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Preliminary communication

A MILD PHASE TRANSFER SYNTHESIS OF THE YLID ADDUCT $(CO)_4FeCH_2P(C_6H_5)_3$ FROM IRON PENTACARBONYL AND DICHLOROMETHANE: EVIDENCE FOR THE TRANSIENT GENERATION OF THE TETRACARBONYL FERRATE ANION $Fe(CO)_4{}^{2-}$

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Summary

The ylid adduct $(CO)_4FeCH_2P(C_6H_5)_3$ (I) was rapidly produced (along with $(CO)_4FeP(C_6H_5)_3$) by introducing iron pentacarbonyl into the following phase transfer system under nitrogen: $CH_2Cl_2/P(C_6H_5)_3$; $H_2O/NaOH$ 1 *M*, $Bu_4N^+{}_2SO_4{}^{2-}$ Production of I goes through the transient generation of the tetracarbonyl ferrate anion $Fe(CO)_4{}^{2-}$, which reacts with the dichloromethane.

A common route to ylid adducts of general formula $(CO)_x(M)C(R'R'')PR_3$ involves the direct attack of a phosphorus ylid on the metal carbonyl [1]. Since this method fails for iron pentacarbonyl [2,3], an elegant new strategy was designed recently, starting from iron tetracarbonyl disilane complexes and aldehydes R'COR'' (R'' = H); the parent complex $(CO)_4FeCH_2PR_3$ was not described, however [4]. We report here a very mild synthesis of the complex $(CO)_4FeCH_2P(C_6H_5)_3$ (I) under phase transfer conditions [5] (reaction 1).

$$Fe(CO)_5 \xrightarrow[H_2O/NaOH\ 1\ M,\ (Bu_4N^+)_2SO_4{}^{2-}]{CH_2Cl_2/P(C_6H_5)_3} \underset{(I)}{(CO)_4FeCH_2P(C_6H_5)_3} \qquad (1)$$

A two phase system consisting of dichloromethane (10 ml, containing 2 mmol of $Fe(CO)_5$ and 2 mmol of $P(C_6H_5)_3$ and water (10 ml, containing 10 mmol of NaOH and 2 mmol of $Bu_4N^+HSO_4{}^-$ was stirred (1100 rpm) for twenty minutes at +10°C under nitrogen. The IR spectrum of the organic layer showed the complete disappearance of $Fe(CO)_5$ and the appearance of new bands which turned out to be essentially those of the ylid I. This complex was isolated in pure form as very air-sensitive yellow crystals (25%) [6] along with $(CO)_4FeP(C_6H_5)_3$ (II) (16%) [7]. Similar results were obtained starting from the preformed tetra-

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carbonylferrate anion III (as the disodium salt [8]) under anhydrous conditions, although the reaction time was much longer (72 h) (reaction 2).

$$\underset{\text{(III)}}{\mathrm{Fe(CO)_4^{2-}}} + \mathrm{CH_2Cl_2} + \mathrm{P(C_6H_5)_3} \xrightarrow{\mathrm{Bu_4N^+Br^-}} \mathrm{I} + \mathrm{II} \qquad (2)$$

By treating the previous liquid—liquid two phase system (without $Fe(CO)_5$) with dry, preformed $Na_2Fe(CO)_4$, complex I could be isolated from the organic layer after 15 min stirring. Thus, in this system, reaction 2 is faster than protonation (which would give the hydridoanion $HFe(CO)_4^-$ (IV). In system 1, replacing $Fe(CO)_5$ by preformed $Bu_4N^+HFe(CO)_4^-$ [9] gave no reaction, and no isotopic exchange of the hydridic proton of IV occurred when D_2O was used instead of H_2O; this rules out phase transfer production of III via deprotonation of IV. These results strongly suggest that the very basic anion $Fe(CO)_4^{2-}$ (III) (about the same base strength as OH^- [10]) is transiently generated under the phase transfer conditions described here [11]. In the case of the reaction scheme of the hydroxide anion with iron pentacarbonyl, there is strong support for the intermediacy of the anionic hydroxycarbonyl species V, although this has never been observed directly (reaction 3) [12,13].

$$\begin{tikzcd}
\mathrm{Fe(CO)_5} \arrow[r, "OH^-"] & \underset{\text{(V)}}{|\mathrm{Fe(CO)_4COOH^-}|} \arrow[r, "OH^-", "A"'] \arrow[dr, "B"', "-CO_2"] & \underset{\text{(VI)}}{|\mathrm{Fe(CO)_4CO_2^{2-}}|} \arrow[dr, "-CO_2"] & \\
 & & \underset{\text{(IV)}}{\mathrm{HFe(CO)_4^-}} & \underset{\text{(III)}}{\mathrm{Fe(CO)_4^{2-}}} \arrow[l, "H^+"']
\end{tikzcd} \qquad (3)$$

The mechanism of the subsequent decarboxylation was controversial until recently, but recent reports, supported by kinetic measurements [12] or gas phase studies [13], strongly suggest that, in agreement with our findings, pathway A is the correct one; decarboxylation of the hydroxycarbonyl V requires prior deprotonation with a strong base. Consequently, according to this scheme, the more basic anion $Fe(CO)_4^{2-}$ (III) is generated before the less basic one $HFe(CO)_4^-$ (IV) [14]. Since under phase transfer conditions reaction 3A probably occurs on the organic side of the liquid—liquid interface, this prevents anion III from further protonation and allows it to react quickly, as a tetrabutylammonium salt, with the organic solvent CH_2Cl_2. Generation of the ylide I could then be accounted for by reaction 4, although it is still not clear whether the reaction goes through the intermediacy of the unknown carbene VIII (pathway A) or by nucleophilic displacement on the anionic species VII (pathway B).

$$\begin{tikzcd}
\underset{\text{(III)}}{\mathrm{Fe(CO)_4^{2-}}} + \mathrm{CH_2Cl_2} \arrow[r] & \underset{\text{(VII)}}{\mathrm{(CO)_4FeCH_2Cl^-}} \arrow[r, "-Cl^-", "A"'] \arrow[d, "B", "P(C_6H_5)_3,\ -Cl^-"'] & \underset{\text{(VIII)}}{\mathrm{(CO)_4FeCH_2}} \arrow[dl, "P(C_6H_5)_3"] \\
 & \underset{\text{(I)}}{\mathrm{(CO)_4FeCH_2P(C_6H_5)_3}} &
\end{tikzcd} \qquad (4)$$

Due to the importance of the tetracarbonyl ferrate dianion III in synthesis [15], its transient generation in mild phase transfer conditions should have a great potential. In addition to the example described here, others have already been described [16,17] or are under study.

References and notes

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6 I: m.p. 110—112°C dec. Anal. Found: C, 62.21; H, 3.74; Fe, 12.3; P, 7.14. $C_{23}H_{17}FeO_4P$ calcd.: C, 62.19; H, 3.86; Fe, 12.57; P, 6.97. *m/e* $C_{23}H_{17}FeO_4P$ calcd. 444.2103; found 444. IR, $\nu(C{\equiv}O)$ (cm^{-1}, CH_2Cl_2): 2020 m, 1930 m, 1905 vs; (KBr) 2020 m, 1930 m, 1905 s, 1880 vs. ^1H NMR (CD_2Cl_2, −25°C, δ relative to external TMS): $FeCH_2$ 1.56 (d, 2H, *J*(PH) 12.50 Hz). ^{31}P NMR (CD_2Cl_2, −20°C, δ from external H_3PO_4) 36.6. ^{13}C NMR (CD_2Cl_2, −20°C δ relative to external TMS): $FeCH_2$ −16.18 (d, *J*(CP) 29.30 Hz). These spectral data are in good agreement with those given in ref. 4 for similar ylid adducts, which are best described as dipolar structure $(CO)_4Fe^{-}CH(R)^{+}P(C_6H_5)_3$.
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$$H_2Fe(CO)_4 \rightleftarrows H^+ + HFe(CO)_4^-, \qquad pK_{a_1}\ 4.0\ (20^\circ C)$$

$$HFe(CO)_4^- \rightleftarrows H^+ + Fe(CO)_4^{2-}, \qquad pK_{a_2}\ 12.7\ (20^\circ C)$$

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