å, b = 11.890 (2) Å, c = 15.712 (3) Å, α = 95.05 (1)°, β = 83.49 (1)°, γ = 92.04 (2)°, V = 2092.5 Å^3, D_{calcd} = 1.301 g cm^{-3}, Z = 2, μ(Mo K$_\alpha$) = 4.8 cm^{-1}, $F(000)$ = 852, Syntex P2$_1$ diffractometer, Mo K$_\alpha$ radiation, λ = 0.71069 Å, graphite monochromator, T = 22 °C. 6558 independent reflections of which 4733 "observed" with I ≥ 2.0 $\sigma(I)$ (ω scan, $\Delta\omega$ = 0.9°, 0.9–29.3° min^{-1}, ((sin θ/λ)$_{max}$ = 0.572, *hkl* range +12, ±13, ±17). Lp, but no absorption correction, solution by direct methods (MULTAN 80), R = 0.063, R_w = 0.068, w = 1/σ^2 (F$_0$) for 532 refined parameters in two large blocks (SHELX-76). Thereby all non-H atoms were treated anisotropically; a rotational disorder of the *tert*-butyl groups was modeled as six half-occupancy C atoms with alternative atoms in different blocks. Phenyl H atoms were included at their calculated positions into structure factor calculation (U_{iso} = 0.08 Å^2), and those of the methyl groups were neglected. A final difference map ($\Delta\rho_{max/min}$ = +0.69/-0.49 e Å^{-3} indicated possible disorder of the acyl ligand by yielding alternative sites for atoms O1, C2, and O2. Refinement attempts failed due to low occupation of these positions, however. See note at the end of the paper for supplementary material.

(15) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

(16) (a) Schubert, U., in ref 2, p 73. (b) Schubert, U. *Coord. Chem. Rev.* **1984**, *55*, 261.

(17) Block, T. F.; Fenske, R. F.; Casey, C. P. *J. Am. Chem. Soc.* **1976**, *98*, 441.

Scheme II

$$2 + EX \xrightarrow[-[(CH_3)_4N]X]{} (CO)_4Fe{=}C\begin{smallmatrix} C-C(CH_3)_3 \\ \parallel \\ O \\ \diagup \\ OE \end{smallmatrix}$$

4-6

7-9

	E	ν_{CO}
7	C_2H_5	2070 m, 2025 s, 2000 vs[a]
8	$Si(CH_3)_3$	2067 m, 2015 s, 1990 vs[b]
9	CH_3CO	2076 m, 2020 s, 1998 vs[b]

The observed molecular geometry of the ferrate anion amply supports that bonding in the Fe–C(O)–C(O)–*t*-Bu framework is largely σ for the Fe–C and C–C bonds, whereas the carbonyl bonds have a large additional π-component, as expected. There is, however, some indication for a minor π-contribution, especially to the Fe–C1 bond. Finally, it should be noted that there are no additional close contacts of the carbonyl oxygen atoms in the crystal structure of **3**. In alkali-metal salts of acylmetalates tight ion pair formation with close M–O$_{acyl}$ contacts is observed with subsequent implications for the molecular structure and bonding.[18]

Acylferrates are known to react with electrophiles in two different ways: Addition to the acyl oxygen atom yields neutral oxycarbene complexes according to the original Fischer synthesis.[19,20] Addition to the metal center, on the other hand, is generally followed by reductive elimination leading to carbonyl compounds.[13] The competition of these two pathways depends both on the electrophile and the solvent.[21] The acylferrate **2** reacts with a series of electrophiles such as ethyl fluorosulfonate (**4**) in ether/HMPT (4/1), chlorotrimethylsilane (**5**), or acetyl chloride (**6**) in methylene chloride at low temperature (–50 °C) to give red solutions.[22] The products **7–9** can be characterized by IR spectroscopy (Scheme II), but elude isolation due to their pronounced thermolability which results in decomposition on warming above –40 °C or even on evaporation of the solvent.

The ν_{CO} spectra of the products obtained from the reaction mixtures are characteristic for (CO)$_4$FeL complexes. They indicate that the electrophile is added to the acyl oxygen functionality and thus are compatible with the formulation of the products as tetracarbonyl pivaloyl carbene complexes.

(18) Ginsburg, R. E.; Berg, J. M.; Rothrock, R. K.; Collman, J. P.; Hodgson, K. O.; Dahl, L. F. *J. Am. Chem. Soc.* **1979**, *101*, 7218 and references cited therein.
(19) Fischer, E. O.; Beck, H. J.; Kreiter, C. G.; Lynch, J.; Müller, J.; Winkler, E. *Chem. Ber.* **1972**, *105*, 162.
(20) Conder, H. L.; Darensbourg, M. Y. *Inorg. Chem.* **1974**, *13*, 506.
(21) Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* **1983**, *105*, 4099.
(22) In a typical experiment, acylferrate **2** (0.3 g, 0.84 mmol) is dissolved in 10 mL of CH₂Cl₂ and cooled to –55 °C. Addition of (CH₃)₃SiCl (1.72 g, 16 mmol) leads to a dark red solution. After 3 h, the solution is concentrated at –55 °C to a volume of 2 mL while unreacted **2** precipitates and can be removed. Further evaporation of the solvent results in decomposition.

Novel C-Alkylation of a CO-Bridged Dinuclear Iron Carbonyl Anion: A New Synthesis of Fe₂(CO)₆ Complexes Containing a Bridging Acyl Ligand
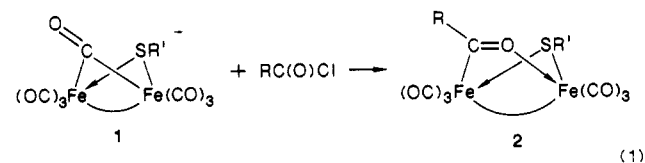
Dietmar Seyferth* and Colin M. Archer

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Summary: The reaction of anionic iron carbonyl complexes which contain a bridging CO ligand of type [Et₃NH][(μ-CO)(μ-R′S)Fe₂(CO)₆] with alkyl- and arylmercuric halides, RHgX, gives products which contain a bridging acyl ligand in place of the bridging CO, (μ-RCO)(μ-R′S)Fe₂(CO)₆. With vinylic and alkynylmercurials, the bridging CO ligand is displaced and products of type (μ-σ,π-CH=CHR)(μ-R′S)Fe₂(CO)₆ and (μ-σ,π-C≡CR)(μ-R′S)Fe₂(CO)₆ are obtained. In contrast, reaction of [Et₃NH][(μ-CO)(μ-R′S)Fe₂(CO)₆] with [Et₃O][BF₄] gives a bridging alkoxycarbyne complex, (μ-EtOC)(μ-R′S)Fe₂(CO)₆.

We report here the first examples of what may be a general and potentially useful new reaction: the alkylation and arylation by RHgX *at carbon* of a CO ligand of a dinuclear transition-metal carbonyl anion which contains a bridging CO ligand. The product is a neutral complex which has a bridging acyl group in place of the original bridging CO ligand. The class of transition-metal anions used in this study are of the type [(μ-CO)(μ-R′S)Fe₂(CO)₆]⁻ (**1**) which, as we have reported earlier,[1] are easily prepared by reaction of Fe₃(CO)₁₂ with mercaptide ion (best generated in situ by the action of triethylamine on a mercaptan, R′SH, in THF). Among several reactions of **1** which we described were those with allyl chloride, propargyl bromide, and acyl chlorides. In these, the organic electrophile displaced the bridging CO ligand to form a new, neutral dibridged Fe₂(CO)₆ complex, e.g., eq 1.

$$\underset{\textbf{1}}{\begin{smallmatrix}O\\ \parallel \\ C \\ (OC)_3Fe{-}Fe(CO)_3 \\ \diagup SR' \end{smallmatrix}}^{-} + RC(O)Cl \longrightarrow \underset{\textbf{2}}{\begin{smallmatrix} R \\ \diagdown \\ C{=}O \quad SR' \\ (OC)_3Fe{-}Fe(CO)_3 \end{smallmatrix}} \qquad (1)$$

Anions of type **1**, we have found, undergo a novel reaction with alkyl- and arylmercuric halides which results in C-alkylation of a CO ligand to give a μ-acyl complex (eq 2). In a typical reaction, a red-brown solution of the

$$\begin{smallmatrix}O\\ \diagdown \\ C \quad SR' \\ (OC)_3Fe{-}Fe(CO)_3 \end{smallmatrix}^{-} + RHgX \longrightarrow$$

$$\underset{(OC)_3Fe{-}Fe(CO)_3}{\begin{smallmatrix} R \\ \diagdown \\ C{=}O \quad SR' \end{smallmatrix}} + Hg + X^- \qquad (2)$$