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$CpFe(CO)_2H$: a Reassessment of the Literature

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The compound $CpFe(CO)_2H$ (*I*) was first reported in 1959 [1]; it was described as a yellow liquid, unstable at room temperature with respect to decomposition, *i.e.*

$$\underset{I}{2CpFe(CO)_2H} \longrightarrow H_2 + [CpFe(CO)_2]_2 \qquad (1)$$

Possibly because of this claim of lability of *I*, which has often been reiterated in the literature, relatively few investigations have been carried out on the compound [2]. It has been synthesized in a variety of ways, including treatment of $Na[CpFe(CO)_2]$ with acetic acid [4] and t-butyl chloride [5], and of $CpFe(CO)_2Cl$ with sodium borohydride [1, 6]. Reactions with phosphorus donors [7], an alkyne (CF_3C_2H) [8], an alkene (CH_2CHCN) [9] and a conjugated diene (C_4H_6) [10] have also been briefly mentioned in the literature, as has the photochemistry of *I* [11].

During the course of an investigation of the chemistry of *I*, however, we have found that the compound is in fact *not* unduly thermally labile, but can be maintained in solution for at least several hours at room temperature. The opportunity is thus offered to study with ease the chemistry of *I* in some detail, and we report herein some of our initial findings. In doing so, we correct/reinterpret several claims in the literature.

Synthesis and Stability of *I*

A very convenient synthesis of *I* involves treatment of $Na[CpFe(CO)_2]$ with acetic acid. The yellow hydride can then be obtained in high yield and *temporarily* pure of the dimer, $[CpFe(CO)_2]_2$, by distillation [5, 6] or by elution with light petroleum ether through an activated alumina column. Within minutes, however, the purified materials invariably turn brown because of the formation of small amounts of the deep red dimer [12], although the degradation process soon stops and the proportion of *I* remains constant thereafter. Indeed, solutions of *I* in toluene or mesitylene have been maintained unchanged for 3 hours at 65 °C. While we do not know the reason(s) for the conversion of *I* to dimer, it would appear that traces of O_2 are not involved. Although exposure to air of solutions of *I* does appear to result in conversion to $[CpFe(CO)_2]_2$ [13], the reaction is much slower than is the initial, partial conversion of freshly prepared *I* to $[CpFe(CO)_2]_2$.

Substitution Reactions of Tertiary Phosphines

We have found, as shown by Kalck and Poilblanc [7], that *I* reacts rapidly with PMe_2Ph in a variety of solvents (C_6H_6, THF, $CHCl_3$) at 0 °C, as in (2):

$$I + PMe_2Ph \longrightarrow CpFeCO(PMe_2Ph)H + CO \qquad (2)$$

The reaction is thus much more facile than are substitution reactions of the corresponding alkyl compounds $CpFe(CO)_2R$, which involve prior dissociation of CO [14]. By analogy with the similar substitution reactions of $HRe(CO)_5$ [15] and $CpW(CO)_3H$ [16], however, (2) may involve a chain radical mechanism, initiated by as yet unidentified adventitious radicals [17]:

$$I + R\cdot \longrightarrow RH + CpFe(CO)_2\cdot \qquad (3)$$

$$CpFe(CO)_2\cdot + PMe_2Ph \longrightarrow CpFeCO(PMe_2Ph)\cdot + CO \qquad (4)$$

$$CpFeCO(PMe_2Ph)\cdot + I \longrightarrow CpFeCO(PMe_2Ph)H + CpFe(CO)_2\cdot \qquad (5)$$

$$\Big\downarrow {+PMe_2Ph}$$

Etc.

As halogenated solvents are known to act as spin traps for the $CpFe(CO)_2\cdot$radical [18–22], it might be thought unlikely that the chain reaction described above would proceed uninterrupted in chloroform. However, it is also quite likely that the substitution reaction (4) of the 17 electron radical would be rapid [23], and thus conceivably competitive with reaction with chloroform. Accordingly we have studied the photolysis of $[CpFe(CO)_2]_2$ in the presence of a 5-fold excess of PMe_2Ph in chloroform under conditions [29] in which the $CpFe(CO)_2\cdot$ radical is gener-

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ated [21]. The photochemical reaction was followed by IR spectroscopy, and it was clear that the starting material (ν(CO) = 2010, 1965, 1775 cm^{-1}) was converted to both $CpFe(CO)_2Cl$ (ν(CO) = 2055, 2010 cm^{-1}) and $CpFeCO(PMe_2Ph)Cl$ (ν(CO) = 1961 cm^{-1}), the latter being the product expected from reaction of the substituted radical, $CpFeCO(PMe_2Ph)\cdot$, with chloroform. Thus it is clear that reaction of $CpFe(CO)_2\cdot$ with PMe_2Ph can be competitive with reaction with chloroform, and that the sequence (3)–(5) may occur in that solvent.

Reactions of *I* with Alkenes and Alkynes

As mentioned above, *I* has been reported to react thermally with CF_3C_2H [8], CH_2CHCN [9] and C_4H_6 [10] to give vinyl and alkyl products expected from 'insertion'. We find that *I* reacts similarly in benzene with $MeO_2CC_2CO_2Me$ and styrene within 30 min and 6 hours, respectively as in (6) and (7):

$$I + MeO_2CC_2CO_2Me \longrightarrow CpFe(CO)_2C(CO_2Me){:}CHCO_2Me \qquad (6)$$

$$I + PhCHCH_2 \longrightarrow CpFe(CO)_2CHMePh \qquad (7)$$

The new vinyl compound has been characterized by IR and ^1H NMR spectroscopy, and by elemental analysis, the 1-phenethyl compound by comparison of its spectroscopic properties with data from the literature [30].

Interestingly, reactions (6) and (7) and the reaction of *I* with butadiene [10], at least, are all completed in too short a time to involve a normal migratory insertion mechanism following substitution of CO by the alkene [31]. A more plausible mechanism for the reactions would involve the intermediacy of a radical pair followed by radical coupling, *i.e.*

$$I + PhCHCH_2 \longrightarrow [CpFe(CO)_2\cdot,\cdot CHMePh] \longrightarrow CpFe(CO)_2CHMePh \qquad (8)$$

This type of reaction is believed to be involved in the stoichiometric aromatic alkene hydrogenations by $HCo(CO)_4$ [32], $HMn(CO)_5$ [32] and $CpM(CO)_3H$ (M = Mo, W) [33], and in the formation of $PhMeCHCOCo(CO)_4$ from styrene and $HCo(CO)_4$ in the presence of CO [34]. The fact that styrene and acrylonitrile give branched rather than linear products means that the reactions have mechanisms fundamentally different from the well-known alkene and alkyne hydrostannation reactions [35, 36],

$$R_3SnH + PhCH{=}CH_2 \longrightarrow R_3SnCH_2CH_2Ph \qquad (9)$$

which involve radical abstraction of hydrogen from R_3SnH to initiate a chain process via $R_3Sn\cdot$ radicals; as shown in (9), primary alkyl products are generally formed [37].

Instead, the chemistry of reactions (6) and (7) may exemplify alkene and alkyne hydrometallation reactions of a type which are complementary to the well-known 'migratory insertion' reactions [31], and which have not been hitherto recognized. The mechanism may well be general for reactions of hydridic hydrides with electrophilic alkenes and alkynes, and in cases where the spins of the radical pair intermediate can couple to form a metal–carbon bond as in (8). Indeed, in some cases, it seems likely that both hydrogenation and coupling can occur. We note that $CpW(CO)_3H$ reacts with $MeO_2CC_2CO_2Me$ to give the vinyl compound $CpW(CO)_3C(CO_2Me){:}CHCO_2Me$ [38], although reaction with α-methylstyrene results in hydrogenation of the alkene [33]. Similarly, *I* reacts with butadiene to give a 2-butenyl complex, while $MeCpFe(CO)_2H$ hydrogenates cyclopentadiene to cyclopentene [4]. We also find that the reaction of *I* with styrene in benzene produces a small amount of ethylbenzene, suggesting that not every radical pair formed in (8) proceeds to coupled product. The observation that both (6) and (7) proceed in chloroform suggests that coupling probably occurs within the solvent cage rather than after diffusion from the cage, as the $CpFe(CO)_2\cdot$ radicals may otherwise be scavenged by solvent (see above).

The 1,4-addition reported for the reaction of *I* with butadiene [10] is consistent with a radical process [39] although, by analogy with the hydrostannation of butadiene [40], one might expect more than one isomer of the product 2-butenyl complex. We find, by selective decoupling of the 200 MHz ^1H spectrum, that two products are formed, the *cis*- and *trans*-isomers [41].

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