

Preliminary communication

REACTIVITY MODES OF BRIDGED BIMETALLIC $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_2\text{-}\mu\text{-dppe}$ WITH ELECTROPHILES. PREPARATION AND REACTIONS OF BIMETALLIC HYDRIDE COMPLEXES

S.J. LaCROCE, K.P. MENARD, and A.R. CUTLER*

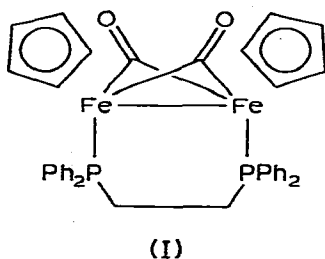
Department of Chemistry, Wesleyan University, Middletown, Connecticut 06457 (U.S.A.)

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Summary

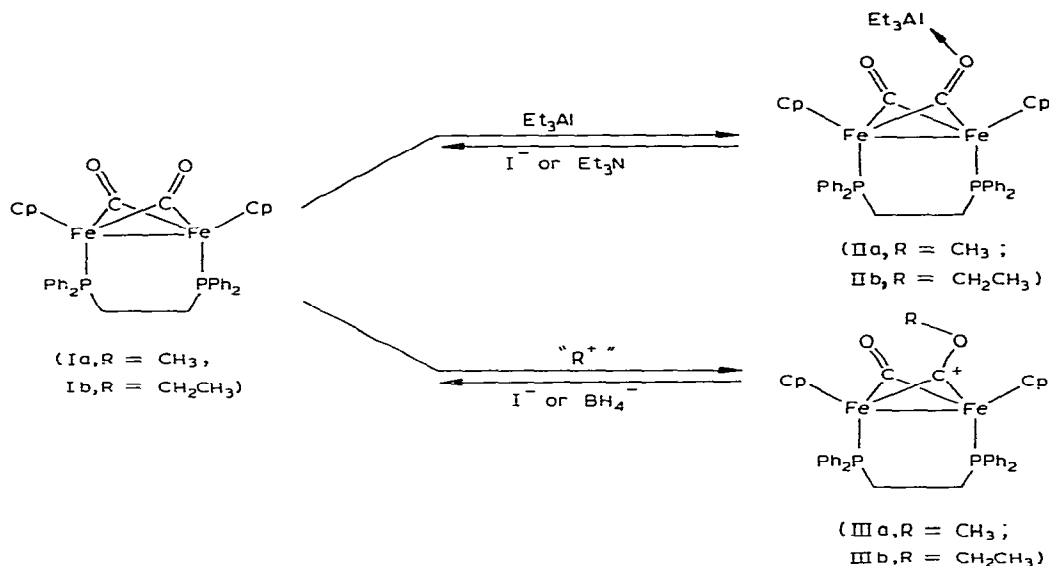
The complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_2\text{-}\mu\text{-dppe}$ (dppe = ethane-1,2-bisdiphenylphosphide) (I) reacts with electrophiles through a $\mu\text{-CO}$ and forms Lewis acid O-adducts with alkylating reagents (giving cationic μ_2 -alkoxycarbyne compounds) or with alkylaluminum compounds. Treatment of I with acid affords a stable μ_2 -hydride salt (IV), $[\text{CpFe}(\text{CO})]_2(\mu_2\text{-H})(\mu_2\text{-dppe})^+$, which serves as an intermediate in the stepwise hydrogenation (reversibly) of I to a bridged bimetallic dihydride, $[\text{CpFe}(\text{CO})\text{H}]_2\text{-}\mu_2\text{-dppe}$. This dihydride serves as a hydride donor, regenerating IV, towards Ph_3C^+ or $\text{CpFe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CH}_2)^+$ hydride acceptors. The necessity of the $\mu_2\text{-dppe}$ as a "mechanical linkage" in facilitating some bimetallic reactions is also established.

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



*Cp represents $\eta^5\text{-C}_5\text{H}_5$, 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 $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ [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.



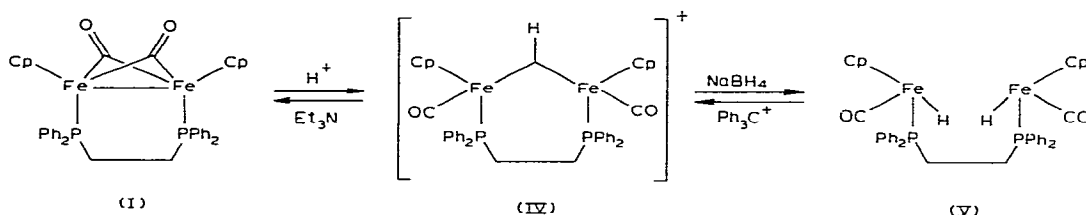
O-alkylated adducts III represent the first examples of either strictly bimetallic or cationic complexes possessing a μ_2 -alkoxycarbyne ligand. Examples of neutral and anionic μ_2 -alkoxycarbyne complexes have been prepared by alkylation of μ_2 -carbonyls on several anionic cluster systems [3]. Cationic binuclear iron complexes containing a bridging alkylidyne ligand $\mu_2\text{-CR}[\text{Cp}_2\text{Fe}_2(\text{CO})_3]^+$ have also been recently reported [4]. Until now, binuclear organometallic complexes bearing $\mu\text{-CO}$ ligands that are sufficiently nucleophilic for O-alkylation and conversion to μ -alkoxycarbyne groups have not been reported.

The reduction of $\mu_2\text{-CO}$ groups to $\mu_2\text{-C}_1$ 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 $\mu\text{-CO}$ on I followed by hydride addition at the activated $\mu\text{-C}$ 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 $\mu\text{-CO}$. Continuing studies are attempting to establish the appropriate Lewis acid activator and hydride donor for reduction of $\mu_2\text{-CO}$ ligands to $\mu_2\text{-carbene}$ 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, $\nu_{\text{CO}}(\text{CH}_2\text{Cl}_2)$ 1953 cm^{-1} . Treatment of I in CH_2Cl_2 with $\text{HBF}_4 \cdot \text{OME}_2$, followed by precipitation with ether, affords a green-air stable product (IV) in 90% yield: NMR (acetone) δ -36.8 ppm (t, $J = 28\text{ Hz}$, 1H, $\mu_2\text{-H}$). One equivalent of triethylamine or even iodide (albeit slowly) quantitatively effects deprotonation of IV to I in CH_2Cl_2 solution. Analogous cationic $\mu_2\text{-hydride}$ compounds generated by protonation of a metal—metal bond have been detected for $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ [6] in acidic media and isolated from other bimetallic complexes [7].



The cationic $\mu_2\text{-hydride}$ 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* $\text{CpFe}(\text{CO})\text{Ph}_3\text{P}(\text{H})$ (VI) [8]: NMR, VI (C_6H_6): δ -12.7 ppm (d, $J = 74\text{ Hz}$, Fe—H), V (C_6H_6): δ -13.1 ppm (d, $J = 74\text{ Hz}$, 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.

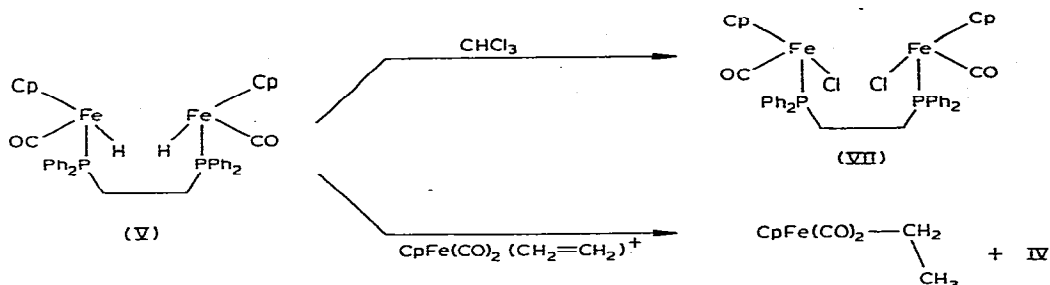
One equivalent of trityl carbocation or of the $\eta^2\text{-ethylene}$ complex $\text{CpFe}(\text{CO})_2\text{-(CH}_2=\text{CH}_2)^+$ in CH_2Cl_2 rapidly and quantitatively converts V to IV. The reduction of the ethylene complex to the $\eta^1\text{-ethyl}$ compound $\text{CpFe}(\text{CO})_2\text{CH}_2\text{CH}_3$ corresponds to intermolecular transfer of hydride from a transition organometallic-hydride complex to a coordinated ligand**.

Interconversions between $\text{I} \rightleftharpoons \text{IV} \rightleftharpoons \text{V}$ 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 $\text{CpMo}(\text{CO})_3\text{H}$, 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 $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ [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 $[\text{CpFe(CO)Ph}_3\text{P}]_2\text{H}^+$, proved difficult as it readily decomposes to $\text{CpFe(CO)}_2\text{Ph}_3\text{P}^+$. An analogous μ_2 -H cation, $[\text{CpMo(CO)}_3]_2\text{H}^+$, has been reported as the result of the reaction of $\text{CpMo(CO)}_3\text{H}$ (two equivalents) with Ph_3C^+ [12]. Preliminary results are also in accord with VI interacting with one equivalent of either CpFe(CO)_3^+ or $\text{CpFe(CO)}_2\text{THF}^+$ and generating $\text{CpFe(CO)}_2\text{H}-\text{Fe(CO)-Ph}_3\text{PCp}^+$, before decomposing to $\text{CpFe(CO)}_2\text{Ph}_3\text{P}^+$ and $\text{Cp}_2\text{Fe}_2(\text{CO})_4$. $\text{CpFe(CO)}_2\text{Ph}_3\text{P}^+$ results from the known decomposition of $\text{CpFe(CO)Ph}_3\text{P}^+$ [13], and $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ comes from $\text{CpFe(CO)}_2\text{H}$ [14]. Clearly the dppe mechanical linkage within IV retards the detrimental dissociation to the neutral metal hydride and cationic coordinatively unsaturated halves, $\text{CpFe(CO)H}-\text{PPh}_2\text{CH}_2-\text{CH}_2\text{PPh}_2-\text{Fe}^+(\text{CO})\text{Cp}$, which prevails for the unlinked μ -H cations.

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