Reaction of (η^3-Acryloyl)tricarbonylferrate with Acyl Halides giving 1:1 Adducts, the Halogenodicarbonyl(η-2-acyloxy)ferracyclopent-2-en-5-onates

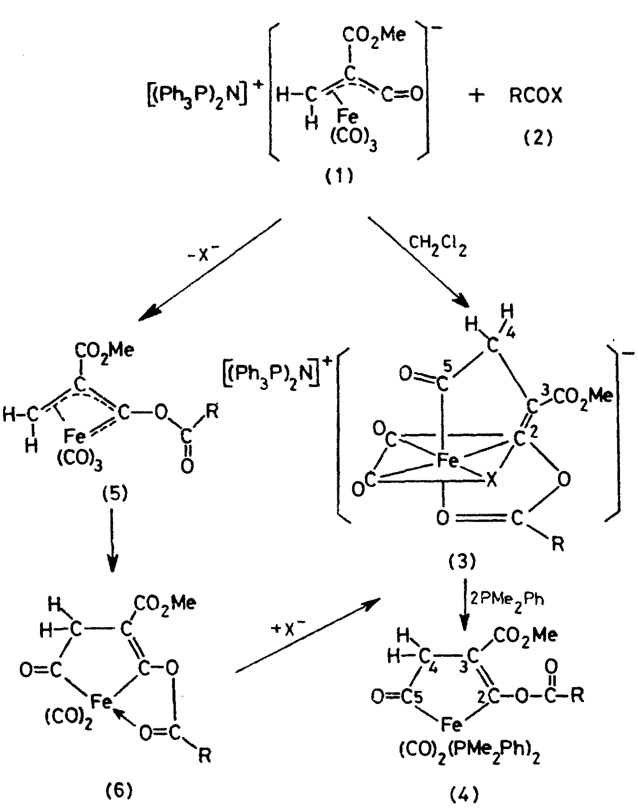
By Take-aki Mitsudo,* Hiroyoshi Watanabe, Yoshihisa Watanabe, and Yoshinobu Takegami

(*Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto* 606, *Japan*)

Summary The (η^3-acryloyl)tricarbonylferrate (**1**) reacted with the acyl halides (**2**) affording the unexpected 1:1 adducts, which were deduced to be the novel halogenodicarbonyl(η-2-acyloxy)ferracyclopent-2-en-5-onates (**3**) derived by the carbonylation of an η^3-vinylcarbene ligand.

The reactions of acylcarbonylmetallates with acyl halides are useful in organic syntheses.[1] Recently the first examples of η^3-acryloylferrates (**1**) were prepared by the reaction of $[FeH(CO)_4]^-$ with acetylenic compounds; alkylation of (**1**) afforded the first η^3-vinylcarbene iron complexes.[2] We now report an unexpected reaction of (**1**) with acyl halides giving the corresponding 1:1 adducts, which were deduced to be novel halogenodicarbonylferracyclopent-2-en-5-onate (1—) complexes containing an additional five-membered chelate ring.

The acryloylferrate[2] (**1**) in CH_2Cl_2 was treated with the acyl halides (**2a**—**e**) (3 mmol) (Scheme) at 0 °C for 30 min. Addition of diethyl ether gave yellow crystals of (**3a**—**e**) in yields of 36—85%. On the basis of the following observations, spectral data, and the 18-electron rule, (**3a**—**e**) were deduced to be 1:1 adducts, the bis(triphenylphosphine)iminium halogeno(dicarbonyl)-η-(2-acyloxy)-3-methoxycarbonylferracyclopent-2-en-5-onates.† The i.r. spectrum of (**3a**) showed two bands in the region typical of terminal metal carbonyl groups in negatively charged complexes (1998 and 1930 cm^{-1}).[3] The spectrum also showed ester ν(C=O) at 1688 cm^{-1},[2] ν(C=O) (*C*-co-ordinated to Fe) at 1660 cm^{-1}, ν(C=O) (*O*-co-ordinated to Fe) at 1636 cm^{-1},[4] and ν(C=C) at 1600 cm^{-1}. The far-i.r. spectra of (**3a**—**c**) showed absorptions at 270, 219, and 181 cm^{-1} respectively showing the presence of an Fe—halogen bond.[5] The ^1H n.m.r. spectrum of (**3a**) exhibited an AB quartet at δ 3·62 (1H) and 3·20 (1H) ($|J|$ 19·0 Hz) due to nonequivalent sp^3 CH_2 protons‡ in addition to signals for MeCO, MeO, and $[PPN]^+$. The ^{13}C n.m.r. spectrum of (**3a**) showed four signals characteristic of a ferracyclopentenone ring: sp^3 CH_2 at δ 62·4 [t, *J*(C–H) 128·9 Hz], $2 \times =C$ at δ 110·4 (s) and 219·0 (slightly broad), and acyl–iron *C*=O at δ 265·7 p.p.m. [t, *J*(CCH) 5·9 Hz]. Spectral data for (**3b**–**e**) were entirely analogous to those for (**3a**). Complex (**3a**) reacted with 2 mol. equiv. of PMe_2Ph at 25 °C affording pale yellow crystals of the bisdimethylphenylphosphine-ferracyclopentenone† (**4**) (yield 27%) (Scheme) [i.r.: ν(C=O) 1690, 1738 (ester), and 1630 (*C*-co-ordinated); ν(C=C) 1550 cm^{-1}; n.m.r. ($CDCl_3$; Me_4Si) ^1H, 2·71 and 3·51 ($|J|$ 21·0 Hz, $-CH_2-$); ^{13}C, 60·1 (t, C-4), 124·4 (s, C-3), 207·9 (s, C-2), and 274·5 p.p.m. (m, J_{C-P} 24·4 Hz, C-5)]. Co-ordination of the 2 PMe_2Ph groups caused the dissociation of the halide ion and the carbonyl group of the enol ester.



Scheme

a; R = Me, X = Cl
b; R = Me, X = Br
c; R = Me, X = I
d; R = Et, X = Cl
e; R = Pr^n, X = Cl

The formation of (**3**) by the reaction of (**1**) with (**2**) may be rationalized as follows. The (η^3-acyloxyvinylcarbene)-iron complex (**5**) is first formed by acylation on the acyl oxygen atom of the acryloyl group. Co-ordination of the

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† Satisfactory analytical data have been obtained.

‡ The absence of a symmetry plane including the methylene carbon proved that the stereochemistry of (**3**) is as shown in the Scheme.

carbonyl of the ester may then cause migratory insertion of a carbonyl group into the methylene carbon–iron bond§ affording the unstable unsaturated complex (**6**) whose vacant site may be occupied by a halide ion to give (**3**).

The complexes (**3**) and (**4**) are to our knowledge the first examples of well characterized ferracyclopent-2-en-5-one complexes which are the keto-form of the 'ferrole' (ferracyclopenta-2,4-diene-2,4-diol) complexes[6] derived by the reaction of acetylenes with alkali–$Fe(CO)_5$.

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§ The reaction of [1—3-η-(1-methoxycarbonyl)methoxycarbene]tricarbonyliron with 2 mol. equiv. of PMe_2Ph also gives a ferracyclopent-2-en-5-one complex, the structure of which was determined by *X*-ray analysis. Spectral data for this complex fully corresponded with those for (**3**) and (**4**) (T. Mitsudo, T. Sasaki, Y. Watanabe, Y. Takegami, K. Nakatsu, K. Kinoshita, and Y. Miyagawa, unpublished work). During this reaction the zerovalent iron complex (**1**) is oxidized to a divalent complex. A similar oxidation was observed in the reaction of an (η^3-vinylcarbene)iron complex with CO or PR_3: T. Mitsudo, T. Sasaki, Y. Watanabe, Y. Takegami, S. Nishigaki, and K. Nakatsu, *J.C.S. Chem. Comm.*, 1978, 252.

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