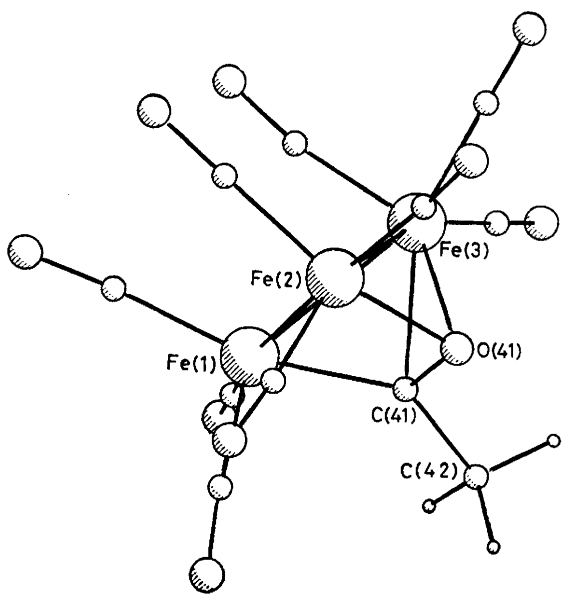
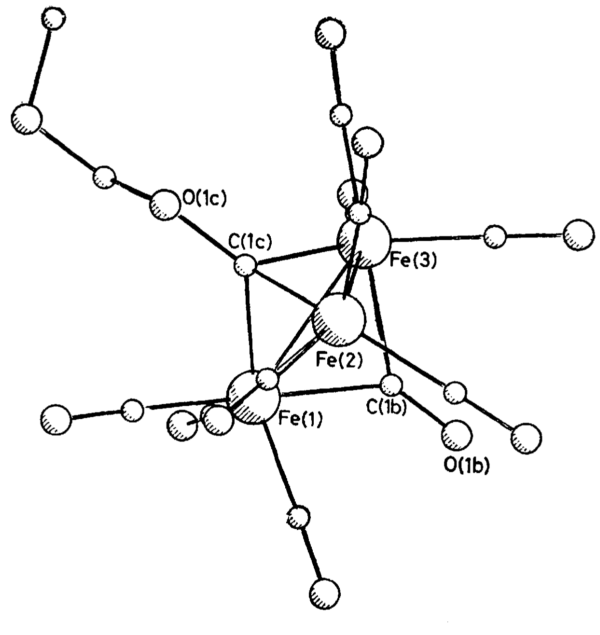
Interaction of Alkyl Halides with the Di-ironoctacarbonylate Anion: the Crystal Structures of the Tetraethylammonium Salts of the μ-Acetyl-$C^1(Fe^1, Fe^2)O(Fe^1, Fe^3)$-nonacarbonyl-*triangulo*-triferrate and μ_2-Carbonylnonacarbonyl-μ_3-2,4-dioxapentylidyne-*triangulo*-triferrate Anions

By WAI-KWOK WONG and GEOFFREY WILKINSON
(*Chemistry Department, Imperial College, London,* SW7 2AY)
and ANITA M. R. GALAS, MICHAEL B. HURSTHOUSE, and MARK THORNTON-PETT
(*Chemistry Department, Queen Mary College, Mile End Road, London,* E1 4NS)

Summary The di-iron carbonylate anion $[Fe_2(CO)_8]^{2-}$ reacts with methyl iodide and with chloromethyl methyl ether to give, respectively, the tri-iron cluster anions $[Fe_3(CO)_9(\mu\text{-MeCO})]^-$ and $[Fe_3(CO)_9(\mu\text{-CO})(\mu^3\text{-COCH}_2\text{OMe})]^-$, the former having a new type of bridging acetyl group.



(1)

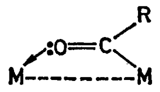


(2)

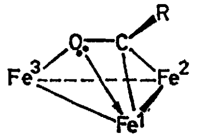
FIGURE. The structures of the anions in compounds (**1**) and (**2**). Some important bond lengths (Å) and angles (°) are: (**1**) Fe(1)–Fe(2) 2·592(2); Fe(1)–Fe(3) 2·541(3); Fe(2)–Fe(3) 2·478(3); Fe(1)–C(41) 1·89(1); Fe(3)–C(41) 1·97(1); Fe(2)–O(41) 1·93(1); Fe(3)–O(41) 1·98(1); C(41)–O(41) 1·31(2); C(42)–C(41)–O(41) 114(1); (**2**) Fe(1)–Fe(2) 2·558(5); Fe(1)–Fe(3) 2·565(5); Fe(2)–Fe(3) 2·553(5); Fe(1)–C(1b) 1·960(11); Fe(3)–C(1b) 1·985(13); C(1b)–O(1b) 1·18(2); Fe(1)–C(1c) 1·979(11); Fe(2)–C(1c) 1·831(12); Fe(3)–C(1c) 2·006(11); C(1c)–O(1c) 1·36(1).

THE reaction of carbocation-generating reagents such as $MeSO_3F$, Me_3OBF_4, or MeI, with metal carbonylate anions gives rise to σ-alkyl compounds. For polynuclear anions the oxygen atom of carbon monoxide may be attacked as in the reactions of $[Fe_3(CO)_{11}]^{2-}$,[1] $[Fe_4(CO)_{13}]^{2-}$,[2,3] and their derivatives, leading to the formation of bridging COR groups. The interaction of di-iodomethane with $[Fe_2(CO)_8]^{2-}$ gives the bridged methylene complex $Fe_2(CO)_8(\mu\text{-}CH_2)$.[4] However, the interaction of $(Et_4N)_2[Fe_2(CO)_8]$ in tetrahydrofuran with methyl iodide and with chloromethyl methyl ether leads in both cases to tri-iron cluster anions whose structures have been characterised spectroscopically and by single crystal *X*-ray study† and are shown in the Figure.

The methyl iodide product $(Et_4N)[Fe_3(CO)_9(MeCO)]$, (**1**), has an acetyl group of a new type. Bridging acyls that have been structurally characterised[5] show the ligand to be bound to two metal atoms as in (A), whereas in compound (**1**) the situation is that in (B), although the C–O bond still retains some double bond character. If we consider the oxygen atom to contribute three electrons to the cluster *via* donation from the lone pair to Fe^1, then the 18-electron rule is satisfied. This acetyl can be specified as being μ-MeCO–$C^1(Fe^1, Fe^2)O(Fe^1, Fe^3)$.



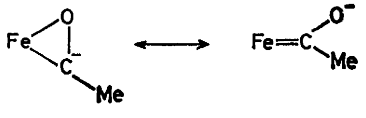
(A)



(B)

The compound (**2**), by contrast, has a bridging alkylidyne, μ_3-$COCH_2OMe$ group and is similar to the μ_3-COMe analogue.[1] Such groups have been obtained by carbocation attacks on the more basic bridging CO groups in polynuclear anions,[1–3] but $[Fe_2(CO)_8]^{2-}$ is said not to have such groups.[6] Although Me_3OBF_4 and $MeSO_3F$ (in benzene) can attack at the metal in, *e.g.*, *trans*-$IrCl(CO)(PPh_3)_2$,[7] it is unlikely that an $FeCH_2OMe$ group is involved. There is no precedent for alkyl transfers from metal to oxygen of CO, although those to carbon to give acyls are well established.[8]

Chloromethyl methyl ether in tetrahydrofuran presumably acts as a carbocation and attacks the oxygen of CO whereas the 'softer' methyl iodide attacks the metal (possibly initially *via* the iodine atom) to give an iron methyl. If the acyl formed by transfer had the forms (C), attack by a neutral iron carbonyl species produced in the reaction could lead to compound (**1**).



(C)

---

† *Crystal data:* (**1**) $C_{19}H_{23}Fe_3NO_{10}$, $M = 592{\cdot}98$, orthorhombic, space group $Pna2_1$, $a = 16{\cdot}559(2)$, $b = 11{\cdot}986(2)$, $c = 12{\cdot}142(2)$ Å, $Z = 4$, $D_c = 1{\cdot}63$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 17{\cdot}4$ cm^{-1}. 2273/3654 observed $[I > 1{\cdot}5\sigma(I)]$ diffractometer data, $R = 0{\cdot}068$. (**2**) $C_{21}H_{25}Fe_3NO_{12}$, $M = 651{\cdot}01$, monoclinic, space group $P2_1/n$, $a = 12{\cdot}806(2)$, $b = 14{\cdot}922(2)$, $c = 15{\cdot}098(2)$ Å, $\beta = 105{\cdot}34(2)°$, $Z = 4$, $D_c = 1{\cdot}55$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 15{\cdot}2$ cm^{-1}. 2677/4580 observed $[I > 1{\cdot}5\sigma(I)]$ data, $R = 0{\cdot}080$. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

As precedent, the formation of $[HFe_3(CO)_{11}]^-$ from $[HFe_2(CO)_8]^-$ is believed[9] to involve neutral species produced in fragmentation reactions; it is also possible that reactions in the present complicated systems (the yields are only *ca.* 30%) could also produce CO-bridged species which could be attacked by CH_2OMe^+.

We thank the S.R.C. for support.

(*Received*, 15*th October*, 1980; *Com.* 1113.)

---

[1] H. A. Hodali and D. F. Shriver, *Inorg. Chem.*, 1979, **18**, 1236.

[2] E. M. Holt, K. Whitmire, and D. F. Shriver, *J. Chem. Soc., Chem. Commun.*, 1980, 778, 780.

[3] P. A. Dawson, B. F. G. Johnson, J. Lewis, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1980, 781.

[4] C. E. Sumner, P. E. Riley, R. E. Davis, and R. Pettit, *J. Am. Chem. Soc.*, 1980, **102**, 1752.

[5] J. R. Blickensderfer, C. B. Knobler, and H. D. Kaesz, *J. Am. Chem. Soc.*, 1975, **97**, 2686.

[6] K. Farmery, M. Kilner, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc. A*, 1969, 2339.

[7] D. Strope and D. F. Shriver, *J. Am. Chem. Soc.*, 1973, **95**, 8197; *Inorg. Chem.*, 1974, **13**, 2652; J. L. Petersen, T. E. Nappier, Jr., and D. W. Meek, *J. Am. Chem. Soc.*, 1973, **95**, 8195.

[8] F. Calderazzo, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 299; J. P. Collman, and L. S. Hegedus, 'Principles and Applications of Organotransition Metal Chemistry,' University Science Books, Mill Valley, California, 1980.

[9] J. P. Collman, R. G. Finke, P. L. Matlock, R. Walren, R. G. Komoto, and J. I. Brauman, *J. Am. Chem. Soc.*, 1978, **100**, 1119.