Metal to Carbene 1,2 Hydrogen Migration in the Protonation of a Fischer-type Carbene Iron(0) Complex

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Protonation of the 1,3-dithiol-2-ylidene iron(0) complex (**2a**) occurs at the carbene carbon centre, but proceeds *via* a *trans* hydrido-carbene intermediate, isomerization into the *cis* derivative, and metal to carbene carbon 1,2 hydrogen shift.
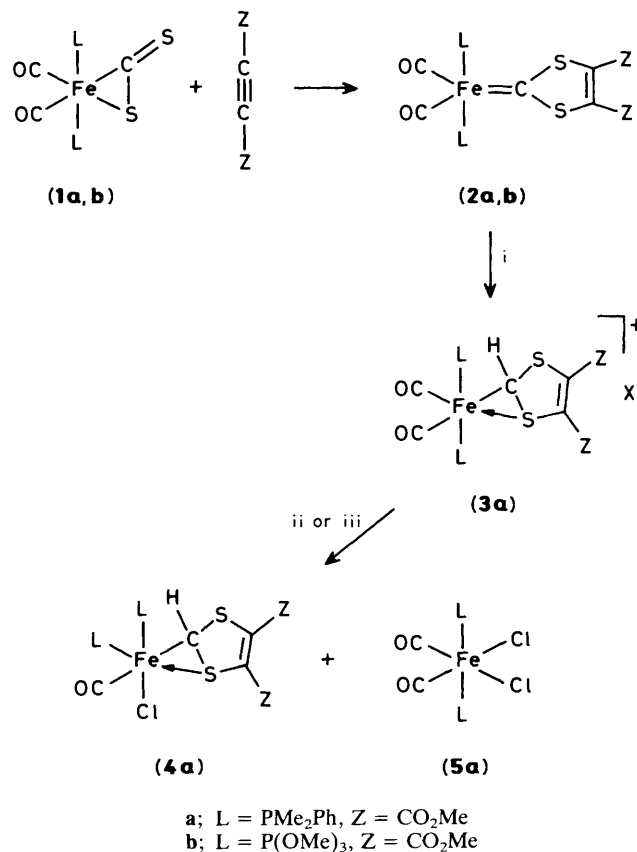
The reactivity of carbene–metal complexes of later transition metals is dominated by the electrophilic character of the carbene carbon atom.[1] However, it has been shown recently that the reactivity of the carbene–metal moiety is strongly related to the oxidation state of the metal: two examples of low valent carbene complexes of group 8 metals, in which the carbene carbon adds electrophiles such as H^+, Ag^+, or $HgCl_2$,[2,3] have been reported. In addition, theoretical calculations on chromium(0) and iron(0) 'Fischer-type' carbene complexes predict that the carbene carbon bears a negative charge and that the electrophilic reactivity at the carbene carbon is not charge controlled but frontier orbital controlled.[4] In contrast, it has been reported that an electron-rich Fe^0 carbene complex[5] adds $HgCl_2$ at the metal atom and

(I)   (II)

protonation of anionic carbene complexes of the type [M(carbene)(CO)$_2$C$_5$H$_5$]$^-$ (M = Mo, W) occurs at the metal site rather than at the carbene carbon site.[6] To determine whether protonation occurs at the metal (I) or at the carbene carbon (II) of low valent carbene–metal complexes we have investigated the protonation of carbene–iron(0) complexes, and we now report that (i) the protonation occurs at the carbene carbon atom but (ii) proceeds via hydrido-carbene intermediates.

Electron rich, 1,3-dithiol-2-ylidene iron(0) complexes (2) are readily obtained by cycloaddition of activated alkynes to the corresponding (η^2-CS$_2$) iron complexes.[7] The protonation of complex (2a) (L = PMe$_2$Ph) has been investigated using CF$_3$CO$_2$H and monitored by n.m.r. spectroscopy. To the carbene complex (2a), made in situ by addition of dimethylacetylene dicarboxylate to complex (1a) at room temperature in CD$_2$Cl$_2$, one equivalent of CF$_3$CO$_2$H is added rapidly. A colour change, from brown to red, occurs instantaneously, leading to the stable cationic complex (3a), as characterised by ^{1}H and ^{13}C n.m.r. spectroscopy (Scheme 1).† In the ^{1}H n.m.r. spectrum a triplet is observed at δ 4.93 corresponding to the (methyne) proton resonance coupled to two phosphorus nuclei (J_{PH} 1.8 Hz), but no hydride resonance in the high field region is detected. The origin of this signal from the proton of CF$_3$CO$_2$H is easily demonstated by the n.m.r. spectra of (2a) protonated with CF$_3$CO$_2$D, which does not show any resonance in the δ 5 region. In addition, inequivalence of the two ester methyl groups is observed, in agreement with the proposed structure (3a). Co-ordination of one sulphur atom to the iron is necessary to achieve an 18 electron configuration and thus induces the disymmetry of the 1,3-dithiol cyclic ligand. The assignment of the protonated species to (3a) is confirmed by the ^{13}C n.m.r. spectrum, which shows inequivalent CO$_2$Me groups and a C–H resonance at δ 52.10 with a $^1J_{CH}$ coupling constant of 181.0 Hz. This reaction appears to

(1a, b)   (2a, b)

(3a)

ii or iii

(4a)   (5a)

a; L = PMe$_2$Ph, Z = CO$_2$Me
b; L = P(OMe)$_3$, Z = CO$_2$Me

Scheme 1. Reagents and conditions: i, HX (X$^-$ = Cl$^-$, CF$_3$CO$_2^-$, BF$_4^-$, PF$_6^-$), room temp.; ii, (X$^-$ = Cl$^-$), CH$_2$Cl$_2$, 40 °C, 1 h; iii, (X$^-$ = BF$_4^-$), Bu$_4$NCl, CH$_2$Cl$_2$, 40 °C, 1 h.

afford the same cation (3a) whatever the acid used, e.g. with a co-ordinating or non-co-ordinating anion. Indeed, treatment of (2a) with one equivalent of HX (X = Cl, BF$_4$, PF$_6$) at room temperature in diethyl ether, gives an orange precipitate whose i.r. and ^{1}H n.m.r. spectra agree with the structure (3a) (X = Cl, BF$_4$, PF$_6$).‡

Treatment of the cation (3a) (X = BF$_4$) with Bu$_4$NCl in CH$_2$Cl$_2$ at reflux gives a mixture of neutral compounds (4a) and (5a) (Scheme 1). They can be directly obtained by treating (2a) with HCl followed by heating the CH$_2$Cl$_2$ solution. After 1 h of reflux the two compounds are isolated by silica gel column chromatography: a yellow derivative (5a)‡ (22%) and a brown air sensitive compound identified as (4a)‡ (20%) by i.r. and n.m.r. spectroscopy.† Of interest is the ^{1}H and ^{13}C n.m.r. spectrum of (4a) which shows two doublets of doublets at δ 61.70, assigned to a C–H carbon coupled with two cis phosphorus nuclei (J_{PC} 26.6, 13.8 Hz) and with the proton ($^1J_{CH}$ 171.0 Hz).

The mechanism of the protonation of (2a) at the carbene carbon was investigated by variable temperature ^{1}H n.m.r. spectroscopy in CD$_2$Cl$_2$. At −80 °C the high field region shows two triplets (A) at δ −10.70 (J_{PH} 35.0 Hz) and (B) at δ −8.30 (J_{PH} 43.0 Hz) in the ratio (A):(B) = 80:20. Raising the temperature to −50 °C leads to a decrease in the intensity of (A) and an increase in that of (B) [(A):(B) = 7:93]. Further warming to −20 °C results in a complete conversion of (A) into (B) (Figure 1). The highest field triplet (A) can be

† Selected spectroscopic data: (3a) (X$^-$ = PF$_6^-$) v (CO) (CH$_2$Cl$_2$) 2025 s and 1970 vs, v (C=O) 1740 vs cm^{-1}; ^{1}H n.m.r. (X$^-$ = CF$_3$CO$_2^-$), δ (CD$_2$Cl$_2$, 308 K, 80 MHz) 7.54 (m, 10H, Ph), 4.93 (t, 1H, J_{PH} 1.8 Hz, CH), 3.84 (s, 3H, OMe), 3.82 (s, 3H, OMe), 1.89 (d, 12H, J_{PH} 8.8 Hz, PMe); ^{13}C n.m.r. δ (CD$_3$CN, 243 K, 75.5 MHz) 208.5 (dd, J_{PC} 28.8 and 32.2 Hz, CO), 207.7 (dd, J_{PC} 30.5 and 33.1 Hz, CO), 161.4 (s, CO$_2$Me), 160.5 (s, CO$_2$Me), 150.8 (s, C=C), 55.0 (s, MeO), 54.7 (s, MeO), 52.1 (dd, J_{PC} 5.0 and 10.1 Hz, CH).

(4a) v (CO) (Nujol) 1910 vs, v (C=O) 1740, 1710 vs cm^{-1}; ^{1}H n.m.r. δ (C$_6$D$_6$, 305 K, 80 MHz) 7.16 (m, 10H, Ph), 4.75 (t, 1H, J_{PH} 2.9 Hz, CH), 3.28 (s, 3H, OMe), 1.71 (t, 6H, J_{PH} 8.4 Hz, PMe), 1.36 (d, 3H, J_{PH} 9.0 Hz, PMe), 1.32 (d, 3H, J_{PH} 9.6 Hz, PMe); ^{13}C n.m.r. δ (CD$_2$Cl$_2$, 298 K, 75.5 MHz) 201.6 (dd, J_{PC} 27.6 and 35.4 Hz, CO), 161.9 (s, CO$_2$Me), 161.1 (s, CO$_2$Me), 150.6 (s, C=C), 61.7 (dd, J_{PC} 26.6 and 13.8 Hz, CH); ^{31}P n.m.r. δ (C$_6$D$_6$, 305 K, 32.4 MHz) 36.7, 16.2 p.p.m. (J_{PP} 14.7 Hz).

(5a) v (CO) (Nujol) 2040 vs, 1975 vs cm^{-1}; ^{1}H n.m.r. δ (CDCl$_3$, 308 K, 60 MHz) 7.57 (m, 10H, Ph), 2.06 (virtually-coupled triplet, 12H, J_{PH} 10.0 Hz, PMe).

(8a) v (CO) (CH$_2$Cl$_2$) 2055 vs, 1995 s, v (C=O) 1740 vs cm^{-1}; ^{1}H n.m.r. δ (CD$_3$CN, 297 K, 300 MHz) 7.28 (m, 10H, Ph), 3.96 (s, 3H, OMe), 3.88 (s, 3H, OMe), 1.94 (m, 12H, PMe); ^{13}C n.m.r. δ (CD$_3$CN, 297 K, 75.5 MHz) 263.2 (t, J_{PC} 21.2 Hz, Fe=C), 209.9 (t, J_{PC} 21.2 Hz, CO), 208.2 (t, J_{PC} 21.2 Hz, CO), 159.2 (s, CO$_2$Me), 158.8 (s, CO$_2$Me), 155.8 (s, C=C), 154.6 (s, C=C), 55.2 (s, OMe), 55.1 (s, OMe), 14.5 (t, J_{PC} 17 Hz, PMe), 13.3 (t, J_{PC} 17 Hz, PMe).

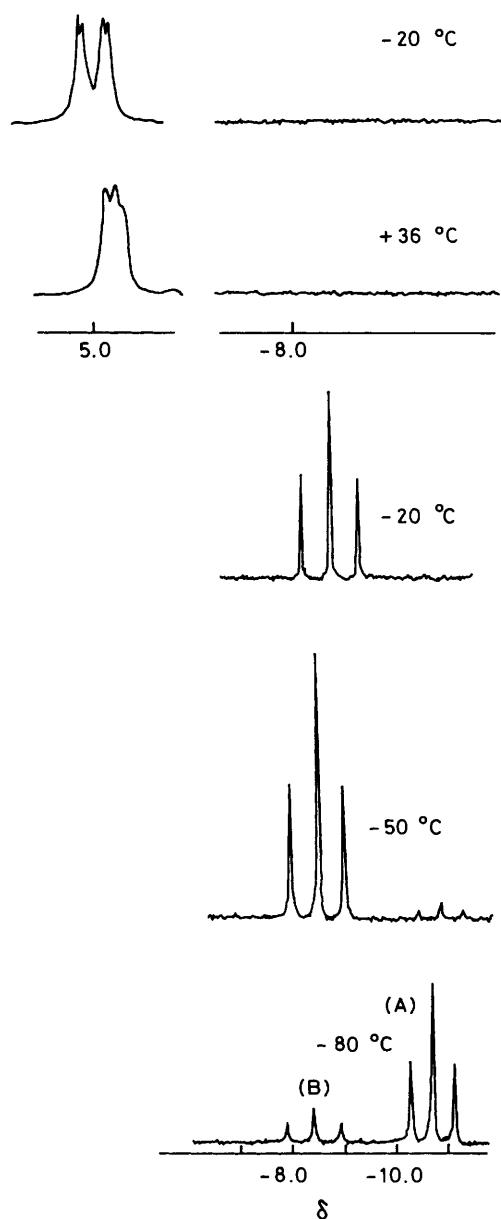‡ Satisfactory analytical data were obtained for these products.

Figure 1. Variable temperature ^{1}H n.m.r. experiment on (2a) in acid solution. The top spectrum is obtained after cooling the solution from 36 to $-20\,°C$ and shows that the conversion of (7a) into (3a) is irreversible.

assigned to the hydrido-carbene complex (6a), resulting from the protonation of the iron centre *trans* to the electron releasing carbene ligand. This proton addition can be related to the co-ordination of the Lewis acid $HgCl_2$ to (2a), which has been shown to give a stable binuclear complex $Cl_2HgFe(CO)_2(PMe_2Ph)_2\{CS_2C_2(CO_2Me)_2\}$ with the position of the $HgCl_2$ unit *trans* to the carbene ligand.[5] The triplet (B) can be assigned to *cis* isomer (7a). Observation of a high $^2J_{PH}$ value rules out any contribution of CH agostic bonding in (6a) and (7a). Structure (7a) is strongly supported by a quenching experiment: protonation of (2a) with $HBF_4\cdot Et_2O$ in CD_2Cl_2 at $-10\,°C$ followed by addition of CCl_4 gives a yellow salt which is formulated as the *cis* chlorocarbene complex (8a)‡ by i.r., and ^{1}H and ^{13}C n.m.r. spectroscopy (Scheme 2).† Of particular interest are the low field resonance at δ 263.2 typical
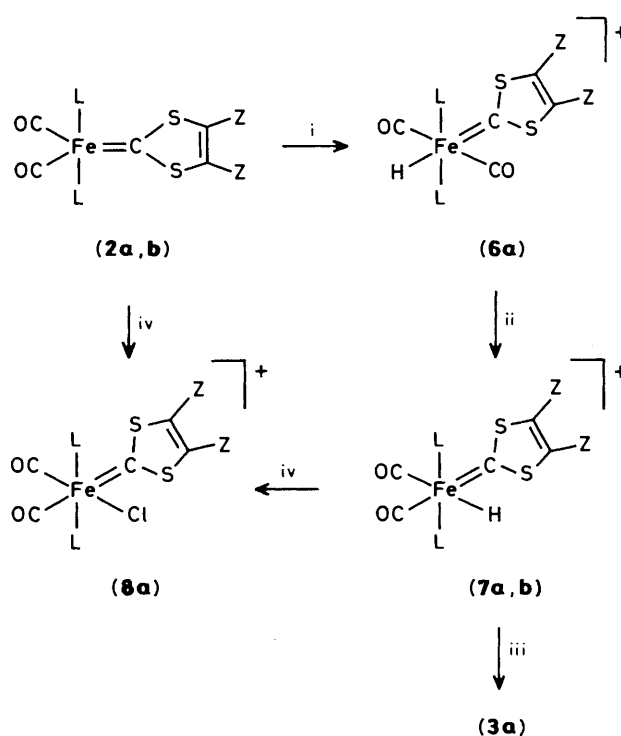
Scheme 2. *Reagents and conditions:* i, CF_3CO_2H, CD_2Cl_2, $-80\,°C$; ii, warm to $-50\,°C$; iii, CD_3CN, $-30\,°C$ then warm to room temp.; iv, $HBF_4\cdot OEt_2$, $CH_2Cl_2-CCl_4$, $-10\,°C$.

of a carbene carbon and the inequivalency of the olefinic and ester carbons of the 1,3-dithiol-2-ylidene ligand which establish that the carbene ligand is contained in the symmetrical plane of the octahedron.

Owing to the instability of (7a) in chlorinated solvents, the dynamic ^{1}H n.m.r. experiment between $-30\,°C$ and $+36\,°C$ was performed in CD_3CN. Protonation of (2a) with CF_3CO_2H at $-30\,°C$ leads to (7a) [δ -8.21 (Fe–H, t, J_{PH} 43.5 Hz)]. Warming at 36 °C results in a complete conversion of (7a) into (3a) [δ 5.20 (C–H, t, J_{PH} 1.9 Hz)] (Scheme 2). This demonstrates the 1,2 shift of the hydrogen from the iron to the *cis* carbene carbon atom.

When the protonation of (2a) is performed at room temperature in CD_2Cl_2 and the ^{1}H n.m.r. spectrum recorded successively at $+30$, 0, and $-20\,°C$, the triplet at δ 4.93 progressively transforms into a doublet of doublets at δ 4.96 [1H, J_{PH} 0.9 and 4.4 Hz], compatible with a geometrical isomerization of the complex (3a), but no signals appear in the high field region (Figure 1). This demonstrates the irreversibility of the conversion (7a) → (3a).

The stability of the hydrido-carbene species is strongly dependent on the electron donating effect of the phosphorus ligand L: protonation of complex (2b), containing the less basic trimethylphosphite rather than PMe_2Ph, with CF_3CO_2H in CD_3CN at $-30\,°C$ gives rise to the hydrido-carbene complex (7b), as suggested by the presence in the ^{1}H n.m.r. spectrum of a triplet at δ -7.56 (J_{PH} 54.1 Hz). On warming to 36 °C, the high field triplet is still present and no resonance in the δ 5 region is observed. In this case the complex (7b) is stable and no 1,2 hydrogen shift occurs below 36 °C.

Some indirect evidence of a reversible 1,2 hydrogen shift between alkyl and hydrido-carbene complexes has been reported.[8—12] The above study is to our knowledge the first *direct* evidence of the conversion of a carbene hydride intermediate into a metal alkyl complex.[13]

In conclusion we have shown that (i) the protonation of metal carbene complex does not take place directly at the carbene carbon site, but the initial site of protonation is always the metal centre giving a hydrido-carbene complex (I); (ii) with weak electron-donor ligands on the metal this *cis* hydrido species is the thermodynamic product; and (iii) with strong electron donor ligands the intermediate (I) leads, *via* a 1,2 hydrogen shift, to the carbene carbon protonated species (II), in the reverse process of α-elimination of an alkyl group.

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