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The reduction of bridged carbonyl groups as a new route to μ-methylene complexes of iron

Giancarlo Ortaggi and Roberto Paolesse *
Centro C.N.R. di Studio sui Meccanismi di Reazione, c/o Dipartimento di Chimica,
Università "La Sapienza", P. le Aldo Moro 2, 00185 Roma (Italy)

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Abstract

Reduction of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)_2$ and of its methylcyclopentadienyl derivative by calcium tetrakis(isopropoxy)alanate has given the corresponding $\mu\text{-}CH_2$ compounds, which were separated into the two geometrical isomers. The cobalt complex $(Ph_3P)_2Co_2(CO)_6$ gives $(Ph_3P)Co(CO)_3CH_3$. The role played by the presence of terminal carbonyl groups seems to rule out a direct reduction of μ-CO group to methylene group, but the reaction offers a new and rapid route to μ-methylene compounds.

Introduction

The involvement of methylene coupling as a mechanism of chain growth in the metal surface-catalyzed Fischer–Tropsch reaction has stimulated investigations of the chemistry of polinuclear alkylidene and alkylidyne complexes [1,2].

Considerable attention has been given to the preparation of bis-(η^5-cyclopentadienyl)-μ-methylene diiron tricarbonyl, $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ (**1**) by Casey [3], Pettit [4] and Ziegler [5], who independently described three methods of preparation of this compound. Casey and Pettit used condensation of two monomers to give **1**, whereas Ziegler carried out a Wittig reaction on the dimer $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)_2$ (**2**).

Results and discussion

We have now discovered a new convenient route to **1** that apparently involves direct reduction of a μ-CO group to the $\mu\text{-}CH_2$ function by calcium tetrakis(isopro-

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* Present address: Dipartimento di Scienze e Tecnologie Chimiche, II Università degli Studi di Roma "Tor Vergata", V. Orazio Raimondo, 00173 Roma (Italy).

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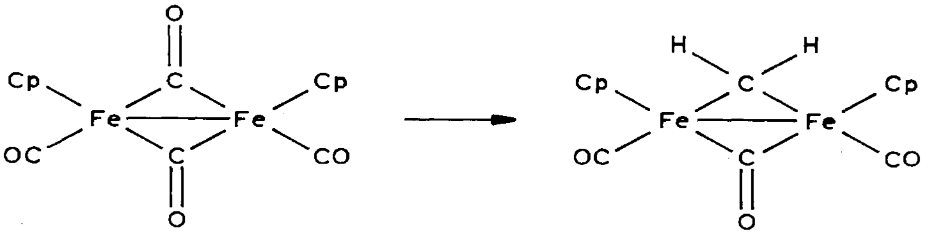
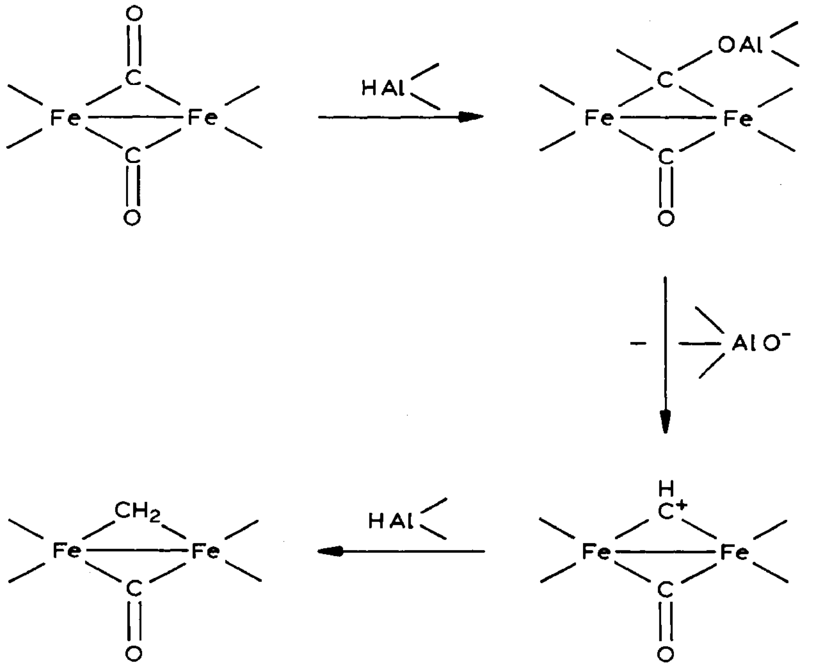
poxy)alanate [6], $Ca[Al(O\text{-}i\text{-}Pr)_2H_2]_2$ (commercially available as CAP-AL, Enichimica) (eq. 1).



(2) (1) (1)

The direct reduction of **2** by CAP-AL offers three major points of interest: (i) the reaction takes place quite rapidly and with good yields (ca. 70%, based on the starting dimer recovery), especially when compared with those from previously published methods; (ii) the reactivities of the bridged carbonyl groups towards reduction appear to be higher than those of the terminal ones. Since the analogous dimer $C_2H_4[(Ph)_2PFe(\eta^5\text{-}C_5H_5)(CO)]_2$ (3) does not react with $LiAlH_4$ or with CAP-AL, we conclude that at least one terminal carbon monoxide group is necessary for the reduction of bridged carbonyl group, probably furnishing the primary site of attack for the hydride. This suggestion is in agreement with some examples given in the literature [7]. In keeping with this, the terminal carbonyl groups of $Cr(CO)_6$ and $Mo(CO)_6$ are reduced by CAP-AL to methyl groups [8]); (iii) The μ-CO is converted to a μ-CH_2 rather than a μ-CHOH bridging group. This



Scheme 1

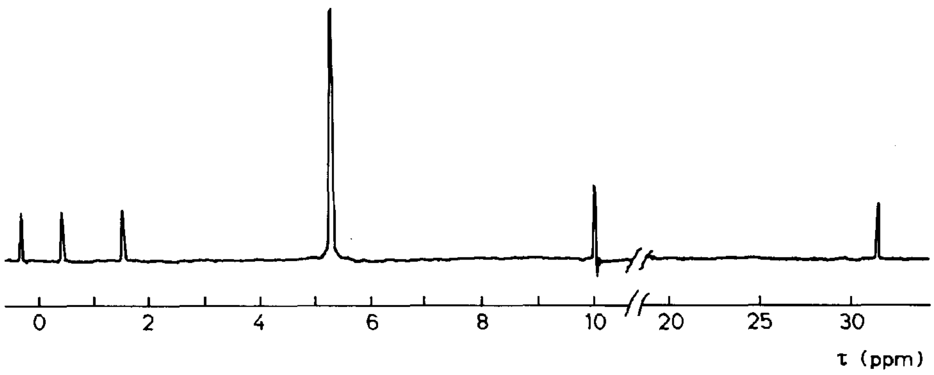


Fig. 1. ^{1}H NMR spectrum of compound **5**.

may be accounted for by assuming that in the intermediate departure of AlO^- group is facilitated by the stability of the μ-$\overset{+}{\mathrm{C}}$H-carbocation [9*] (Scheme 1).

Complex **2** can also be reduced by $LiAlH_4$ but in this case the yields of the μ-methylene complex are low (ca. 20%), and the predominant product is (η^5-C_5H_5)Fe(CO)$_2$CH$_3$ (**4**). This is due to the opening of the dimetallacyclopropane ring by the $LiAlH_4$; in effect **1** immediately reacts with $LiAlH_4$ at room temperature to give **4**. CAP-AL undergoes the same reaction more slowly than $LiAlH_4$, and use of $LiAlD_4$ gave the compound containing the CD_3 group.

These results show that hydride donors can open the dimetallacyclopropane ring despite the high negative charge on the μ-CH_2 carbon [10], and that the rupture of the μ-CH_2/iron bond is preferred to that of μ-CO/iron bond. They also show that the terminal carbonyls are not directly involved in the reaction with hydrides.

While mechanistic implications of the above reaction need further investigation, other information has been obtained by the isolation during the chromatographic separations of an intermediate which gives the ^{1}H NMR spectrum shown in Fig. 1. The most relevant features are the continued presence of the μ-CH_2 structure, as evidenced by the signals in the 0–2 τ region (mixture of *cis* and *trans* isomers), and the presence of an hydridic metal-linked hydrogen revealed by the peak at 30.5 τ. On the basis of the position of this signal, which strongly suggests that the hydrogen is linked to both the iron atoms (μ-H) [11], and from the presence of three signals in the 0–2 τ region, we formulate this intermediate as a mixture of *cis* and *trans* $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\mu\text{-}H)]^-$. (A plausible structure is represented by **5**).

The isolation of the binuclear H-bridged species and the incorporation of deuterium of $LiAlD_4$ are consistent with the transfer of H^- to the terminal carbonyl with the formation of an anionic formyl complex that undergoes deinsertion to the μ-H complexes, with the breaking of the iron–iron bond. A methylene-hydride/methyl tautomerism, which has been suggested to be characteristic of dimetallacyclopropanes containing metal-bound hydrogen ligands [12–14], leads to the formation of the methyl group.

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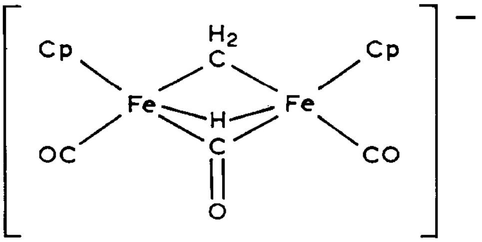
* Reference number with asterisk indicates a note in the list of references.



(5)

Because of the commercial availability of **2**, its conversion of **2** into **4** provide a faster and more convenient route to **4** than those previously described [15].

The selective reducing properties of CAP-AL have been successfully utilized in the preparation of $(\eta^5\text{-}CH_3C_5H_4)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ from the corresponding dicarbonyl complex.

The reduction of $(Ph_3P)_2Co_2(CO)_6$ (**6**) by CAP-AL affords the monomer $(Ph_3P)Co(CO)_3CH_3$ (**7**). The course of the reaction may be reasonably interpreted in terms of the intermediate formation of the μ-methylene complex **8**, which is rapidly reduced to the methyl derivative by the excess of reagent. Thus the behaviour of the cobalt dimer **6** is quite similar to that of the iron dimer **2**.

Experimental

All reactions were carried out under nitrogen. Solvents were dried over Na/K alloy. CAP-AL was purchased as toluene solution from Assoreni, $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)_2$ and $(Ph_3P)_2Co_2(CO)_6$ were obtained from Strem Chemical Company and used without further purification. $(\eta^5\text{-}CH_3C_5H_4)_2Fe_2(CO)_2(\mu\text{-}CO)_2$ [2] and $C_2H_4[(Ph_2P)Fe(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]$ were prepared and purified by literature methods.

IR spectra were recorded on a Perkin–Elmer model 983 spectrophotometer as $CHCl_3$ solutions. NMR spectra were recorded on a Bruker WP 80 SY instrument with $CDCl_3$ solutions containing tetramethylsilane as internal standard.

Preparation of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$

A toluene solution of CAP-AL (4.8 ml, 11 mmol) was added dropwise to an anhydrous diethyl ether solution of **2** (1 g, 2.8 mmol) and the mixture was stirred for 1 h. After hydrolysis and evaporation of the organic phase, the residue was subjected to chromatography on a silica gel column. Elution with benzene/petroleum ether (1/1) gave three bands: the first contained **4** (0.06 g, 20%) (identical to an authentic speciman [15]); the second band was **1** (0.4 g, 70%), and the third band was the starting dimer (0.43).

As noted by other workers [3–5] the separation of **1** from **2** is difficult, but may be accomplished by treating the crude product mixture with an excess of 1,2-bis(diphenylphosphino)ethane which converts the starting dimer into its diphos derivative, which is easily separated from **1**.

The *cis* and *trans* isomers were separated by chromatography on an alumina column with elution with benzene/petroleum ether (1/1), this yielded the red-violet *trans*-isomer (0.13 g, 33%) and the orange-red *cis*-isomer (0.27 g, 67%).

The spectral data for the two isomers were in full agreement with those previously presented [3–5].

The complex $(\eta^5\text{-}CH_3C_5H_4)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ was prepared analogously from the relevant dimer.

cis-$(\eta^5\text{-}CH_3C_5H_4)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$. IR ν(CO), cm^{-1} $CHCl_3$): 1985s, 1920s, 1785s. ^{1}H NMR (δ, ppm, $CDCl_3$): 2.10 (s, 6H, CH_3); 4.36–4.66 (m, 8H, C_5H_4); 8.50 (s, 1H, CH_2); 9.94 (s, 1H, CH_2).

trans-$(\eta^5\text{-}CH_3C_5H_4)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$. IR ν(CO) cm^{-1}, $CHCl_3$): 1970s, 1900s, 1780s. ^{1}H NMR (δ, ppm, $CDCl_3$): 2.10 (s, 6H, CH_3); 4.36–4.75 (m, 8H, C_5H_4); 9.44 (s, 2H, CH_2).

Reductions of **2** (1 g, 2.8 mmol) with $LiAlH_4$ were carried out as before and gave 0.26 g (70%) of **4** and 0.13 g (20%) of **1**, along with the starting dimer (recovery 0.35 g). Use of minor amounts of $LiAlH_4$ in the reduction gave **1** in the same yield, relative to **4**, but the total conversion of **2** was less.

Preparation of $(Ph_3P)Co(CO)_3CH_3$

A toluene solution of CAP-AL (2.2 ml, 5 mmol) was added to an anhydrous diethyl ether suspension of **6** (1 g, 1.2 mmol). During the reaction the solution became bright yellow and the reagent dissolved almost completely. After hydrolysis, filtration and partial evaporation of the solvent under a stream of nitrogen, the solution was kept at −80 °C to give air-sensitive crystalline yellow material with properties, identical to those of an authentic speciman prepared by the literature method.

Reaction of 1 with hydrides

An excess of $LiAlH_4$ (40 mg, 1.1 mmol) was added to a dry THF solution of **1** (0.2 g, 0.6 mmol). The colour of the solution changed from red to yellow. Hydrolysis and evaporation of solvent afforded **4** (0.05 g, 0.27 mmol) (90% yield calculated for a 1/1 molar ratio).

When the reaction was carried out with CAP-AL the colour change was slow. Hydrolysis and the evaporation of solvent after 1/2 h afforded red crystals which gave the ^{1}H NMR spectrum shown in Fig. 1 (C_6D_6 as solvent). After longer times (3 h) the solution became yellow and the hydrolysis afforded **4**.

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8 Unpublished results from this laboratory.

9 Preliminary experiments show that $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}\overset{+}{C}R)$ cations are appreciably stabilized.

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