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Preparation and Properties of Bis(η^5-cyclopentadienyl)-μ-methylene-diiron Tricarbonyl and Some of Its Derivatives

S. C. Kao,* Paul P. Y. Lu,*† and R. Pettit‡

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

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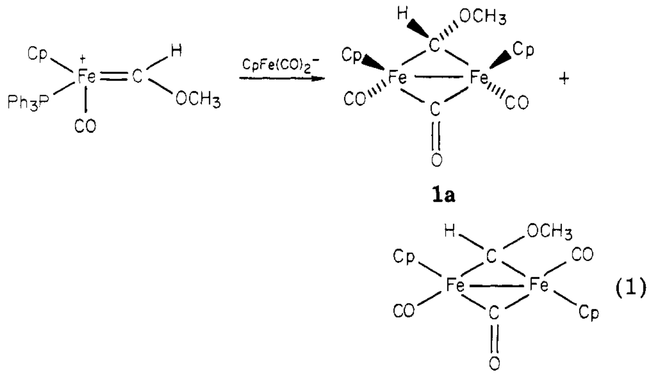
The reaction of $CpFe(CO)(PPh_3)(CHOCH_3)^+BF_4^-$ with $K^+CpFe(CO)_2^-$ leads to the formation of a 3:1 mixture of the cis- and trans-μ-methoxymethylene complex $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHOCH_3)$ (1). This complex reacts with acid or Ph_3C^+ to produce the bridging methylidyne complex $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH)^+$ (7). Treatment of the cationic methylidyne complex 7 with $NaBH_4$ gives a 3.2:1 mixture of the cis and trans parent bridging methylene complex $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ (9). The bridging methylene complex reacts with hydrogen to produce the dihydro form of the methylene ligand. Reaction of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_3)^+BF_4^-$ (6) with base generates the μ-vinylidene complex $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$. The treatment of 6 with $NEt_4HFe(CO)_4$ leads to the formation of a 5:1 mixture of the cis and trans-μ-ethylidene complex $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (11). The ethylidene complex 11 reacts with Ph_3C^+ to give a μ-σ,π-vinyl complex $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}\sigma,\pi\text{-}CHCH_2)^+$ (15). Treatment of 15 with various RLi reagents results in the formation of the corresponding bridging alkylidene complex $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_2R)$.

Introduction

In the previous paper[1] we discussed the preparation and chemical properties of the μ-methylene-diiron octacarbonyl and several of its derivatives. In this paper we discuss the preparation and properties of related systems in which each iron atom carries a cyclopentadienyl ligand, viz., bis(η^5-cyclopentadienyl)-μ-methylene-diiron tricarbonyl. The three compounds of principal interest are the bridging parent methylene system, bridging methoxymethylene complex, and bridging ethylidene complex. The point has been made previously that such bridging methylene systems may serve as useful models for interpretation of the chemistry of several important catalytic processes.

Results and Discussion

Bis(η^5-cyclopentadienyl)-μ-(methoxymethylene)-diiron tricarbonyl (1) is formed as a mixture of cis (a) and trans (b) isomers following reaction of the $CpFe(CO)(PPh_3)(CHOCH_3)^+$ (Cp = η^5-C_5H_5) ion[2] with $CpFe(CO)_2^-$ in acetonitrile at 0 °C (eq 1). A mixture of 1a and 1b was isolated as a stable red solid. The IR spectrum of the methoxy derivative 1 in CH_2Cl_2 displays bands at 1986 (vs), 1941 (m), 1776 (s), and 1080 (m) cm^{-1}, the latter two being indicative of bridging CO and OCH_3 groups, respectively. Separation of 1a and 1b by chromotography at room temperature was not successful. However, both isomers can be distinguished by the ^1H NMR spectroscopy at ambient temperature. In the ^1H NMR spectrum of 1 in $CDCl_3$, the equivalent protons of the two Cp rings of the cis isomer appear as a singlet at δ 4.67 and the nonequivalent protons of the two Cp rings of the trans isomer appear as two very close singlets of equal intensity at δ 4.70 and 4.71, respectively. The chemical shift for the methylene proton which is syn to the Cp rings of the cis form is δ 12.48,[3] and that of the trans form is δ 11.62. The ratio between these two singlets is 3:1 in favor of the cis form. In the ^{13}C NMR spectrum of 1, the methylene carbon resonances appearing at δ 216.7 and 214.0 are assigned to 1a and 1b, respectively.



1a

1b

(1)

The course for the formation of methoxy derivative 1 may involve a nucleophilic addition of $CpFe(CO)_2^-$ on $CpFe(CO)(PPh_3)(CHOCH_3)^+$ to give $Cp_2Fe_2(CO)_3(PPh_3)(\mu\text{-}CHOCH_3)$ followed by dissociation of phosphine ligand and formation of a metal-metal bond. A similar reaction, between the terminal methoxymethylene complex $CpFe(CO)_2(CHOCH_3)^+$ and $CpFe(CO)_2^-$, however, did not produce methoxy derivative 1. The products isolated from this reaction were $[CpFe(CO)_2]_2$ (2) as well as $CpFe(CO)_2CH_3$.[4] This synthetic approach, by combining mononuclear metal carbene complexes with nucleophilic metal species, has been employed by Stone and co-workers[5] in the synthesis of mixed-metal systems of bridging methoxymethylene derivatives.

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† Department of Chemistry, University of California, Los Angeles, CA 90026.

‡ Deceased, December 10, 1981.

(1) Sumner, C. E., Jr.; Collier, J. A.; Pettit, R., manuscript in preparation.

(2) Cutler, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 604–606.

(3) A third isomer in which the methylene proton is anti to both Cp rings was ruled out on the basis of the ^1H NMR data of 1 as compared to other systems of similar structure (e.g., complexes 9 and 11). Failure to observe this isomer might be due to the increased steric hindrance caused by placing three bulky groups (two Cp rings and one OCH_3) on the same side of the molecule.

(4) Yeh, J., unpublished work.

(5) (a) Ashworth, T. V.; Berry, B.; Howard, J. A. K.; Laguna, M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1979**, 43–45. (b) Ashworth, T. V.; Howard, J. A. K.; Laguna, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1953–1960. (c) Berry, M.; Howard, J. A. K., Stone, F. G. A. *Ibid.* **1980**, 1601–1608. (d) Ashworth, T. V.; Berry, M.; Howard, J. A. K.; Laguna, M.; Stone, F. G. A. *Ibid.* **1980**, 1615–1624. (e) Howard, J. A. K.; Mead, K. A.; Moss, J. R.; Navarro, R.; Stone, F. G. A.; Woodward, P. *Ibid.* **1981**, 743–750.

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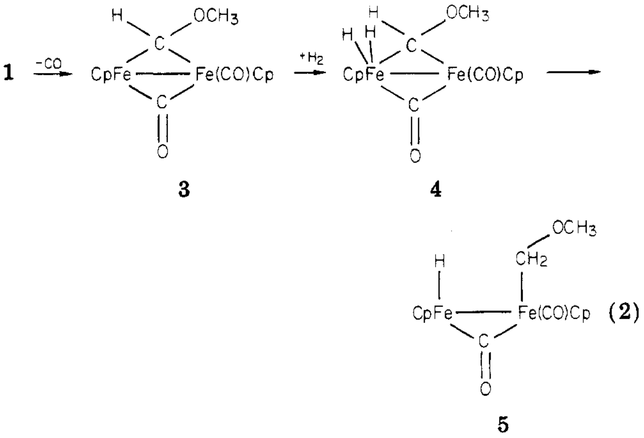
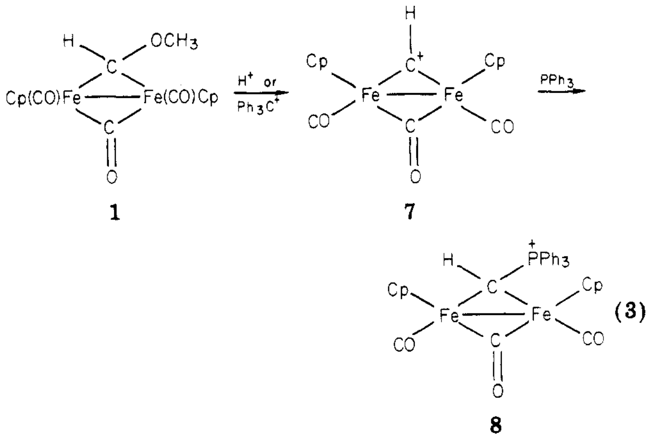
When methoxy derivative **1** is treated with hydrogen (270 psi) at 150 °C in tetrahydrofuran (THF), dimethyl ether and methane are produced, as well as $[CpFe(CO)_2]_2$ (**2**). The dimethyl ether formation may involve prior loss of a CO ligand from **1** to form **3**, which then undergoes oxidative addition of H_2 to give **4**, followed by reductive elimination to the methoxymethyl complex **5** (eq 2). The reductive elimination of **5** would lead to dimethyl ether formation. Such a reaction scheme has been suggested earlier in the hydrogenation reaction of the bridging methylene complex $Fe_2(CO)_8CH_2$.[6] Formation of dimethyl ether from the hydrogenation reaction of methoxy derivative **1** is interesting since compounds of this type may represent a possible building block for small oxygen-containing molecules such as methanol and ethylene glycol.



3 **4** **5**

Treatment of methoxy derivative **1** in CH_2Cl_2 with $HBF_4{\cdot}OEt_2$ at 0 °C gives an intense red solution which readily decomposes with formation of a red-brown precipitate. The IR spectrum of the red solution displays bands at 2050 (vs), 2020 (m), and 1860 (s) cm^{-1}. The resemblence between this IR spectrum and that of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_3)^+BF_4^-$ (**6**)[7] is indicative of the presence of a methylidyne complex $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH)^+BF_4^-$ (**7**) in the solution. The proposed structure of **7** is supported by the ^1H NMR study of the solution at low temperature, as well as by trapping the compound with triphenylphosphine. The ^1H NMR spectrum of **7** in CD_2Cl_2 at −60 °C features a very low-field singlet at δ 22.56 (1 H) for the methine proton and a singlet at δ 5.28 (10 H) for the two cyclopentadienyl ring protons. When the CH_2Cl_2 solution of **7** was quenched with triphenylphosphine, followed by addition of diethyl ether, an α-phosphonium adduct **8** was isolated (eq 3). Complex **8**, obtained as a red-brown solid, was found to exist in the cis form only, as indicated by the spectroscopic studies. The IR spectrum of **8** displays bands at 1993 (vs), 1958 (w), and 1810 (s) cm^{-1}. The ^1H NMR spectrum of **8** features a doublet (1 H, J = 1.5 Hz) at δ 9.96 assigned to the methine proton, a multiplet (15 H) at δ 7.50–8.00 to the aryl protons, and a singlet (10 H) at δ 5.25 attributed to the equivalent protons of the two Cp rings.

Treatment of methoxy derivative **1** dissolved in CH_2Cl_2 (0 °C) with an equal molar amount of $Ph_3{}^+BF_4^-$ produces the similar red solution which, upon treating with triphenylphosphine and diethyl ether, gives the same α-phosphonium complex **8**. It is evident from these observations that both acid and Ph_3C^+ selectively abstract the α-methoxide from methoxy derivative **1** and generate the methylidyne complex **7**. Similar α-alkoxide abstractions have been observed in mononuclear and dinuclear systems for synthesizing terminal methylidene[8] and bridging alkylidyne complexes, respectively.[1,9]



1 **7** **8**

When an acetonitrile solution of compound **7** is treated with sodium borohydride, a red slurry was produced which leaves an orange-red residue upon removal of solvent. Column chromatography of this orange-red residue on alumina results in the isolation of two components. An orange-red solid **9a**, which is the major component, displays IR bands at 1985 (vs), 1940 (m), and 1780 (s) cm^{-1}. The mass spectrum of this compound indicates a parent peak *m/e* at 340 with sequential loss of 3 CO and a mass unit of 14. ^1H NMR of **9a** features three diagnostic downfield singlets at δ 10.33, 9.63, and 8.43. The relative intensity of these peaks, however, varies with time. A steady-state is finally reached, at which point the relative ratio of these three singlets is 1.6:1:1.6. The second component, **9b**, which is isolated as a pink-red solid, also possesses a parent peak at *m/e* 340 in the mass spectrum. In IR, the spectrum of **9b** displays bands at 1985 (vs), 1940 (vs), and 1780 (s) cm^{-1}. ^1H NMR of **9b** also features three diagnostic downfield singlets with the same chemical shifts as that of complex **9a**, but different in relative intensity. The relative intensity of the three singlets again varies with time, and later reach a steady-state with the same ratio as in the case of complex **9a**. On the basis of these spectroscopic studies, compounds **9a** and **9b** were assigned as the cis and trans isomers of the bridging methylene complex $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$.[10] It is also concluded that **9a** and **9b** interconvert in solution with the final equilibrium cis/trans ratio of 3.2:1. The singlet at δ 10.33 is assignable to the proton of the methylene moiety which is syn to the cyclopentadienyl ring in the cis form and the singlet at δ 8.43 to the other proton of the CH_2 moiety.

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(6) Sumner, C. E., Jr.; Riley, P. E.; Davis, R. E.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 1752–1754.

(7) Nitay, M.; Priester, W.; Rosenblum, M. *J. Am. Chem. Soc.* **1978**, *100*, 3620–3622.

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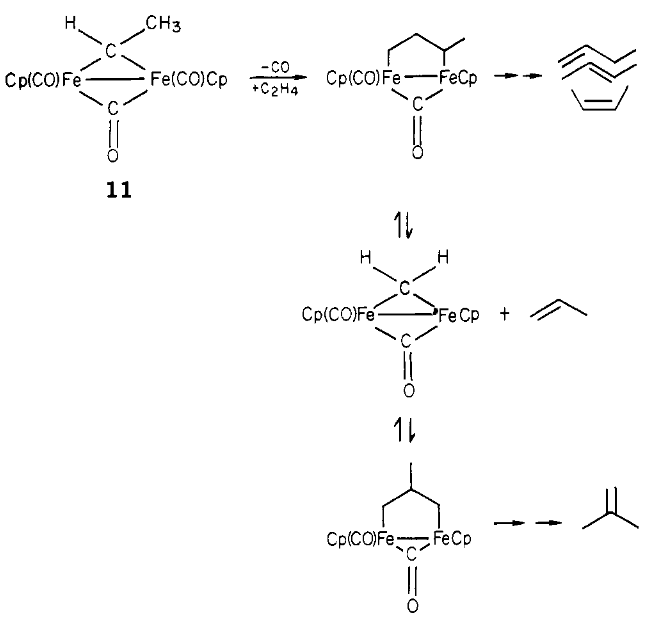
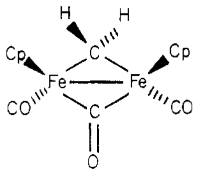
(9) Howard, J. A. K.; Jeffery, J. C.; Laguna, M.; Navarro, R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1981**, 751–762.

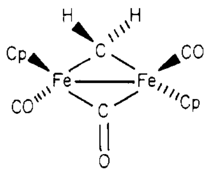
(10) $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ has been prepared by the reaction of $CpFe(CO)L(CH_2Cl)$ (L = CO, PPh_3) and $CpFe(CO)_2K$. Thiel, C. H.; Kao, S. C., unpublished work. This compound has also been recently prepared by the reaction of $[CpFe(CO)_2]_2$ and $CH_2{=}PPh_3$: Korswagen, R.; Alt, R.; Ziegler, M. L. *Angew. Chem.*, in press, as well as by the reaction of $CpFe(CO)_2CH_2O_2CCH_3$ and $CpFe(CO)_2K$: Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.*, submitted for publication and private communication.

Scheme I



The two methylene protons of the trans form experience identical magnetic environment that is assignable to the singlet at δ 9.63.


9a


9b

A ruthenium analogue of **9** has been prepared by Knox and co-workers.[11] Other complexes which possess a CH_2 group bridging two bonded transition-metal atoms have recently been reported.[12]

Treatment of the bridging methylene complex **9** with hydrogen (270 psi) at 150 °C in THF produced methane as well as $[CpFe(CO)_2]_2$. Methane formation may involve the same reaction sequence outlined earlier for the formation of dimethyl ether (eq 2).

We also wish to report a different approach in the transformation of the coordinated carbonyl ligand into the μ-alkylidenes and related novel compounds based on the iron dimer complex **2**.

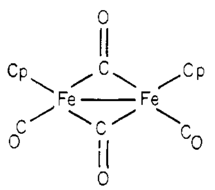
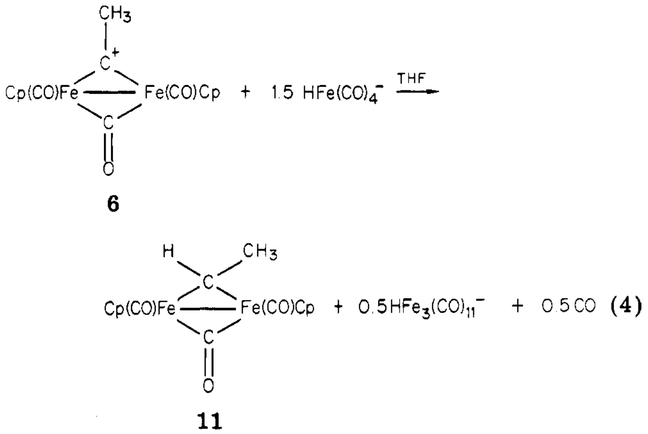

2

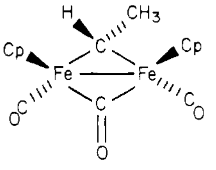
Table I. ^1H NMR Data of Complex $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (**11**) in Benzene-d_6 at 30 °C

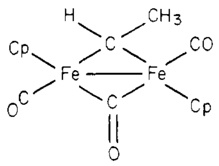
	ratio	δ(CH_3)	δ(C_5H_5)	δ(H)	*J*, Hz
11a	5	3.30 (d, 3 H)	4.16 (s, 10 H)	11.60 (q, 1 H)	8.0
11b	1	3.24 (d, 3 H)	4.28 (s, 5 H) 4.36 (s, 5 H)	10.80 (q, 1 H)	8.0

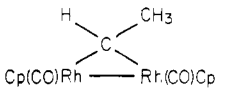
Treatment of **2** with MeLi, followed by acidification, afforded the μ-ethylidyne complex **6**.[7] The reaction of **6** with $NEt_4HFe(CO)_4$ (**10**) produced the desired μ-ethylidene complex **11** (eq 4). The IR absorptions of the carbonyls of **11** are analogous to those of the parent dimer **2** but exhibit a bathochromatic shift presumably due to the weaker π acceptability of the ethylidene group than the carbonyl ligand.

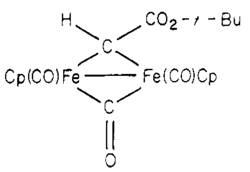


The ^1H NMR spectrum of **11** shows that it is mixture of two isomers designated as **11a** and **11b** (Table I). The three-dimensional X-ray structure of **11a** was performed by Davis and co-workers.[13] Their results indicated that the alkylidene carbon is sp^3 hybridized. The reaction described in eq 4 represents a convenient preparation of a binuclear alkylidene complex from the corresponding alkylidyne complex.[14] A photochemical entry for **11** and its ruthenium analogue was recently reported.[15] One related dirhodium complex **12**[16] and one diiron complex **13**[17] were known.


11a


11b


12


13

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[11] Davies, D. L.; Dyke, A. F.; Knox, S. A. R.; Morris, M. J. *J. Organomet. Chem.* **1981**, *215*, C30–C32.

[12] (a) Review: Herrmann, W. A. *Adv. Organomet. Chem.*, in press. (b) See also: Isobe, K.; Andrews, D. G.; Mann, B. E.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1981**, 809–810. Green, M.; Hankey, D. R.; Murray, M.; Orpen, A. G.; Stone, F. G. A. *Ibid.* **1981**, 688–691. Steinmetz, G. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 1278–1279. Shapley, J. R.; Sievert, A. C.; Chruchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 6975–6977.

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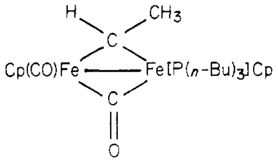
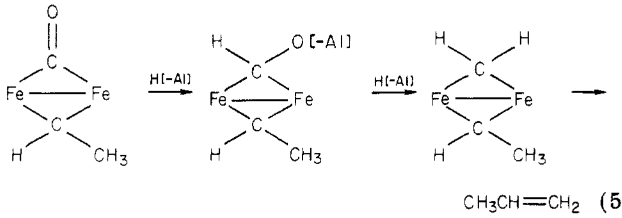
Complex **11** displays cyclopropanation activity. In the presence of acid, styrene is converted into 1-methyl-2-phenylcyclopropane (ca. 5%). This cyclopropanation activity is not observed in the absence of acids, under either thermal or photolytic conditions. It is not yet clear whether this cyclopropanation activity of **11** bears any resemblence to the mononuclear cases.[18]

Photolysis of **11** with P(n-Bu)$_3$ afforded complex **14** based on the spectroscopic data [IR (THF) 1920 (s), 1730 (m) cm^{-1}; ^{1}H NMR (benzene-d_6) δ 0.70–1.70 (m, 48 H, extra hydrogens are due to residual phosphine), 3.56 (d, 3 H, J = 8.0 Hz), 4.26 (m, 5 H), 4.52 (s, 5 H), 8.59 (d of q, 1 H, J_{P-H} = 17.0 Hz, J_{H-CH_3} = 8.0 Hz)]. However, complex **11** did not react with PPh$_3$ either photochemically or upon prolonged heating.



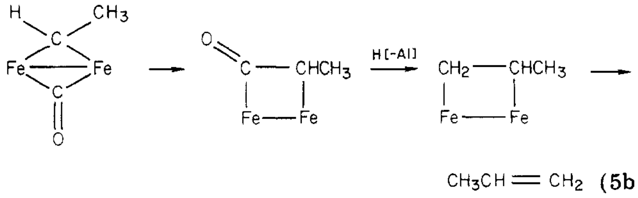
14

Atwood et al. recently reported that hydride reagents (i.e., LiAlH$_4$) could reduce iron dimer complex **2** into C$_1$ to C$_4$ hydrocarbons, with ethylene as the major product in the primary process.[19] The formation of ethylene from **2**, but not from mononuclear model compounds, suggests the process of methylidene coupling as in the hydride reduction of metal carbonyls.[20] We anticipated that complex **11** and LiAlH$_4$ would produce mainly C$_3$ primary product(s), provided that the coupling mechanism of alkylidenes is operative (eq 5a). Indeed, **11** and LiAlH$_4$ did afford C$_1$ to C$_4$ hydrocarbons (40% yield). The relative distribution was methane (7.3%), ethylene (1.4%), ethane (3.5%), propene (64.7%), propane (7.9%), 1-butene (10.1%), and n-butane (5.2%). However, an alternative mechanism involving CO insertion into iron–alkylidene bond is also reasonable (eq 5b), as in the mononuclear cases of Mn and Ni.[21]



(5a)

H[-Al] ≡ LiAlH$_4$
other ligands on complex 11 omitted for clarity



(5b)

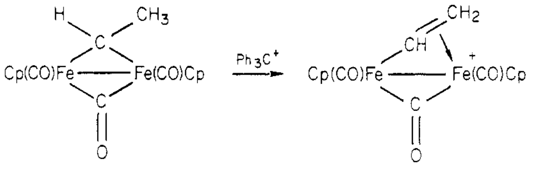
H[-Al] ≡ LiAlH$_4$
other ligands on complex 11 omitted for clarity

Compound **11** was allowed to react with CO and H$_2$ at 600 psi and 165 °C. The gas phase presented trace amounts of methane, ethylene, propene, and propane. In the solution phase, the dimer complex **2** and cyclopentadiene were observed. Most significantly, propanal (ca. 10%) was also detected. One possible mechanism for the formation of propanal is analogous to the one proposed for the formation of acetaldehyde from the diiron octacarbonyl μ-methylene complex with H$_2$.[6] With H$_2$ alone, the reaction of **11** produced ethane, and no propanal could be detected.

When the μ-ethylidene complex **11** was treated with ethylene, methane (trace), propene (3.6%), and C$_4$ hydrocarbons (2.2%) were obtained. Of the C$_4$'s, 1-butene, 2-butene, and even isobutylene were observed. The presence of propene and isobutylene is explicable by a binuclear olefin methathesis (Scheme I).

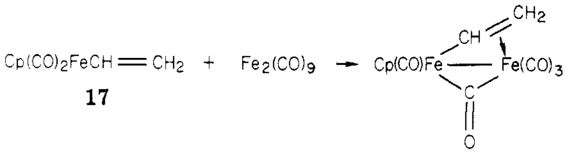
Olefin metathesis involving bimetallocycloalkanes was recently proposed to occur over ditungsten complexes.[22] Pettit et al. reported that the reaction between ethylene and μ-CH$_2$ iron complex afforded propene, and the intermediacy of a binuclear metallocycle was suggested.[6] The recent isolation of a dicobalt cyclopentane complex substantiates the plausibility of binuclear metallocycles in the μ-alkylidene–olefin interaction.[23]

β-Hydride abstraction of metal alkyls and its reverse reaction are well-known processes in mononuclear organometallic complexes.[24] When the μ-ethylidene compound **11** is treated with trityl cation (Ph$_3$C$^+$BF$_4^-$), a purple solid **15** is obtained (eq 6). The structure of μ-σ,π-vinyl complex **15** was deduced from spectroscopic and elemental analyses. The infrared spectum of **15** is analogous to the μ-ethylidyne cation **6**, whereas the ^{1}H NMR spectrum reveals the characteristic ABX pattern for the vinylic protons and two Cp signals (vide infra). ^{13}C NMR studies verified the presence of α-vinylic carbon (δ 184.94 (d)) and β-vinylic carbon (δ 64.77 (t)). One related neutral compound **16** was reported, which is prepared from the thermal reaction between mononuclear vinyl complex **17** and Fe$_2$(CO)$_9$ (eq 7).[25] The reverse reaction of Equation 6, complex **15** with NaBH$_4$, gives back the μ-ethylidene complex **11**. The reaction of complex **15** with organolithium RLi (R = CH$_3$, n-Bu) produced the corresponding μ-CHCH$_2$R complexes **18**. Even more surprising is that



(6)

11 **15**



(7)

17

16

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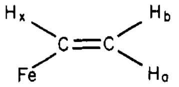
Table II. Characterization of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_2R)$ (18)

	mp, °C	high-resoln mass spectrosc		IR, cm^{-1}	^1H NMR, δ (benzene-d_6)
		calcd	found		
18a, R = CH_3	170–171 dec	367.9797	367.9808	1975 (s)[a] 1935 (w) 1778 (m)	1.41 (t, 3 H, J = 7.6 Hz) 3.27 (d of q, 2 H, J = 7.6, 7.9 Hz) 4.19 (s, 10 H) 11.40 (t, 1 H, J = 7.9 Hz)
18b, R = n-Bu	120–122 dec	410.0267	410.0278	1976 (s)[a] 1934 (w) 1775 (m)	0.75–2.14 (m, 9 H) 3.39 (d of t, 2 H, J = 7.9, 8.4 Hz) 4.25 (s, 10 H) 11.67 (t, 1 H, J = 8.4 Hz)
18c, R = OCH_3	115–116 dec	383.9746	383.9755	1978 (s)[b] 1938 (m) 1788 (m)	3.51 (s, 3 H) 4.55 (d, 2 H, J = 7.8 Hz) 4.79 (s, 10 H) 11.40 (t, 1 H, J = 7.8 Hz)

[a] In CH_2Cl_2. [b] In THF.

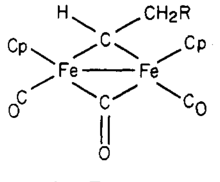
Table III. ^1H NMR Data of $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)]^+BF_4^-$ (15) and Related Complexes[a]



		δ(Ha)	δ(Hb)	δ(Hx)	δ(Cp)	J_{ab}	J_{ax}	J_{bx}
15A	$(CD_3)_2CO$; CD_3CN (−20 °C)	2.98	5.15	12.75	5.58 5.76	2.3	16.2	9.0
15B	CD_3CN	5.53	5.80	7.13	4.83 4.88	2.0	12.0	7.0
17	$CDCl_3$	5.42	5.90	7.14	4.81	1.4	17.4	9.0
16	$CDCl_3$	1.70	2.20	10.91	5.00	1.4	11.8	7.3

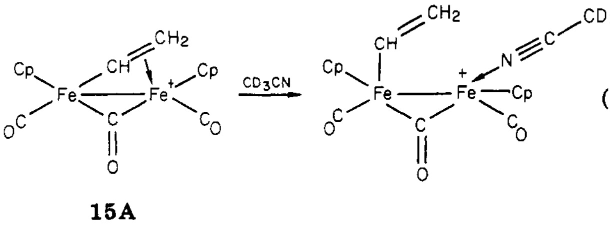
[a] J (coupling constant) in Hz. 15 is not soluble in $CDCl_3$.

complex 15 reacts with methanol to give novel μ-$CHCH_2OCH_3$ complex, which in turn can be converted back to 15 upon treatment with acid. The characterizations of compounds 18 are listed in Table II.



18a, R = CH_3
b, R = n-Bu
c, R = OCH_3

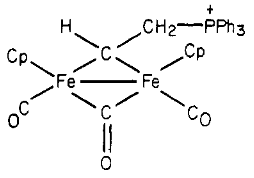
An intriguing phenomenon was observed during the ^1H NMR studies on the μ-vinyl complex 15. Two types of ^1H NMR ABX-pattern spectra can be observed from the vinylic protons in 15. A freshly prepared sample of 15 in acetonitrile-d_3 at <−10 °C shows the first type (15A-type) spectrum; upon warming to ambient temperature in the probe (ca. 30 °C), a second type (15B-type) spectrum is observed (see Table III). This transformation was found to be irreversible. In acetone-d_6, 15 displays A-type spectrum (−30 to +30 °C). Addition of an equal volume of acetonitrile-d_3 to the acetone-d_6 solution of 15 can cause the B-type spectrum to develop. Both A- and B-type spectra, along with the spectra of the two model compounds 16 and 17, are listed in Table III. The similarity of 15A with 16 and 15B with 17, in terms of δ and/or J values suggest the following transformation (eq 8).



(8)

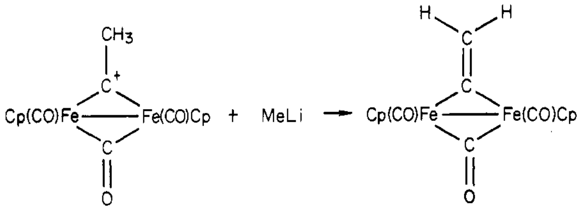
15A

When triphenylphosphine (1.1 equiv) was added to an acetone solution of 15, a binuclear complex 19 was obtained. ^1H NMR and IR data suggest structure 19 [IR (acetone) 1985 (vs), 1940 (w), 1793 (m) cm^{-1}; ^1H NMR (CD_3CN) δ 4.65 (s, 10 H), 4.99 (d of d, 2 H, J = 14.1, 7.5 Hz), 7.63–8.28 (m, 15 H), 10.88 (d of t, 1 H, J = 17.7, 7.5 Hz)].



19

μ-Hydroxycarbene complexes and their possible role(s) in the hydrogenation of carbon monoxide have received much attention recently.[26] We have attempted to prepare bridging hydroxycarbene complexes. μ-Ethylidyne complex 6 was reacted with $NH_4^+OH^-$ and afforded a red, neutral complex. Spectroscopic evidence suggests that it is not the expected μ-hydroxycarbene complex but rather the new μ-vinylidene complex 20. Complex 20 was found to be best prepared from the reaction of 6 with methyllithium (eq 9). Very recently, Stone and co-workers also observed complex 20 by using basically the same approach.[27] A preparation of the ruthenium analogue of 20 has also been reported.[28]



(9)

6 20

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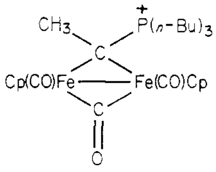
When HBF_4 was added to **20**, the μ-ethylidyne complex **6** was obtained. Complex **6** could be transformed into the μ-ethylidene complex **11** as described in eq 4. This represents an example of the transformation of a *gem*-dimetalloalkene into the corresponding *gem*-dimetalloalkane. Reduction of the μ-vinylidene complex **20** by molecular hydrogen afforded ethane, parent dimer **2**, and a tetramer, $Cp_4Fe_4(\mu_3\text{-}CO)_4$; no μ-ethylidene complex **11** was observed, which is stable under the reaction conditions.

Finally, the reaction of complex **6** with $P(n\text{-}Bu)_3$ affords the new phosphonium complex **21** as evidenced by the spectroscopic data [IR (CH_3CN) 1990 (s), 1950 (w), 1798 (m) cm^{-1}; ^1H NMR (CD_3CN) δ 1.00–2.00 (m, 27 H), 2.94 (d, 3 H, J_{P-H} = 21.3 Hz), 5.15 (s, 10 H)].



21

We have demonstrated the feasibility of transforming the carbonyl ligand into a series of bridging organic species—namely, the alkylidene and related ligands. Their chemical behaviors might serve as models for the coordination of hydrocarbon moieties on metal surfaces.

Experimental Section

General Procedure. Melting points were obtained on a Fischer-Johns melting point apparatus and were uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 257 or 298 grating infrared spectrophotometer.

Nuclear magnetic resonance spectra were recorded on a Perkin-Elmer R-12 (60 MHz), or a Varian EM-390 (90 MHz), or Nicolet NT-200 (200 MHz) spectrophotometer. Mass spectra were recorded on a Du Pont Model 491 low-resolution mass spectrometer and a Model 110B high-resolution mass spectrometer. Microanalyses were performed by Chemalytics, Inc., Tempe, AZ, and by Galbraith Laboratories, Knoxville, TN. Gas chromatography–mass spectroscopy analyses were performed on a Finnigan Model 4023 Automated GC-MS with Incos data system. Columns used in the GC and GC–MS studies are (1) 5 ft × $^1/_8$ in. Porapak Q on 80/100 Chromosorb W, (2) 7 ft × $^1/_8$ in. 0.18% picric acid on Carbopak C, and (3) 50-m sp-2100 on fused silica capillary column. Pressure reactions were run in a 58-mL stainless steel (T-304) autoclave equipped with star-head magnetic stirring bar. Standard Schlenk techniques for handling air-sensitive compounds as described by Brown[29] and Schriver[30] were routinely followed. Reactions were run under argon, unless otherwise specified. $C_5H_5Fe(CO)(PPh_3)(CHOCH_3)^+BF_4^-$,[2] $C_5H_5Fe(CO)_2K$,[31] $NEt_4HFe(CO)_4$ (**10**),[32] and $Ph_3C^+BF_4^-$ [33] were prepared according to literature procedures.

Preparation of $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHOCH_3)$ (1). To a solution of $C_5H_5Fe(CO)(PPh_3)(CHOCH_3)^+BF_4^-$ (2.72 g, 5.01 mmol) in CH_3CN (30 mL) at 0 °C was added $C_5H_5Fe(CO)_2K$ (1.10 g, 5.00 mmol) in CH_3CN (20 mL). The mixture was stirred for 3 h, and a brown residue was obtained after the solvent was removed; the residue was extracted with benzene and chromatographed on alumina. Four components were isolated from the column: (1) $C_5H_5Fe(CO)(PPh_3)H$[34] (0.103 g, 5.00%, eluted with 50% hexane/benzene), (2) $[C_5H_5Fe(CO)_2]_2$ (0.884 g, 47.6%, eluted with benzene), (3) $(C_5H_5)_2Fe_2(CO)_3(PPh_3)$[35] (0.293 g, 9.94%, eluted with 10% diethyl ether/benzene), and (4) a cis/trans isomeric mixture of **1** (0.460 g, 24.8%, eluted with 50% diethyl ether/benzene). Recrystallization of **1** from CH_2Cl_2/hexane gave air-stable red crystals: mp 170–173 °C dec; IR (CH_2Cl_2) 1986 (vs), 1941 (m), 1776 (s), 1080 (m) cm^{-1}; ^1H NMR ($CDCl_3$) **1a**, δ 3.90 (s, 3 H), 4.67 (s, 10 H), 12.48 (s, 1 H); **1b**, δ 4.00 (s, 3 H), 4.70 (s, 5 H), 4.71 (s, 5 H), 11.62 (s, 1 H); ^{13}C NMR (CD_2Cl_2): **1a**, δ 63.9 (OCH_3), 86.9 (C_5H_5), 216.7 (μ-$CHOCH_3$), 212.0 (CO), 275.9 (μ-CO); **1b**, δ 64.6 (OCH_3), 88.3 (C_5H_5), 90.1 (C_5H_5), 214.0 (μ-$CHOCH_3$), 212.0 (CO), 275.9 (μ-CO); mass spectrum, *m/e* 370 (M^+), 342, 314, 286. Anal. Calcd for $C_{15}H_{14}Fe_2O_4$: C, 48.70; H, 3.81; Fe, 30.18. Found: C, 48.66; H, 3.82; Fe, 29.91.

Hydrogenation of $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHOCH_3)$ (1). A solution of **1** (0.050 g, 0.13 mmol) in THF (15 mL) was placed in a 58-mL stainless-steel autoclave and charged with hydrogen (270 psi). The reactor was heated at 150 °C for 3 h. VPC analysis of the gas phase over the reaction mixture revealed the presence of dimethyl ether (15%) and methane (5%). The IR spectrum of the liquid phase indicated $[C_5H_5Fe(CO)_2]_2$ (50%) and unreacted **1** (20%) as the products.

Reaction of $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHOCH_3)$ (1) with $HBF_4{\cdot}OEt_2$. To a solution of **1** (0.050 g, 0.13 mmol) in CH_2Cl_2 (15 mL) at 0 °C was added $HBF_4{\cdot}OEt_2$ (slight excess). An intense red solution was developed immediately which decomposed readily with the formation of a brown precipitate. The IR spectrum of the red solution displayed bands at 2050 (vs), 2020 (m), and 1860 (s) cm^{-1}.

In another experiment, **1** (0.020 g, 0.052 mmol) was dissolved in CD_2Cl_2 (approximately 1 mL) and treated with a threefold excess of $HBF_4{\cdot}OEt_2$ at –60 °C. The ^1H NMR spectrum of the resulting red solution at –60 °C featured a singlet at δ 22.56 (1 H) and a singlet at δ 5.24 (10 H).

Preparation of $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHPPh_3)^+BF_4^-$ (8). To a solution of **1** (0.100 g, 0.270 mmol) and triphenylphosphine (0.080 g, 0.30 mmol) in CH_2Cl_2 (25 mL) at –20 °C was added $HBF_4{\cdot}OEt_2$ (slight excess). The red-brown solution which resulted was stirred for 15 min, and the solvent was removed. The resulting red-brown solid, when recrystallized from CH_2Cl_2/Et_2O, afforded 0.15 g (85%) of a dark red crystalline solid: mp 200 °C dec; IR (CH_2Cl_2) 1993 (vs), 1958 (w), 1810 (s) cm^{-1}; ^1H NMR (acetone-d_6) δ 5.25 (s, 10 H), 7.50–8.00 (m, 15 H), 9.96 (d, 1 H, J_{P-H} = 1.5 Hz). Anal. Calcd for $C_{32}H_{26}BF_4Fe_2O_3P$: C, 55.86; H, 3.81; P, 4.50. Found: C, 56.12; H, 4.04; P, 4.51.

Reaction of $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHOCH_3)$ (1) with $Ph_3C^+BF_4^-$. To a solution of **1** (0.050 g, 0.13 mmol) in CH_2Cl_2 (15 mL) at 0 °C was added $Ph_3C^+BF_4^-$ (0.045 g, 0.13 mmol) in CH_2Cl_2 (5 mL). An intense red solution was developed immediately which decomposed readily with the formation of a brown precipitate. The IR spectrum of the red solution displayed bands at 2050 (vs), 2020 (m), and 1860 (s) cm^{-1}. When this solution was treated with triphenylphosphine (0.040 g, 0.15 mmol) in CH_2Cl_2 (5 mL) and followed by adding diethyl ether, a red-brown solid was isolated which was identified to be **8** (0.065 g, 70%).

Preparation of $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ (9). To a solution of **1** (0.100 g, 0.270 mmol) in CH_2Cl_2 (15 mL) at –20 °C was added $HBF_4{\cdot}OEt_2$ (slight excess). The resulting red solution was stirred for 1 min and the solvent removed. A solution of $NaBH_4$ in CH_3CN was added, and the reaction mixture was stirred for 30 min at room temperature. Removal of the solvent gave an orange-red residue which was then extracted with benzene and subjected to separation on alumina. Two components were isolated from the column: (1) a pink-red solid (0.015 g, 16%, eluted with 50% hexane/benzene) which was found to be predominant of the trans isomer **9b** of the title compound and (2) an orange-red solid (0.038 g, 41%, eluted with benzene) which was identified as predominant of the cis form **9a** of the title compound. Although **9a** and **9b** are separable by column, they interconvert each other in solution with the final equilibrium cis/trans ratio of 3.2:1.0. Recrystallization of **9** from hexane at –78 °C gave orange-red solids: mp 160–164 °C dec; IR (CH_2Cl_2) 1985 (vs), 1940 (s), 1780

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(s) cm^{-1}; ^{1}H NMR ($CDCl_3$) **9a**, δ 4.73 (s, 10 H), 8.43 (s, 1 H), 10.33 (s, 1 H); **9b**, δ 4.76 (s, 10 H), 9.63 (s, 2 H); ^{13}C NMR ($CDCl_3$) **9a**, δ 86.8 (C_5H_5), 138.8 (CH_2), 212.8 (CO), 272.0 (μ-CO); **9b**, δ 88.8 (C_5H_5), 142.0 (CH_2), 213.8 (CO), 274.0 (μ-CO); mass spectrum, m/e 340 (M^+), 326, 312, 298, 284, 270, 256, 242; high-resolution mass spectrum (HRMS) calcd for $C_{14}H_{12}Fe_2O_3$, 339.9484, found, 339.9495.

Hydrogenation of $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ (9). A solution of **9** (0.050 g, 0.13 mmol) in THF (15 mL) was placed in a 58-mL stainless-steel autoclave and charged with hydrogen (270 psi). The reactor was heated at 150 °C for 3 h. VPC analysis of the gas phase over the reaction mixture revealed the presence of methane (50%). The IR spectrum of the liquid phase indicated $[C_5H_5Fe(CO)_2]_2$ as the only product (60%).

Preparation of $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_3)^+BF_4^-$ (6).[7] To a solution of **2** (7.24 g, 20.4 mmol) in THF (250 mL) at −20 °C was added methyllithium (25 mL, 1.5 M in diethyl ether) with stirring. The reaction solution was stirred for 10 min and was allowed to warm to room temperature. An aqueous HBF_4 (12 g, 48%) was added slowly at 0 °C. Gas formation was evident. The reaction solution was stirred for 15 min more and warmed to room temperature for an additional 30 min while solids precipitated out. The solid was filtered and washed several times with benzene and pentane. The deep brick-red crystals were subjected to high vacuum overnight (1 mm, room temperature). The resulting crystals were analytically pure, and the yield was 3.68 g (40.8%): IR (CH_3CN) 2040 (vs), 2020 (m), 1855 (s) cm^{-1}; ^{1}H NMR (CD_3CN) δ 5.06 (s, 3 H), 5.36 (s, 10 H). Anal. Calcd for $C_{15}H_{13}BF_4Fe_2O_3$: C, 40.97; H, 2.98; Fe, 25.40. Found: C, 40.74; H, 3.03; Fe, 27.15.

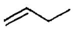
Preparation of $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (11). In a flask (A) was placed **6** (2.27 g, 5.16 mmol) and THF (80 mL). In another flask (B) was placed $NEt_4HFe(CO)_4$ (2.46 g, 9.25 mmol) and THF (70 mL). Both flasks were cooled at −78 °C. The solution in flask B was added to flask A via a cannula under argon. The reaction solution was allowed to stir for 10 min, and the solvent was removed on a rotary evaporator. The resulting dark red residue was extracted several times with benzene (120 mL). Benzene was removed, and the residue was vacuum dried. The residue was subjected to column chromatography (silica gel, 2.5 cm × 30 cm). Benzene eluted first a purplish red band **11b** and then an orange-red band **11a** (the former converted to the latter color even at 0 °C under argon). Removing the solvent from the orange-red band afforded an analytically pure title compound (1.65 g, 90.3%): mp 166 °C dec; a molecular ion peak (m/e 354) was observed; IR (THF) 1974 (vs), 1937 (m), 1784 (s) cm^{-1}; ^{13}C NMR (acetone-d_6) **11a**, δ 43.0 (CH_3), 88.0 (C_5H_5), 172.1 ($CHCH_3$), 214.8 (CO), 274.7 (μ-CO). Anal. Calcd for $C_{15}H_{14}Fe_2O_3$: C, 50.89; H, 3.98; Fe, 31.55. Found. C, 50.80; H, 3.87; Fe, 31.27.

Preparation of $(C_5H_5)_2Fe_2(CO)[P(n\text{-}Bu)_3](\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (14). In a 6 in. × 0.5 in. quartz tube were placed **11** (0.142 g, 0.400 mmol), $P(n\text{-}Bu)_3$ (1.00 mL, 4.02 mmol), and benzene (10 mL). The tube was placed in a Rayonet RS—preparation photochemical reactor—and photolyzed for 10 h (no **11** was observed in the IR spectrum then). Solvent was removed via a rotary evaporator and then a high vacuum pump overnight. The title complex is green.

Reaction of $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (11) with Styrene in the Presence of Acid. In a 10 × 1.5 cm test tube were placed **11** (0.100 g, 0.282 mmol) and p-dioxane (6.0 mL). To this solution was added styrene (40 μL, 0.35 mmol), and the reaction solution was stirred for 1 h at room temperature. The solution was then checked by GC (SP-2100) for 1-methyl-2-phenylcyclopropane, and no trace was observed. The reaction solution was then cooled to −78 °C, and aqueous HBF_4 (0.50 mL, 48%) was added. Upon warming to room temperature, the solution was checked by GC as above, and 1-methyl-2-phenylcyclopropane (5%) was observed. Authentic 1-methyl-2-phenylcyclopropane was prepared by the literature method.[36]

Reaction of $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (11) with $LiAlH_4$. In a 50-mL flask with one septum-covered side arm were placed **11** (0.177 g, 0.500 mmol) and $LiAlH_4$ (0.501 g, 13.2 mmol). The reaction flask was evacuated and cooled at −78 °C. Through the side arm was introduced THF (10 mL), and the reaction solution was allowed to warm slowly to room temperature (time, T = 0:00). The gaseous products as analyzed by GC were listed in Table IV. Complex **2** was also tested under the same conditions and was found to produce C_1 to C_4 hydrocarbons, with C_2H_4 as the major product of the primary process.

Table IV

T	C_1	C_2H_4	C_2H_6	α-C_3H_6	C_3H_8		
0:00[a]	–	–	–	–	–	–	–
1:50[b]	53.5	3.1	8.7	32.7	–	–	–
2:15	8.4	1.6	3.7	65.2	7.3	9.1	4.7
2:42[c]	7.3	1.4	3.5	64.7	7.0	10.1	5.2
5:25	9.0	1.2	4.2	61.4	9.2	9.7	5.4
10:30	8.7	0.9	4.8	85.7		+	+
20:45[d]	9.4	0.4	5.1	56.9	12.8	9.3	6.1

[a] Only THF was observed. [b] Solution color changed from red to green. [c] 40% absolute yield. [d] The IR spectrum of the reaction solution indicated the presence of $C_5H_5(CO)_2Fe^-Li^+$.

Reaction of $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (11) with CO/H_2. Compound **11** (0.043 g, 0.12 mmol) in p-dioxane (6 mL) was charged with CO and H_2 (1:1, 600 psi) and heated at 165 °C for 16 h. The IR spectrum of the solution indicated mainly $[C_5H_5Fe(CO)_2]_2$ and $Fe(CO)_5$. Products in the gas phase were methane, ethane, propene, and propane. The solution phase showed ethane (trace) and propanal (9.0–10.0%), as verified by GC and GC-MS analysis on Porapak Q and SP-2100 columns. The same reaction without CO afforded ethane as the only product.

Reaction of $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (11) with C_2H_4. Complex **11** (0.219 g, 0.618 mmol) in p-dioxane (18 mL) was charged with C_2H_4 (450 psi) and heated at 160 °C for 10 h. Methane (trace), propene (2.6%), and C_4 hydrocarbons (2.2%) were obtained, along with cyclopentadiene, $Fe(CO)_5$ as analyzed by GC. The C_4 hydrocarbons were further analyzed on Carbopak C and SP-2100 to identify 1-butene, 2-butene, and isobutylene.

Preparation of $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)^+BF_4^-$ (15). Complex **11** (0.395 g, 1.12 mmol) in CH_2Cl_2 (25 mL) was added to $Ph_3C^+BF_4^-$ (0.405 g, 1.23 mmol) in CH_2Cl_2 (25 mL) at 0 °C. The reaction solution was stirred for 30 min, and the IR spectrum indicated that a cationic species was present. The solution was allowed to warm to room temperature, and the volumn of the solution was reduced to ca. half on a rotary evaporator. Diethyl ether (30 mL) was added to precipitate a deep purple solid. The solid was collected, washed with ether, and dried under high vacuum to afford an analytically pure **15** (0.440 g, 89.8%): IR (CH_3CN) 2050 (s), 2025 (sh), 1969 (m) cm^{-1}; ^{13}C NMR (acetone-d_6) δ 64.2 ($CH{=}CH_2$), 89.6 (C_5H_5), 92.7 (C_5H_5), 185.8 ($CH{=}CH_2$), 213.9 (CO), 243.6 (μ-CO). Anal. Calcd for $C_{15}H_{13}BF_4Fe_2O_3$: C, 40.97; H, 2.98; F, 17.28; Fe, 25.40; B, 2.45. Found: C, 40.76; H, 3.06; F, 17.09; Fe, 25.19; B, 2.67.

Reaction of $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)^+BF_4^-$ (15) with CH_3Li and n-BuLi. (a) CH_3Li. CH_3Li (0.30 mL, 1.6 M in diethyl ether) was introduced to a solution of **15** (0.177 g, 0.403 mmol) in CH_2Cl_2 (50 mL) at −78 °C. The reaction solution was stirred for 40 min and then warmed to room temperature for 0.5 h. The solvent was removed, and the residue was extracted with benzene (60 mL). After removal of benzene the residue was subjected to column chromatography [Florisil, hexane/benzene (2:1)]. A bright orange-red solid of $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_2CH_3)$ was obtained (0.12 g, 82%) after workup.

(b) n-BuLi. The bright orange-red $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}CH(CH_2)_4CH_3]$ (yield 80%) was prepared similarly as in a, mp 120–122 °C dec.

Reaction of $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)^+BF_4^-$ (15) with CH_3OH. On top of a Florisil column (1.8 × 10 cm) was placed complex **15** (0.184 g, 0.418 mmol). Methanol was applied to eluted the column and a red band developed. This methanol band was collected and concentrated to afford orange-red crystals of $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_2OCH_3)$ (0.158 g, 98%).

Reaction of $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH{=}CH_2)^+BF_4^-$ (15) with PPh_3. Complex **15** (0.431 g, 0.979 mmol) in acetone (25 mL) was added to PPh_3 (0.257 g, 0.981 mmol) at room temperature. The purple reaction solution turned red within 3 min, and the IR spectrum of the solution indicated that a new binuclear species

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[36] Dilling, W. F. *J. Org. Chem.* **1966**, *29*, 260–264.

had formed. The solvent was removed to yielded a red-orange solid. Further dried under high vacuum for 20 h to afford 0.550 g (79.9%) of $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCH_2PPh_3)^+BF_4^-$ (**19**).

Preparation of $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$ (20). CH_3Li (2.2 mL, 1.6 M in diethyl ether) was slowly added to a solution of **6** (1.52 g, 3.45 mmol) in CH_2Cl_2 (50 mL) at -78 °C and stirred for 30 min. CH_2Cl_2 was removed, and the resulting residue was dried under high vacuum. The solid residue was taken up in benzene (70 mL) and filtered. Removal of benzene from the filtrate afforded 1.13 g (93%) of an orange-red solid of the title compound, mp 153-155 °C dec. A molecular ion (352) was observed in the mass spectrum: IR (benzene) 1995 (s), 1958 (w), 1795 (m) cm^{-1}; ^1H NMR (benzene-d_6) δ 4.25 (s, 10 H), 6.97 (s, 2 H). Anal. Calcd for $C_{15}H_{13}Fe_2O_3$: C, 51.19; H, 3.44; Fe, 31.74. Found: C, 50.97; H, 3.53; Fe, 30.98.

Reaction of $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C{=}CH_2)$ (20) with HBF_4. A solution of aqueous HBF_4 (0.1 mL, 48%) in acetic anhydride (1.0 mL) was added to a solution of **20** (0.100 g, 0.285 mmol) in THF (40 mL) at 0 °C. The solution was warmed to room temperature and stirred for 20 min while a shining brick-red precipitate started falling out. The solid was collected and washed with THF. Application of high vacuum to remove the residual solvent afforded 0.051 g (40.8%) of complex **6**.

Reaction of $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_3)^+BF_4^-$ (6) with $P(n\text{-}Bu)_3$. $P(n\text{-}Bu)_3$ (0.13 mL, 0.519 mmol) was added to a solution of **6** (0.22 g, 0.50 mmol) in acetonitrile (20 mL) at room temperature. IR spectrum of the solution indicated the formation of a new carbonyl species within 5 min. Removal of the solvent afforded a red complex of $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}CCH_3P(n\text{-}Bu)_3]^+BF_4^-$ (*21*) (0.26 g, 81%). Anal. Calcd for $C_{27}H_{40}BF_4Fe_2O_3P$: C, 50.50; H, 6.27; Fe, 17.39; P, 4.82. Found: C, 50.37; H, 6.05; Fe, 17.10; P, 4.64.

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Registry No. 1a, 81616-44-6; **1b**, 81654-89-9; **2**, 12154-95-9; **3**, 81616-45-7; **4**, 81616-46-8; **5**, 81616-47-9; **6**, 81616-49-1; **7**, 81616-50-4; **8**, 81616-52-6; **9a**, 79839-80-8; **9b**, 79896-43-8; **10**, 25879-01-0; **11a**, 75811-60-8; **11b**, 75829-77-5; **14**, 81616-53-7; **15**, 75818-23-4; **18a**, 81616-54-8; **18b**, 81616-55-9; **18c**, 81616-56-0; **19**, 81616-58-2; **20**, 76722-37-7; **21**, 81616-60-6; $C_5H_5Fe(CO)(PPh_3)(CHOCH_3)^+BF_4^-$, 81616-61-7; $C_5H_5Fe(CO)_2K$, 60039-75-0.

Tridentate Amido Phosphine Derivatives of the Nickel Triad: Synthesis, Characterization, and Reactivity of Nickel(II), Palladium(II), and Platinum(II) Amide Complexes

Michael D. Fryzuk,* Patricia A. MacNeil, Steven J. Rettig, Anthony S. Secco, and James Trotter

Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T IY6

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Deprotonation of $HN(SiMe_2CH_2PPh_2)_2$ (**4**) with *n*-butyllithium generates $LiN(SiMe_2CH_2PPh_2)_2$ (**5**), a tridentate, uninegative ligand which contains both the *hard* amido donor and *soft* phosphine donors. The reaction of **5** with each of $NiCl_2 \cdot DME$ (DME = dimethoxyethane), $PdCl_2(PhCN)_2$, and $K[PtCl_3(C_2H_4)]$, generates the corresponding diamagnetic chloro amide derivatives $[MClN(SiMe_2CH_2PPh_2)_2]$ (M = Ni, **6**; M = Pd, **7**; M = Pt, **8**). The X-ray structure of the nickel derivative **6** (space group $P\bar{1}$ (C_i^1, No. 2) a = 10.091 (3), b = 10.224 (3), c = 17.234 (4) Å; α = 81.06 (2), β = 78.51 (2), γ = 65.93 (3)°; Z = 2; R = 0.029 (R_w = 0.040)) indicates a slightly distorted square-planar geometry with trans phosphine donors. The backbone of the ring is puckered generating near C_2 symmetry in the solid state; however, the ^1H NMR is consistent with C_{2v} symmetry in solution which can be explained by a rapid conformational flipping of the ligand backbone. The X-ray structure of the corresponding palladium derivative **7** (space group $P\bar{1}$; a = 11.539 (1), b = 15.368 (2), c = 10.949 (2) Å; α = 92.92 (1), β = 104.09 (1), γ = 84.74 (1)°; Z = 2; R = 0.022 (R_w = 0.031)) also indicates trans phosphines in a square-planar array but with no puckering of the backbone of the ligand. The neutral amine **4** acts as a bidentate ligand via donation through the phosphines to produce the dichloro derivatives $[MCl_2NH(SiMe_2CH_2PPh_2)_2]$ (M = Ni, **9**; M = Pd, **10**; M = Pt, **11**). The X-ray structure of the nickel derivative **9** (space group $P\bar{1}$; a = 10.2224 (1), b = 10.5719 (8), c = 17.770 (2) Å; α = 72.978 (6), β = 78.424 (6), γ = 61.864 (8)°; Z = 2; R = 0.031 (R_w = 0.039)) displays a distorted tetrahedral geometry with no evidence of interaction between the amine portion of the backbone and the metal. Both the palladium, **10**, and platinum, **11**, derivatives are assumed to be square-planar with cis disposed phosphine donors on the basis of ^1H FT NMR studies. All three dichloro derivatives, **9**, **10**, and **11**, are cleanly converted to the corresponding chloro amide complexes, **6**, **7**, and **8**, by treatment with NEt_3 in toluene; this reaction requires prior coordination of the phosphine donors in order to activate the distal N-H bond. Metathesis with a number of simple Grignard reagents occurs only for the nickel and palladium chloro amide derivatives, **6** and **7**, to generate the metal-carbon bonded complexes $[M(R)N(SiMe_2CH_2PPh_2)_2]$ (M = Ni or Pd; R = CH_3, $CH{=}CH_2$, $CH_2CH{=}CH_2$, or C_6H_5). The platinum chloride bond of **8** does not undergo metathesis with Grignards and, in addition, is not abstracted with Ag^+; consistent with this is the Pt-Cl stretching frequency of 317 cm^{-1} which is indicative of a weak trans influence for the $^-N(SiR_3)_2$ ligand.

Introduction

The stability and reactivity of transition-metal complexes are a function of both the position of the metal in the transition series and the nature of the complexing ligands. While the former provides for a gratifying diversity of chemical behavior across the transition series, it is the latter feature which allows the reactivity patterns of a given transition metal to be fine tuned. Indeed, an enormous amount of effort has gone into the design and synthesis of new ligands[1] and new combinations of ligands[2]

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