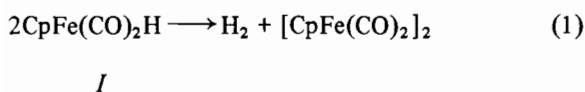


CpFe(CO)<sub>2</sub>H: a Reassessment of the LiteratureSTUART B. FERGUSSON, LAURA J. SANDERSON,  
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The compound CpFe(CO)<sub>2</sub>H (*I*) was first reported in 1959 [1]; it was described as a yellow liquid, unstable at room temperature with respect to decomposition, *i.e.*



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)<sub>2</sub>] with acetic acid [4] and *t*-butyl chloride [5], and of CpFe(CO)<sub>2</sub>Cl with sodium borohydride [1, 6]. Reactions with phosphorus donors [7], an alkyne (CF<sub>3</sub>-C<sub>2</sub>H) [8], an alkene (CH<sub>2</sub>CHCN) [9] and a conjugated diene (C<sub>4</sub>H<sub>6</sub>) [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)<sub>2</sub>] with acetic acid. The yellow hydride can then be obtained in high yield and *temporarily* pure of the dimer, [CpFe(CO)<sub>2</sub>]<sub>2</sub>, by distillation [5, 6] or by elution with light petroleum ether through an activated alumina column.

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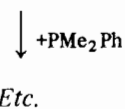
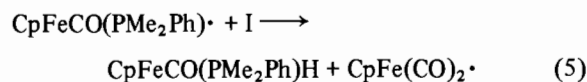
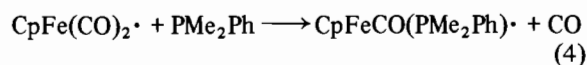
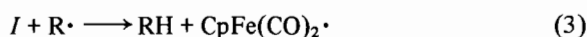
Within minutes, however, the purified materials invariably turn brown because of the formation of small amounts of the deep red dimer [12], although the degradation process soon stops and the proportion of *I* remains constant thereafter. Indeed, solutions of *I* in toluene or mesitylene have been maintained 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<sub>2</sub> are not involved. Although exposure to air of solutions of *I* does appear to result in conversion to [CpFe(CO)<sub>2</sub>]<sub>2</sub> [13], the reaction is much slower than is the initial, partial conversion of freshly prepared *I* to [CpFe(CO)<sub>2</sub>]<sub>2</sub>.

## Substitution Reactions of Tertiary Phosphines

We have found, as shown by Kalck and Poilblanc [7], that *I* reacts rapidly with PMe<sub>2</sub>Ph in a variety of solvents (C<sub>6</sub>H<sub>6</sub>, THF, CHCl<sub>3</sub>) at 0 °C, as in (2):



The reaction is thus much more facile than are substitution reactions of the corresponding alkyl compounds CpFe(CO)<sub>2</sub>R, which involve prior dissociation of CO [14]. By analogy with the similar substitution reactions of HRe(CO)<sub>5</sub> [15] and CpW(CO)<sub>3</sub>H [16], however, (2) may involve a chain radical mechanism, initiated by as yet unidentified adventitious radicals [17]:

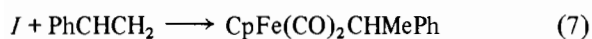
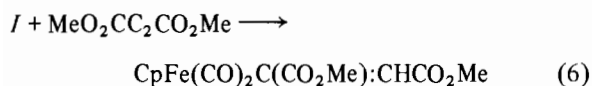


As halogenated solvents are known to act as spin traps for the CpFe(CO)<sub>2</sub>· radical [18–22], it might be thought unlikely that the chain reaction described above would proceed uninterrupted in chloroform. However, it is also quite likely that the substitution reaction (4) of the 17 electron radical would be rapid [23], and thus conceivably competitive with reaction with chloroform. Accordingly we have studied the photolysis of [CpFe(CO)<sub>2</sub>]<sub>2</sub> in the presence of a 5-fold excess of PMe<sub>2</sub>Ph in chloroform under conditions [29] in which the CpFe(CO)<sub>2</sub>· radical is gener-

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

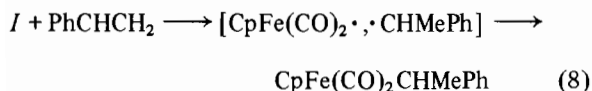
### Reactions of *I* with Alkenes and Alkynes

As mentioned above, *I* has been reported to react thermally with  $\text{CF}_3\text{C}_2\text{H}$  [8],  $\text{CH}_2\text{CHCN}$  [9] and  $\text{C}_4\text{H}_6$  [10] to give vinyl and alkyl products expected from 'insertion'. We find that *I* reacts similarly in benzene with  $\text{MeO}_2\text{CC}_2\text{CO}_2\text{Me}$  and styrene within 30 min and 6 hours, respectively as in (6) and (7):

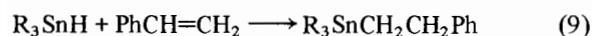


The new vinyl compound has been characterized by IR and  $^1\text{H}$  NMR spectroscopy, and by elemental analysis, the 1-phenethyl compound by comparison of its spectroscopic properties with data from the literature [30].

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.*



This type of reaction is believed to be involved in the stoichiometric aromatic alkene hydrogenations by  $\text{HCo}(\text{CO})_4$  [32],  $\text{HMn}(\text{CO})_5$  [32] and  $\text{CpM}(\text{CO})_3\text{H}$  ( $\text{M} = \text{Mo}, \text{W}$ ) [33], and in the formation of  $\text{PhMe-CHCOCo}(\text{CO})_4$  from styrene and  $\text{HCo}(\text{CO})_4$  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],



which involve radical abstraction of hydrogen from  $\text{R}_3\text{SnH}$  to initiate a chain process via  $\text{R}_3\text{Sn}\cdot$  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  $\text{CpW}(\text{CO})_3\text{H}$  reacts with  $\text{MeO}_2\text{CC}_2\text{CO}_2\text{Me}$  to give the vinyl compound  $\text{CpW}(\text{CO})_3\text{C}(\text{CO}_2\text{Me})\text{:CHCO}_2\text{Me}$  [38], although reaction with  $\alpha$ -methylstyrene results in hydrogenation of the alkene [33]. Similarly, *I* reacts with butadiene to give a 2-butenyl complex, while  $\text{MeCpFe}(\text{CO})_2\text{H}$  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  $\text{CpFe}(\text{CO})_2\cdot$  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  $^1\text{H}$  spectrum, that two products are formed, the *cis*- and *trans*-isomers [41].

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### References

- 1 M. L. H. Green, C. N. Street and G. Wilkinson, *Z. Naturforsch.*, **14b**, 738 (1959).
- 2 Indeed, a search of literature reveals fewer than 30 publications dealing directly with *I*, in stark contrast with the voluminous literature on the analogous alkyl compounds [3].
- 3 See, for instance, M. D. Johnson, 'Comprehensive

- Organometallic Chemistry', G. Wilkinson, F. G. A. Stone and E. W. Abel, Eds.; Pergamon Press, New York, 1982, Vol. 4, p. 331.
- 4 T. H. Whitesides and J. Shelly, *J. Organomet. Chem.*, **92**, 215 (1975).
  - 5 M. L. H. Green and P. L. I. Nagy, *J. Organomet. Chem.*, **1**, 58 (1963).
  - 6 A. Davison, J. A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, 1133 (1963).
  - 7 P. Kalck and R. Poilblanc, *C. R. Hebd. Acad. Sci., Ser. C*, **274**, 66 (1972).
  - 8 D. A. Harbourn and F. G. A. Stone, *J. Chem. Soc. (A)*, 1765 (1968).
  - 9 J. K. P. Ariyaratne and M. L. H. Green, *J. Chem. Soc.*, 274, 66 (1963).
  - 10 M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963).
  - 11 R. J. Kazlauskas and M. S. Wrighton, *Organometallics*, **1**, 602 (1982).
  - 12 It is presumably this observation which has led in the past to the hypothesis that (1) occurs readily.
  - 13 Solutions of  $[\text{CpFe}(\text{CO})_2]_2$  are also somewhat air sensitive, yielding unidentified brown precipitates.
  - 14 A. Wojcicki, *Adv. Organomet. Chem.*, **12**, 31 (1974).
  - 15 B. H. Byers and T. L. Brown, *J. Am. Chem. Soc.*, **99**, 2527 (1977).
  - 16 N. W. Hoffman and T. L. Brown, *Inorg. Chem.*, **17**, 613 (1978).
  - 17 An interesting, as yet not understood, clue to the identity of the catalytic species is that it appears to be destroyed by acetic acid. Solutions of *I* containing acetic acid are inert to  $\text{PMe}_2\text{Ph}$ .
  - 18 H. B. Abrahamson and M. S. Wrighton, *Inorg. Chem.*, **17**, 1003 (1978).
  - 19 J. V. Caspar and T. J. Meyer, *J. Am. Chem. Soc.*, **102**, 7794 (1980).
  - 20 C. Giannotti and G. Merle, *J. Organomet. Chem.*, **105**, 97 (1976).
  - 21 H. B. Abrahamson, M. C. Palazzotto, C. L. Reichel and M. S. Wrighton, *J. Am. Chem. Soc.*, **101**, 4123 (1979).
  - 22 B. Collan and A. R. Manning, *J. Chem. Soc., Chem. Commun.*, 263 (1983).
  - 23 There is considerable evidence in the literature [15, 16, 24–28] that 17 electron species are generally exceedingly labile.
  - 24 S. B. McCullen, H. W. Walker and T. L. Brown, *J. Am. Chem. Soc.*, **104**, 4007 (1982).
  - 25 Q.-Z. Shi, T. G. Richmond, W. C. Troglor and F. Basolo, *J. Am. Chem. Soc.*, **104**, 4033 (1982).
  - 26 R. H. Magnuson, R. Meirowitz, S. J. Zulu and W. P. Giering, *Organometallics*, **2**, 460 (1983).
  - 27 A. Poë and C. Sekhar, *J. Chem. Soc. Chem. Commun.*, 566 (1983).
  - 28 J. W. Hershberger, R. J. Klingler and J. K. Kochi, *J. Am. Chem. Soc.*, **105**, 61 (1983).
  - 29 Hanovia lamp 20 cm from a Pyrex flask containing approximately millimolar concentrations of the reactants, stirred under nitrogen.
  - 30 J. J. Alexander and A. Wojcicki, *Inorg. Chim. Acta*, **5**, 655 (1971).
  - 31 J. P. Collman and L. S. Hegeudus, 'Principles and Applications of Organotransition Metal Chemistry', University Science Books, Mill Valley, California, 1980, pp. 291–294.
  - 32 T. E. Nalesnik, J. H. Freudenberger and M. Orchin, *J. Molec. Catal.*, **16**, 43 (1982), and references therein.
  - 33 R. L. Sweany, D. S. Comberrel, M. F. Dombourian and N. A. Peters, *J. Organomet. Chem.*, **216**, 57 (1981).
  - 34 F. Ungváry and L. Markó, *Organometallics*, **1**, 1120 (1982).
  - 35 W. P. Neumann, 'The Organic Chemistry of Tin', Wiley, New York, 1970.
  - 36 A. G. Davis and P. J. Smith, in 'Comprehensive Organometallic Chemistry'; G. Wilkinson, F. G. A. Stone and E. W. Abel, Eds., Pergamon Press, New York, 1982, Vol. 2, p. 519.
  - 37 Furthermore, hydrostannation reactions are generally accelerated by radical initiators such as AIBN. In contrast, (7) is retarded by AIBN, apparently because of competing styrene polymerization.
  - 38 R. M. Laine and P. C. Ford, *J. Organomet. Chem.*, **124**, 29 (1977).
  - 39 P. I. Abell, in 'Free Radicals', J. K. Kochi, ed., Wiley, New York, 1973, Vol. II, p. 64.
  - 40 R. H. Fish, H. G. Kuivila and I. J. Tyminski, *J. Am. Chem. Soc.*, **89**, 5861 (1967).
  - 41 The original NMR study [10] was carried out on the neat compound, a viscous oil, at 40 MHz, thus explaining why only one isomer was detected.