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SHORT COMMUNICATION

Evidence for an iron–carbene complex*

It has been observed that the stretching frequency of the acyl C=O group in some transition metal–acetyl complexes, M–COMe, occurs near 1660 cm^{-1} which is unusually low for a ketonic C=O stretch[1,2]. Several authors have suggested that the lowering may arise by donation of electrons from the metal via π-bonding to the carbonyl group causing a reduction in the C=O bond character and an increase of electron density on the carbonyl oxygen[1,2]. We have prepared the air-stable, red brown, triphenylphosphine derivative π-$C_5H_5FeCOPh_3PCOMe$ (I) and find the ν(C=O) at 1608 cm^{-1} which is a very low value, even compared with ν(C=O) 1652 cm^{-1} for the analogous dicarbonyl π-$C_5H_5Fe(CO)_2COMe$(II)**. This observation is consistent with the hypothesis of metal–carbon π-bonding and since triphenylphosphine is a more basic ligand than carbon monoxide the ν(C=O) would be expected to be lower in the complex (I).

We have investigated the reaction of complexes (I) and (II) with proton acids since in these complexes the oxygen of the carbonyl C=O group would be expected to be more basic than usual. The complex (I) in petroleum protonates when treated with either dry hydrogen chloride or hydrogen bromide forming cream-yellow powders. Prolonged standing in vacuum or washing the powders with ether removes the hydrogen halide forming the parent complex (I). Analysis of the hydrogen bromide derivative shows a stoicheiometry consistent with the formulation π-$C_5H_5FeCOPh_3PCOMe \cdot HBr$ (III). The rapid dissociation of the complex (III) in solutions precludes determination of its conductivity.

The infrared spectra of the hydrogen halide adducts show *inter alia* that there is no ν(C=O); there are broad bands at 3400–2900 cm^{-1} and at 1650 cm^{-1} which may be assigned to O–H stretching and bending frequencies respectively; finally the terminal carbonyl stretch, occurs at 1981 cm^{-1} and is 32 cm^{-1} higher than in the neutral complex (I), which is consistent with there being an increase of positive charge on the iron. The spectra of the deuterium halide products from (I) similarly show the absence of ν(C=O) and a broad O–D stretching frequency appears at 2200–2400 cm^{-1}. Comparison of the proton magnetic resonance spectra of solutions of the complex (I) in trifluoroacetic acid and carbon disulphide show that band due to the π-C_5H_5 hydrogens is shifted to lower fields in the acid solution which is consistent with there being an increased positive charge on the metal in the protonated species. The acid solutions showed no bands assignable to O–H hydrogens, their apparent absence may be due to exchange broadening effects; also there were no bands at high fields assignable to M–H species.

The complex (II) similarly reacts with hydrogen chloride forming a cream-coloured powder, (IV), but it dissociates very readily and it was not possible to keep it

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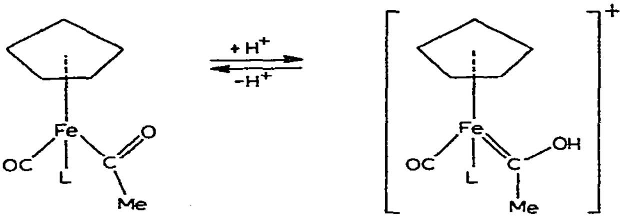
** *Note added in proof.* This compound has been independently reported[5].

pure outside a hydrogen chloride atmosphere. Infrared studies using HCl saturated mulls showed results similar to those found for the protonated complex (II).

The yellow crystalline compound π-$C_5H_5Mo(CO)_2Ph_3PCOMe$ has also been prepared. Its benzene solutions show no reaction with hydrogen chloride.

Recently "carbene" complexes, which contain the system M–C(OR')R have been described[3,4]. We propose by analogy and on the above evidence that the protonated acyl complexes (III) and (IV) contain a similar system, as shown in the figure.



L = CO or Ph_3P

Experimental

Acetyl-π-cyclopentadienyl(triphenylphosphine)iron carbonyl. Methyl-π-cyclopentadienyliron dicarbonyl (2.5 g) and triphenylphosphine (1.7 g) were ground together under nitrogen at 120° for 1 h. The product was washed with light petroleum (2 × 50 ml) and recrystallised from hot petroleum at 100°. (Found: C, 68.7; H, 4.9; Fe, 12.8; mol. wt., 461. $C_{26}H_{23}FeO_2P$ calcd.: C, 68.7; H, 5.1; Fe, 12.3%; mol. wt., 454.)

The complex π-$C_5H_5Mo(CO)_2Ph_3PCOCH_3$ was similarly prepared from π-$C_5H_5Mo(CO)_3Me$ and triphenylphosphine. (Found: C, 61.9; H, 4.4; mol. wt., 511. $C_{27}H_{23}MoO_3P$ calcd.: C, 62.1; H, 4.4%; mol. wt., 522.)

Reaction of π-$C_5H_5FeCOPh_3PCOMe$ with hydrogen halides. Pure π-$C_5H_5FeCOPh_3PCOMe$ (1 g) in petroleum (b.p. 40–60°) was treated with dry hydrogen chloride for 10 min. A cream-yellow powder immediately precipitated which was washed with light petroleum and dried in vacuum for a few minutes. (Found: C, 63.7; H, 4.8, Cl, 7.2. $C_{26}H_{24}ClFeO_2P$ calcd.: C, 63.4; H, 4.9; Cl, 7.3%.)

The bromide analogue was prepared similarly. (Found: C, 57.1, H, 4.8. $C_{26}H_{24}BrFeO_2P$ calcd.: C, 58.5, H, 4.5%.)

Infrared spectra. Spectra were determined on mulls using a Perkin-Elmer 21 instrument. The data are: *π-$C_5H_5FeCOPh_3PCOMe$*: 3070 w^{a}, 2980 w^{b}, 2920 vw^{b}, 2815 w^{b}, 1929 vs^{c}, 1608 s^{d}, 1488 w, 1438 m, 1325 w, 1189 w, 1113 w, 1083 m, 1064 m, 1028 w, 997 w, 908 w, 810 m, 756 w, 695 m, 690 s; *π-$C_5H_5Mo(CO)_2Ph_3PCOMe$*: 3070 w^{a}, 2980 w^{b}, 2810 w^{b}, 1930 vs^{c}, 1845 vs^{c}, 1604 s^{d}, 1481 m, 1440 m, 1335 w, 1307 w, 1263 w, 1180 w, 1159 w, 1092 m, 1064 m, 907 m, 848 m, 758 m, 724 m, 694 m; $[\pi\text{-}C_5H_5FeCOPh_3PC(OH)Me]^+Br^-$: 3400–2800 br^{e}, 3060 w^{a}, 2965 wm^{b}, 2920 w^{b}, 1981 vs^{c}, 1650 br^{f}, 1480 w, 1435 m, 1311 m, 1192 m, 843 w, 755 m, 745 m, 723 m, 695 m. The spectrum of the chloride analogue was apparently identical. a, C–H str. of π-C_5H_5; b, C–H str. of Me; c, C≡O str.; d, C=O str.; e, O–H str.; f, O–H def.

Proton magnetic resonance spectra. Spectra were determined at 40 Mc/sec. on a Perkin–Elmer instrument. Data are given in τ. π-$C_5H_5Fe(CO)_2COMe$ (CS_2) 7.58^{a}, 5.23^{b}; (CF_3COOH) 6.80^{a}, 4.76^{b}. π-$C_5H_5FeCOPh_3PCOMe$ (CS_2) 7.83^{a}, 5.76^{b}, 2.95^{c};

(CF_3COOH) 7.41[a], 5.04[b], 2.44[c]. [π-$C_5H_5FeCOPh_3PCOHMe]^+Br^-$ (SO_2) 7.41[a], 5.04[b], 2.44[c]. Assignments: a, Me; b, π-C_5H_5; c, Ph_3P.

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