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Preliminary communication

EXPLORATORY FLASH VACUUM PYROLYSIS OF SOME CYCLOPENTADIENYLIRON COMPLEXES

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Summary

At 500 °C, flash vacuum pyrolysis of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ provides a rapid, practical synthesis of the tetranuclear complex $(\eta^5\text{-}C_5H_5)_4Fe_4(\mu_3\text{-}CO)_4$: at higher temperatures, ferrocene is formed. Ferrocene itself undergoes little change under flash vacuum pyrolysis conditions, even at 725 °C. Pivaloylferrocene is unchanged at 650 °C but cracks to yield isobutene between 675 and 700 °C; this reaction does not proceed by simple elimination since formylferrocene can be recovered unchanged under flash vacuum pyrolysis conditions which give substantial quantities of isobutene from pivaloylferrocene.

Flash vacuum pyrolysis (FVP) is now a standard technique in organic synthesis [1,2]. However, although FVP has been employed extensively in organosilicon chemistry [3], there have been only sporadic reports of its use in organo-transition metal chemistry [4–7].

One common reaction type in FVP of organic compounds is the elimination of small stable molecules, such as CO, CO_2, N_2, SO_2 or HX (X = halogen). The recorded examples of FVP applications to organo-transition metal systems are largely of this type. They include the elimination of CO from $(\eta^5\text{-}C_5H_5)_3Rh_3(\mu_3\text{-}CO)(PhCCPh)$ with concomitant cleavage of the central carbon–carbon bond in the PhCCPh ligand, to yield $(\eta^5\text{-}C_5H_5)_3Rh_3(\mu_3\text{-}CPh)_2$ [4]; the elimination of SO_2 from η^4-thiophene-*S*,*S*-dioxide in $(\eta^4\text{-}C_4H_4SO_2)Co(\eta^5\text{-}C_5H_5)$ to yield the cyclobutadiene complex $(\eta^4\text{-}C_4H_4)Co(\eta^5\text{-}C_5H_5)$ [6]; and loss of two moles of CO from $(\eta^1\text{-}C_6H_5CH_2)Mn(CO)_5$ to give $(\eta^5\text{-}C_6H_5CH_2)Mn(CO)_3$ [7], which contains the η^5-methylenecyclohexadienyl ligand.

We have now studied the FVP behaviour of some simple η^5-cyclopentadienyliron compounds, including both examples which contain the readily eliminated η^1-CO ligand, and for comparison, those which contain no such ligand.

FVP of the dinuclear complex $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ at 500 °C yielded the tetranuclear complex $(\eta^5\text{-}C_5H_5)_4Fe_4(\mu_3\text{-}CO)_4$ [8,9] in 16.7% yield, along with

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ferrocene in 65.3% yield. At higher temperatures, ferrocene was the only molecular product. Ferrocene itself is highly stable under FVP conditions, and was recovered in 96% yield from a run with the furnace temperature at 675°C and in 86% yield when the temperature was 725°C. Preformed [9] $(\eta^5\text{-}C_5H_5)_4Fe_4(\mu_3\text{-}CO)_4$ was converted under FVP conditions into ferrocene at temperatures as low as 200°C. The reaction sequence, starting with $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$, may therefore be represented as in equation 1:

$$2(C_5H_5)_2Fe_2(CO)_4 \xrightarrow{-2CO} (C_5H_5)_4Fe_4(CO)_4 \xrightarrow{-4CO} 2(C_5H_5)_2Fe + 2Fe \qquad (1)$$

In all FVP processes which yielded ferrocene from either $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ or $(\eta^5\text{-}C_5H_5)_4Fe_4(\mu_3\text{-}CO)_4$, an iron mirror was deposited in the pyrolysis tube. The FVP conversion of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ to $(\eta^5\text{-}C_5H_5)_4Fe_4(\mu_3\text{-}CO)_4$ provides a similar yield of the tetranuclear product to the original solution pyrolysis (14%) [8]: this route however, as well as giving a low yield is extremely lengthy (ca. 20 days), and also requires extensive purification [8]. The recently-described high-yield conversion (56%) [9,10], is shorter (2 days) and requires less work-up. The present vapour-phase route to $(\eta^5\text{-}C_5H_5)_4Fe_4(\mu_3\text{-}CO)_4$, although giving only a modest yield (16.7%), requires only 2–3 hours, and provides, direct from the reactor, crystalline material of high purity which requires no work-up at all.

In contrast to the reaction sequence represented by equation 1, FVP of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$, although readily producing the triply Mo≡Mo bonded $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$ at 350°C, yielded no tractable products other than $Mo(CO)_6$: in particular no molecular species of nuclearity higher than two were observed.

FVP of the sulphur-bridged cyclopentadienyliron complex $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu_2\text{-}SMe)_2$ [11] yielded ferrocene (78%) at much lower temperature (300°C) than did $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$: at much lower FVP temperatures (ca. 120°C) the S-bridged complex underwent conversion to a labile blue complex. This has not yet been isolated in a pure condition, but appears to be neither $(\eta^5\text{-}C_5H_5)_2Fe_2(S_2)(\mu_2\text{-}SMe)_2$ [12] nor $(\eta^5\text{-}C_5H_5)_3Fe_3(S_2)(SMe)$ [12]. On the other hand, we note that in the mass spectrum of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu_2\text{-}SMe)_2$, ions which contain carbonyl ligands are almost entirely absent. Although there is only a crude correlation between mass spectral behaviour and FVP behaviour, this mass spectrum tends to support the idea that the labile blue complex is carbonyl-free.

As an example of a cyclopentadienyliron complex containing no readily extruded ligand, we selected pivaloylferrocene $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4COCMe_3)$, since this is a prototype of other stable $(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_4C(X)CMe_3]$ complexes. The FVP behaviour of pivaloylferrocene showed a very marked dependence upon temperature. At 650°C, the starting complex was recovered unchanged almost quantitatively (94%) while at 675 and 700°C only 8 and 9% were recovered, along with 59 and 32% yields respectively of $Me_2C{=}CH_2$. At 725°C, no isobutene was observed, and only 6% of the pivaloylferrocene was recovered: the rest was wholly decomposed. The minimum temperature for isobutene production was 675°C, and the temperature range over which isobutene was a significant product was no more than 40°C.

At no point was formylferrocene, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CHO)$ observed in the FVP of pivaloylferrocene, although at a temperature of 700°C, which gave a substantial yield of isobutene, formylferrocene was partly (27%) recovered unchanged with the rest fully decomposed. Hence isobutene cannot be formed according to equation 2:

$$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4COCMe_3) \rightarrow (\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CHO) + Me_2C{=}CH_2 \qquad (2)$$

Rather we suggest initial formation of t-butyl radicals: at the temperature required for C–C bond cleavage, major degradation of the other product radicals, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CO^{\bullet})$ and $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4^{\bullet})$ must occur, even though ferrocene itself is stable under these conditions. We now plan to generate ferrocene radicals under much milder FVP conditions.

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