Journal of Organometallic Chemistry, 190 (1980) C79—C83

Preliminary communication

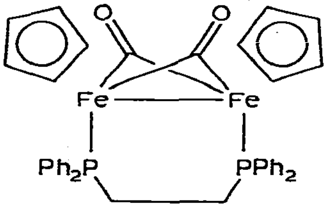
REACTIVITY MODES OF BRIDGED BIMETALLIC $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2\text{-}\mu\text{-}$dppe WITH ELECTROPHILES. PREPARATION AND REACTIONS OF BIMETALLIC HYDRIDE COMPLEXES

S.J. LaCROCE, K.P. MENARD, and A.R. CUTLER*
Department of Chemistry, Wesleyan University, Middletown, Connecticut 06457 (U.S.A.)
(Received January 11th, 1980)

Summary

The complex $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2\text{-}\mu\text{-}$dppe (dppe = ethane-1,2-bisdiphenylphosphide) (I) reacts with electrophiles through a μ-CO and forms Lewis acid O-adducts with alkylating reagents (giving cationic μ_2-alkoxycarbyne compounds) or with alkylaluminum compounds. Treatment of I with acid affords a stable μ_2-hydride salt (IV), $[CpFe(CO)]_2(\mu_2\text{-}H)(\mu_2\text{-dppe})^+$, which serves as an intermediate in the stepwise hydrogenation (reversibly) of I to a bridged bimetallic dihydride, $[CpFe(CO)H]_2\text{-}\mu_2\text{-dppe}$. This dihydride serves as a hydride donor, regenerating IV, towards Ph_3C^+ or $CpFe(CO)_2(\eta^2\text{-}CH_2{=}CH_2)^+$ hydride acceptors. The necessity of the μ_2-dppe as a "mechanical linkage" in facilitating some bimetallic reactions is also established.

We report that $Cp_2Fe_2(\mu\text{-}CO)_2(\mu\text{-dppe})$* (I) [1] exhibits an enhanced bimetallic reactivity towards electrophiles relative to its parent complex, $Cp_2Fe_2(CO)_4$. The μ-dppe ligand both increases the electron density of the bimetallic unit (as reflected in the IR, $\nu_{CO}(CH_2Cl_2)$ 1674 cm^{-1} vs. 1771 cm^{-1} for the analogous μ-CO ligands on $Cp_2Fe_2(CO)_4$), and also serves as a mechanical linkage that associates both halves.

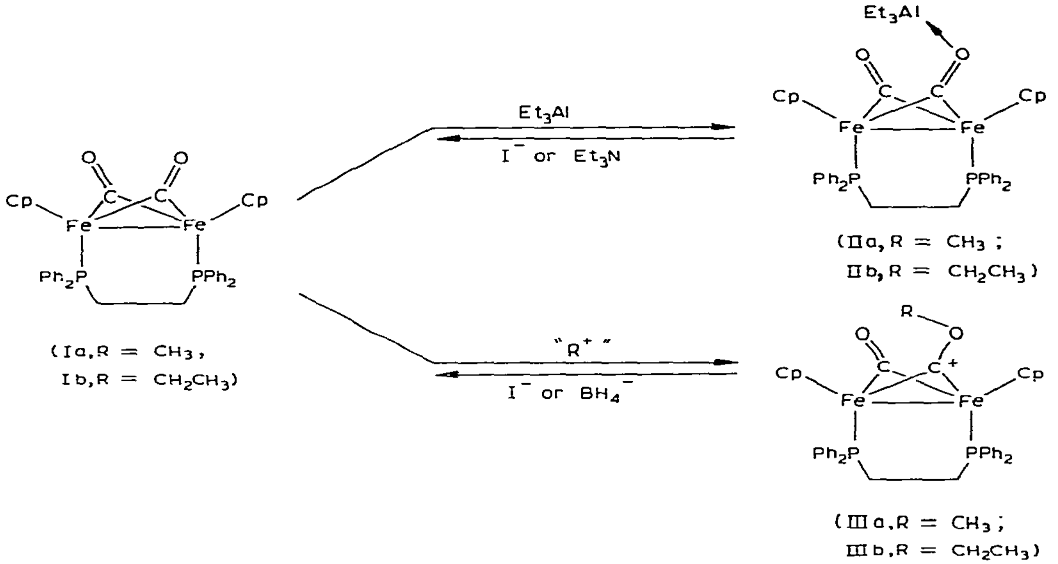


(I)

---

*Cp represents $\eta^5\text{-}C_5H_5$, and dppe depicts ethane-1,2-bisdiphenylphosphide.

Bridging carbonyl ligands generally exhibit Lewis basicity and form Lewis acid O-bonded adducts [2]. Accordingly, titration of bimetallic I with triethylaluminum in CH_2Cl_2 produces the 1:1 adduct II (IR, ν_{CO} shift to 1727 cm^{-1} with one-half intensity), analogous to that established with $Cp_2Fe_2(CO)_4$ [2a]. The interaction of powerful alkylating agents and I, however, leads to isolable cationic adducts III as O-alkylated bridging carbonyl complexes. These O-alkylated adducts (III), μ_2-alkoxycarbyne complexes, quantitatively develop upon treatment of I with trialkyloxonium salts or methyl fluorosulfonate in CH_2Cl_2 (IR: ν_{CO} shift to 1759 cm^{-1} with one-half intensity). Ether precipitation, followed by reprecipitation from acetone-ether, leads to 80% yields of the two salts IIIa,b as air-stable brown solids*. Adduct formation (II or III) reverses upon treatment with one equivalent of iodide or triethylamine.



(Ia, R = CH_3, Ib, R = CH_2CH_3)

(IIa, R = CH_3; IIb, R = CH_2CH_3)

(IIIa, R = CH_3; IIIb, R = CH_2CH_3)

O-alkylated adducts III represent the first examples of either strictly bimetallic or cationic complexes possessing a μ_2-alkoxycarbyne ligand. Examples of neutral and anionic μ_2-alkoxycarbyne complexes have been prepared by alkylation of μ_2-carbonyls on several anionic cluster systems [3]. Cationic binuclear iron complexes containing a bridging alkylidyne ligand μ_2-$CR[Cp_2Fe_2(CO)_3]^+$ have also been recently reported [4]. Until now, binuclear organometallic complexes bearing μ-CO ligands that are sufficiently nucleophilic for O-alkylation and conversion to μ-alkoxycarbyne groups have not been reported.

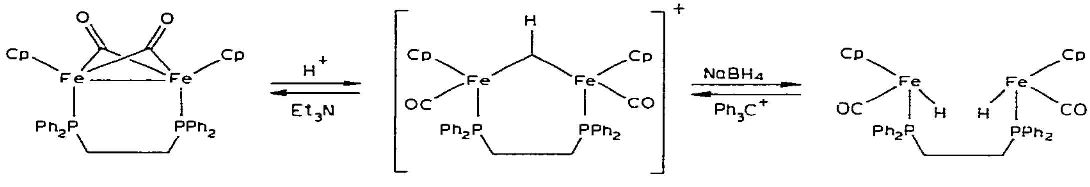
The reduction of μ_2-CO groups to μ_2-C_1 ligands, via μ_2-alkoxy (or -hydroxy) carbyne complexes, represents one approach to catalytic homogeneous hydrogenation of carbon monoxide, or Fischer Tropsch chemistry [5]. We therefore considered the possibility of Lewis acid O-complexation of a μ-CO on I followed by hydride addition at the activated μ-C atom. Borohydride reagents, however, readily react with II or III under a variety of reaction conditions and eliminate the in-

---

*All new compounds gave satisfactory C,H-elemental analyses, IR, and NMR data in accord with the proposed structures.

tact starting dimer I. Diisobutylaluminum hydride reversibly forms a 1 : 1 adduct in CH_2Cl_2 with I (analogous to II), which does not reduce (even with excess aluminum reagent) the μ-CO. Continuing studies are attempting to establish the appropriate Lewis acid activator and hydride donor for reduction of μ_2-CO ligands to μ_2-carbene groups.

The two electron Fe—Fe bond in I exhibits sufficient basicity to undergo protonation and form a cationic bridging hydride compound IV with trifluoroacetic acid: IR, $\nu_{CO}(CH_2Cl_2)$ 1953 cm^{-1}. Treatment of I in CH_2Cl_2 with $HBF_4 \cdot OMe_2$, followed by precipitation with ether, affords a green-air stable product (IV) in 90% yield: NMR (acetone) δ −36.8 ppm (t, J = 28 Hz, 1H, μ_2-H). One equivalent of triethylamine or even iodide (albeit slowly) quantitatively effects deprotonation of IV to I in CH_2Cl_2 solution. Analogous cationic μ_2-hydride compounds generated by protonation of a metal—metal bond have been detected for $Cp_2Fe_2(CO)_4$ [6] in acidic media and isolated from other bimetallic complexes [7].



(I) (IV) (V)

The cationic μ_2-hydride compound IV represents an intermediate stage in the stepwise hydrogenation of a Fe—Fe bond in I to the bimetallic dihydride complex V. Sodium borohydride converts IV in tetrahydrofuran (THF) solution to V, which can be isolated in 62% yield after chromatography on alumina with benzene. The dihydride V is a yellow-air-sensitive solid possessing chemical attributes of the analogous monomer* $CpFe(CO)Ph_3P(H)$ (VI) [8]: NMR, VI (C_6H_6): δ −12.7 ppm (d, J = 74 Hz, Fe—H), V (C_6H_6): δ −13.1 ppm (d, J = 74 Hz, 2H, Fe—H); IR, VI (CH_2Cl_2): ν_{CO} 1915 cm^{-1}, V (CH_2Cl_2): ν_{CO} 1910 cm^{-1}. Thus V also exhibits the free radical reactivity of most transition metal hydrides [10] and instantaneously forms the bimetallic dichloride VII in chloroform.

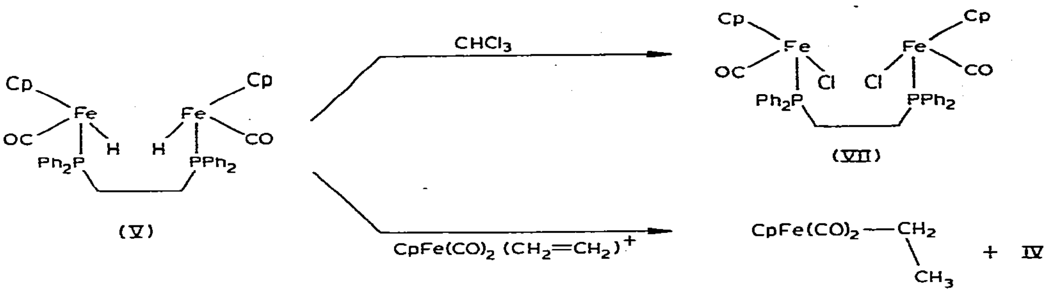
One equivalent of trityl carbocation or of the η^2-ethylene complex $CpFe(CO)_2(CH_2{=}CH_2)^+$ in CH_2Cl_2 rapidly and quantitatively converts V to IV. The reduction of the ethylene complex to the η^1-ethyl compound $CpFe(CO)_2CH_2CH_3$ corresponds to intermolecular transfer of hydride from a transition organometallic-hydride complex to a coordinated ligand**.

Interconversions between I $\rightleftharpoons$ IV $\rightleftharpoons$ V merit consideration for two reasons. (1) Overall conversion of I to V, stepwise hydrogenation of a metal—metal bond, exemplifies separate addition of a Lewis acid and a Lewis base to a metal—metal bond without disrupting the bimetallic unit [7a]. (2) The reverse sequence, V to

---

*A linked bimetallic-dihydride derivative of $CpMo(CO)_3H$, but joined through the Cp rings [9a], also undergoes reactions established for its monomer. Other symmetrical bimetallic dihydride complexes have been reported [7b,9b].

**A publication detailing the use of VI and other mononuclear organometallic hydride complexes in effecting intermolecular hydride transfer to coordinated alkene and carbene ligands is in press [15].



I, may serve as a prototypal mechanism of sequential hydride and proton transfer from two transition metal hydride fragments on adjacent metals in effecting hydrogenation of another coordinated substrate.

Facility of these bimetallic-reaction derives in part from the role of the μ-dppe ligand in associating the two halves of I. Indeed, the pronounced stability of I contrasts the inability to prepare unlinked bis-tertiary phosphine derivatives of $Cp_2Fe_2(CO)_4$ [11]. Attempts at studying μ-hydride complexes analogous with IV, but otherwise lacking the μ-diphosphine, further demonstrates the importance of the μ-dppe mechanical linkage.

Treatment of a yellow CH_2Cl_2 solution of VI with one half equivalent of trityl carbocation generates an emerald green solution and shifts its IR ν_{CO} of 1915 cm^{-1} to 1961 cm^{-1}. Further characterization of this product, tentatively formulated as $[CpFe(CO)Ph_3P]_2H^+$, proved difficult as it readily decomposes to $CpFe(CO)_2Ph_3P^+$. An analogous μ_2-H cation, $[CpMo(CO)_3]_2H^+$, has been reported as the result of the reaction of $CpMo(CO)_3H$ (two equivalents) with Ph_3C^+ [12]. Preliminary results are also in accord with VI interacting with one equivalent of either $CpFe(CO)_3{}^+$ or $CpFe(CO)_2THF^+$ and generating $CpFe(CO)_2$—H—Fe(CO)—Ph_3PCp^+, before decomposing to $CpFe(CO)_2Ph_3P^+$ and $Cp_2Fe_2(CO)_4$. $CpFe(CO)_2Ph_3P^+$ results from the known decomposition of $CpFe(CO)Ph_3P^+$ [13], and $Cp_2Fe_2(CO)_4$ comes from $CpFe(CO)_2H$ [14]. Clearly the dppe mechanical linkage within IV retards the detrimental dissociation to the neutral metal hydride and cationic coordinatively unsaturated halves, $CpFe(CO)H$—PPh_2CH_2-CH_2Ph_2P—$\overset{+}{Fe}(CO)Cp$, which prevails for the unlinked μ-H cations.

Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and to Wesleyan University for support of this research.

References

1 R.J. Haines and A.L. DuPreez, J. Organometal. Chem., 21 (1970) 181; Inorg. Chem., 11 (1972) 330.
2 (a) A. Alich, N.J. Nelson, D. Strope and D.F. Shriver, Inorg. Chem., 11 (1972) 2976; (b) D.F. Shriver, J. Organometal. Chem., 94 (1975) 259; J.R. Wilkinson and L.J. Todd, ibid., 118 (1976) 199.
3 D.F. Shriver, D. Lehman and D. Strope, J. Amer. Chem. Soc., 97 (1975) 1594; H.A. Hodali, D.F. Shriver and C.A. Ammlung, ibid., 100 (1978) 5239; P.D. Gavens and M.J. Mays, J. Organometal. Chem., 162 (1978) 389; B.F.G. Johnson, J. Lewis, A.G. Orpen, P.R. Raithby and G. Süss, ibid., 173 (1979) 187; H.A. Hodali and D.F. Shriver, Inorg. Chem., 18 (1979) 1236.
4 M. Nitay, W. Priester and M. Rosenblum, J. Amer. Chem. Soc., 100 (1978) 3620.
5 (a) J. Keister, J. Chem. Soc. Chem. Commun., (1979) 214; G. Fachinetti, ibid., (1979) 397; G. Mignani, H. Patin and R. Dabard, J. Organometal. Chem., 169 (1979) C19; (b) C. Masters, Adv. Organometal. Chem., 17 (1979) 61.

6 A. Davison, W. McFarlane, L. Pratt and G. Wilkinson, J. Chem. Soc., (1962) 3653; D.A. Symon and T.C. Waddington, J. Chem. Soc. (A), (1971) 953; D.C. Harris and H.B. Gray, Inorg. Chem., 14 (1975) 1215.
7 (a) H. Werner and W. Hoffmann, Ang. Chem. Int. Ed. Engl., 18 (1979) 158; (b) J.J. Bonnet, A. Thorez, A. Maisonnat, J. Galy and R. Poilblanc, J. Amer. Chem. Soc., 101 (1979) 5940; (c) M.P. Brown, R.J. Puddephatt, M. Rashidi and K.R. Seddon, J. Chem. Soc. Dalton Trans., (1978) 516.
8 S. Su and A. Wojcicki, J. Organometal. Chem., 27 (1971) 231; P. Kalck and R. Poilblanc, C.R. Acad. Sci. Paris, 274 (1972) 66; D.L. Reger and E.C. Culbertson, J. Amer. Chem. Soc., 98 (1976) 2789.
9 (a) P.A. Wegner and V.A. Uski, Inorg. Chem., 18 (1979) 646; (b) T.H. Tulip, T. Yamagata, T. Yoshida, R.D. Wilson, J.A. Ibers and S. Otsuka, ibid., 18 (1979) 2239.
10 R.A. Schunn in E.L. Muetterties (Ed.), Transition Metal Hydrides, Marcel Dekker, New York, N.Y., 1971, p. 244.
11 A.J. White, J. Organometal. Chem., 168 (1979) 197; R.J. Haines and A.L. duPreez, Inorg. Chem., 8 (1969) 1459.
12 W. Beck and K. Schloter, Z. Naturforsch. B, 33 (1978) 1214.
13 D.L. Reger, C.J. Coleman and P.J. McElligott, J. Organometal. Chem., 173 (1979) 171.
14 A. Davison, M.L.H. Green and G. Wilkinson, J. Chem. Soc., (1961) 3172.
15 T. Bodnar, S.J. LaCroce and A.R. Cutler, J. Amer. Chem. Soc., in press.