washed with diethyl ether, and recrystallized from acetone/diethyl ether to give **5** (0.084 g, 26%, $[\alpha]^{20}_{D}$ +134° (*c* 3.4, MeCN).

(e) [(2-MeO-5-*endo*-$PPh_3C_6H_6$)$Fe(CO)_3$]PF_6 (11). A stirred suspension of racemic **6b** (0.86 g, 1.31 mmol) in THF (30 mL) was cooled to −60 °C and an excess of BuLi in hexane (2.0 mmol) was added over 1 h to give a deep red solution. A small excess of HPF_6 (5% aqueous, 1.7 mmol) was added dropwise to give a yellow solution which was allowed to warm to room tempearture. After removal of solvent, the yellow gum was dissolved in CH_2Cl_2 (10 mL), filtered, and precipitated by addition of diethyl ether. The small amount of less soluble **6b** was removed by redissolving this crude product in acetone (10 mL). Addition of petroleum ether (10 mL) resulted in separation of **6b** as a brown oil from which the more soluble isomer **11** was readily decanted. Further additions of 40–60 petroleum ether (50 mL) followed by filtration gave **11** (0.61 g, 71%).

(f) Reduction of [(5-*exo*-(PPh_2(Me-(Me_2CH)C_6H_9))$C_6H_7Fe(CO)_3$]BF_4. Finely powdered diastereoisomerically pure **3a**[6] (0.80 g, 1.27 mmol) was suspended in THF (40 mL) at 0 °C, and $LiAlD_4$ (0.092 g, 2.2 mmol) was added in three portions. The reaction mixture was stirred at 0 °C until the infrared spectrum indicated complete consumption of starting material (2 h). The reaction mixture was treated cautiously with 20% sodium potassium tartrate solution (50 mL) and extracted with diethyl ether (3 × 30 mL). Drying over $MgSO_4$ followed by removal of solvent and chromatography of the residue on grade II alumina using petroleum ether (40–60) gave **14** (0.135 g, 48%; $[\alpha]^{20}_{D}$ +4.3 ± 1.5° (*c* 3.3, $CHCl_3$) of a sample which was analytically and spectroscopically pure).

Reduction of a 1:1 diastereoisomeric mixture of [(2-MeO-5-*exo*-(PPh_2(Me(Me_2CH)C_6H_9))C_6H_6)$Fe(CO)_3$]BF_4 (**3b**) with $LiAlD_4$ was complete in 1.5 h. Chromatography on preparative silica gel plates using petroleum ether (40–60) gave (2-$MeOC_6H_6D$)$Fe(CO)_3$ (**12**) (72%) and (1-MeO-C_6H_6D)$Fe(CO)_3$ (**13**) (8%).

The 5-*exo*-deuterio complex **15** was prepared by a literature method.[13]

Acknowledgment. We thank the SERC for support in the form of a studentship (M.J.T.) and Dr. B. E. Mann for his assistance with the 400 MHz proton spectra.

Registry No. 2, 51508-59-9; (2*S*)-(+)-2, 76704-83-1; **3a**, 95463-17-5; (2*S*5*S*)-**3b**, 84525-82-6; **5**, 95406-37-4; (2*S*5*S*)**6a**, 86664-10-0; **6b**, 95463-20-0; (2*S*5*S*)-**6a**, 95463-18-6; **6c**, 95387-14-7; 8, 86664-11-1; **9a**, 86664-12-2; **9b**, 86708-26-1; **10**, 86768-26-5; **11**, 95463-22-2; **12**, 95387-15-8; **13**, 95387-16-9; **14**, 95387-17-0; **15**, 95387-18-1; **16**, 95463-23-3; (2-methoxycyclohexadiene)$Fe(CO)_3$, 12318-19-3; (1-methoxycyclohexadine)$Fe(CO)_3$, 12318-18-2; PPh_3, 603-35-0; $PPhMe_2$, 672-66-2; PPh_2Me, 1486-28-8; benzaldehyde, 100-52-7; formaldehyde, 50-00-0.

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[18] Enantiomerically pure (2*R*) (5*S*) isomer obtained by fractional crystallization has a rotation of −138°: Stephenson, G. R. *Aust. J. Chem.* **1981**, *34*, 2339. The enantiomeric purity of **5** was additionally confirmed by the presence of only two methyl resonances in the ^1H NMR spectrum of the dimethyl malonate adduct in the presence of optically active shift reagent.

Reactivity of Bis(cyclopentadienyl)niobium and -tantalum Hydrides toward Iron Penta-, Nona-, and Dodecacarbonyl. Interaction of a Bridging Carbonyl with an Early Transition Metal and Formation of an O-Metalated Carbyne

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The monohydrides $Cp_2M(CO)H$ ($Cp = \eta^5\text{-}C_5H_5$) and $Cp'_2M(CO)H$ ($Cp' = \eta^5\text{-}C_5H_4CMe_3$) (M = Nb or Ta) react with $Fe_2(CO)_9$ in equimolar ratio to give the Lewis acid-base adducts $Cp_2M(CO)(\mu\text{-}H)Fe(CO)_4$ and $Cp'_2M(CO)(\mu\text{-}H)Fe(CO)_4$. With $Fe_3(CO)_{12}$ or with an excess of $Fe_2(CO)_9$, the polynuclear systems $Cp_2M(CO)[(\mu\text{-}CO)(\mu\text{-}H)Fe_3(CO)_{10}]$ and $Cp'_2M(CO)[(\mu\text{-}CO)(\mu\text{-}H)Fe_3(CO)_{10}]$ which contain a bridging O-metalated carbyne ligand are obtained. When the trihydrides Cp_2MH_3 or Cp'_2MH_3 are treated with $Fe(CO)_5$, $Fe_2(CO)_9$, or $Fe_3(CO)_{12}$, the initial formation of the monohydrides is observed by an "in situ" carbonylation reaction.

Introduction

The research and the improvement of novel systems for the homogeneous reduction of carbon monoxide continue to be an active area of organometallic chemistry.[1] The design of catalysts affording both high selectivity and mild reaction conditions is of considerable economic interest. Of course, this goal needs the knowledge and the understanding of the elementary steps involved in the carbon monoxide hydrogenation. A key step in the reduction pathway is the formation of the first C–H bond; an alternative to insertion of CO into a M–H bond which appears as a highly unfavorable process is the nucleophilic attack by H^- upon a coordinated CO. Stoichiometric reductions of complexed carbon monoxide leading to formyl,[2] hydroxymethyl,[3] or methyl[4] complexes can be performed

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Table I. IR and ^{1}H NMR Data

compound	ν_{CO}[a]	^{1}H NMR[b]		
		Cp or Cp′	$C(CH_3)_3$	M–H
Cp_2TaH_3 (**1a**)		4.77 (s/10)		−1.63 (dd, 2), −3.01 (d, 1)
Cp_2NbH_3 (**1b**)		4.77 (s/10)		−2.6 (dd, 2), −3.6 (d, 1)
Cp'_2TaH_3 (**1′a**)		4.71 (m, 4), 4.62 (m, 4)	1.26 (s/18)	−1.38 (t/2), −2.8 (d, 1)
Cp'_2NbH_3 (**1′b**)		4.74 (s/8)	1.22 (s/18)	−2.51 (t/2), −3.52 (d, 1)
$Cp_2Ta(CO)H$ (**2a**)	1893	4.48 (d/10), 0.8 Hz)		−6.78 (m/1)
$Cp_2Nb(CO)H$ (**2b**)	1906	4.56 (d/10, 0.7 Hz)		−6.37 (m/1)
$Cp'_2Ta(CO)H$ (**2′a**)	1889	4.78 (m/2), 4.20 (m/6), 1.20 (s/18)		−6.65 (m/1)
$Cp'_2Nb(CO)H$ (**2′b**)	1901	4.77 (q/2), 4.50 (q/2), 4.31 (t/4, 2.5 Hz)	1.17 (s/18)	−6.42 (m/1)
$Cp_2Ta(CO)HFe(CO)_4$ (**3a**)	2032 (s), 1950 (vs), 1942 (vs), 1919 (vs)	4.41 (d/10, 0.3 Hz)		−20.53 (m/1)
$Cp_2Nb(CO)HFe(CO)_4$ (**3b**)	2032 (s), 1957 (vs), 1946 (vs), 1917 (vs)	4.51 (d/10, 0.25 Hz)		−21.30 (m/1)
$Cp'_2Ta(CO)HFe(CO)_4$ (**3′a**)	2032 (s), 1950 (vs), 1941 (vs), 1917 (vs)	4.83 (t/4), 4.51 (t/4, 2.6 Hz)	0.88 (s/18)	−20.59 (m/1)
$Cp'_2Nb(CO)HFe(CO)_4$ (**3′b**)	2032 (s), 1956 (vs), 1946 (vs), 1916 (sh)	4.92 (t/4), 4.66 (t/4, 2.6 Hz)	0.81 (s/18)	−22.08 (m/1)
$Cp_2Ta(CO)HFe_3(CO)_{11}$ (**4a**)	2077 (m), 2022 (vs), 2014 (vs), 1992 (vs), 1962 (s), 1945 (s)	4.86 (s/10)		−15.94 (s/1)[c]
$Cp_2Nb(CO)HFe_3(CO)_{11}$ (**4b**)	2077 (m), 2019 (vs), 2013 (vs), 1993 (vs), 1961 (s), 1943 (s)	4.86 (s/10)		−15.81 (s/1)[d]
$Cp'_2Ta(CO)HFe_3(CO)_{11}$ (**4′a**)	2078 (m), 2022 (vs), 2012 (vs), 1990 (vs), 1961 (s), 1942 (s)	5.37 (m/4), 4.97 (m/2), 4.83 (m/2)	0.90 (m/18)	−15.92 (s/1)
$Cp'_2Nb(CO)HFe_3(CO)_{11}$ (**4′b**)	2077 (m), 2020 (vs), 2011 (vs), 1988 (vs), 1961 (s), 1945 (s)	5.62 (m/1), 5.09 (m/1), 4.90 (m/1)	0.81 (s/18)	−15.78 (s/1)

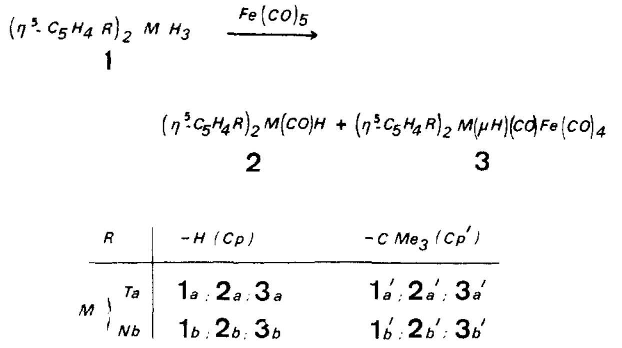
[a] In toluene [b] δ units, parts downfield from internal $SiMe_4$; C_6D_6 was used as a solvent and internal lock and C_6D_5H as an internal standard (δ 7.15). Apparent resonance multiplicity and relative intensity are included in parentheses. [c] Sparingly soluble in C_6D_6. In CD_3COCD_3: δ 6.03 (s/10) and −14.8 (s/1) [d] Sparingly soluble in C_6D_6. In CD_3COCD_3: δ 5.83 (s/10) and −14.8 (s/1).

by using main-group metal hydrides. However, these reducing reagents cannot be used in a catalytic process since they are not formed from H_2. Group 4[16] metal hydrides present reactivity patterns similar to those of boron or aluminium hydrides,[5] and several examples of stoichiometric CO reduction in the titanium and zirconium series have been reported.[6] Nevertheless, the strength of the metal–oxygen bond precludes the use of group 4 metals in a catalytic cycle. With the next group in the periodic table, the hydride complexes Cp_2MH_3 (M = Nb, Ta; Cp = η^5-C_5H_5) were found to possess some hydridic character and to be stable in water or ethanol. This feature prompted Labinger and co-workers to examine the behavior of Cp_2NbH_3 toward several first-row metal carbonyl.[7] We have recently published some reactions of Cp_2TaH_3 and $Cp'_2Ta(CO)H$ (Cp′ = η^5-$C_5H_4CMe_3$) with organometallic fragments leading to bi- and polymetallic species.[8] We describe in this paper the results obtained with niobium and tantalum hydrides in a comparative study between the iron–carbonyl complexes $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$.

Results and Discussion

The addition of $Fe(CO)_5$ to a toluene solution of Cp_2TaH_3 (in 1:1 molar ratio) afforded as major product the hydride carbonyl $Cp_2Ta(CO)H$, identified by ^{1}H NMR and IR spectroscopy (Table I). A careful examination of the reaction mixture by IR revealed the presence in a small amount of a second carbonyl derivative (ν_{CO} = 2032, 1950, 1942, 1919 cm^{-1}) corresponding to structure **3a** (vide infra) (Chart I).

Chart I



A similar reaction occurred with the analogous niobocene trihydride, Cp_2NbH_3. The IR spectrum of the reaction mixture showed carbonyl absorptions at 2032, 1957, 1946, 1917, and 1906 cm^{-1}. The NMR spectrum displayed two doublets in the Cp resonance region at 4.56 (J = 0.7 Hz) and 4.51 (J = 0.25 Hz) ppm and two upfield broadened signals at −6.37 and −21.30 ppm. A selective irradiation of the −6.37 ppm proton signal collapsed the 4.56 ppm doublet to a singlet. A similar experiment demonstrated coupling between the Cp protons at 4.51 ppm and the hydride ligand at −21.30 ppm. These observations are indicative of the presence of two species: resonances at 4.56 and −6.37 ppm are assigned to $Cp_2Nb(CO)H$ (by comparison with an authentic sample); the two other signals are due to binuclear **3b**, first isolated and characterized by a crystal structure determination by Labinger and co-workers.[7c] In Table I, we report its unambigous IR and NMR spectroscopic data.

Upon reaction of $Fe_2(CO)_9$ with Cp_2MH_3 (M = Ta, Nb), the binuclear complexes **3a** or **3b** could be isolated in moderate yield. On monitoring the course of these reactions by IR analysis, it was clearly shown that the hydrides

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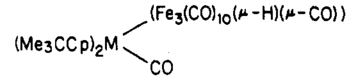
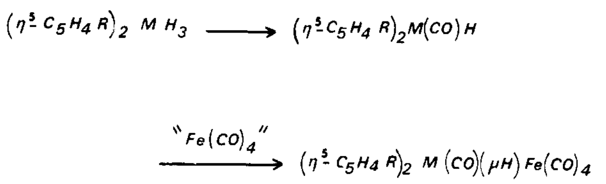
Table II. ^{13}C NMR Data[a] of 4′a and 4′b



	Me_3-C	Cp	$Fe_3(CO)_{10}$	M-CO	μ-CO
4′a (M = Ta)	31.7, 33.1	87.7, 90.2, 98.5, 100, 129.75	210–216[b]	327	345.1 (*J* = 14.7 Hz)
4′b (M = Nb)	31.5, 32.7	92.5, 93, 101.3, 103.2, 129.2	213–214.5[b]	321.6	341.1 (*J* = 14.7 Hz)

[a] In C_6D_6 at 25 °C; δ units referenced to C_6D_6 at δ 128.0. [b] Broadened signal.

Chart II



$Cp_2M(CO)H$ were formed as transitient intermediates. This suggests that these bimetallic compounds are formed via hydrido derivatives **2a** or **2b** and not by a H^- transfer from the trihydrides Cp_2MH_3 as had been postulated previously.[7a] Consistent with this view is the fact that the monohydrides $Cp_2M(CO)H$ (**2a** or **2b**) and $Cp'_2M(CO)H$ (**2′a** or **2′b**) quickly afford the binuclear species $Cp_2M(CO)(\mu\text{-}H)Fe(CO)_4$ (**3a** or **3b**) and $Cp'_2M(CO)(\mu\text{-}H)Fe(CO)_4$ (**3′a** or **3′b**) in nearly quantitative yield when treated with $Fe_2(CO)_9$. We have shown recently that the hydrides $Cp_2M(CO)H$ are able to function as a two-electron donor toward unsaturated organometallic fragments and lead to bimetallic complexes $Cp_2M(CO)(\mu\text{-}H)ML_n$[8] ($ML_n$ = "$Cr(CO)_5$", "$Mo(CO)_5$", "$W(CO)_5$", and "$CpMn(CO)_2$"). To form these acid–base adducts, $Cp_2MCO)H$ can employ either the M–H bonding electron pair (three center, two electron bonds) or the nonbonding pair available in the M^{III} d^2 center. The results reported here are illustrative of a donor–acceptor association with the Lewis acid fragment "$Fe(CO)_4$". Consequently, the overall reaction sequence can be written as shown in Chart II.

During the reaction of Cp'_2MH_3 with $Fe_2(CO)_9$, the competitive formation of the dimer $[Cp'Fe(CO)_2]_2$ was observed. This involves a cyclopentadienyl migration from the hydride complex to an iron carbonyl species (presumably $Fe(CO)_5$). The iron dimer could be isolated by chromatography. Its spectroscopic data are given in the Experimental Section. Such a ligand exchange does not occur in the unsubstituted cyclopentadienyl series.

With $Fe_3(CO)_{12}$, $Cp'MH_3$ or $Cp'_2M(CO)H$ or binuclear $Cp'_2M(CO)(\mu\text{-}H)Fe(CO)_4$ afford, after purification by low-temperature chromatography, red crystalline solids, which are soluble in hydrocarbons or aromatic solvents. In toluene or heptane solution, their IR spectra exhibit a complex pattern in the CO terminal stretching region; no bridging as a carbonyl stretch occurs in the range 1900–1700 cm^{-1} (Figure 1A). In a THF solution, there is no significant change in the carbonyl terminal absorptions but a low-frequency absorption appears at 1745 cm^{-1} indicative of a CO bridge (Figure 1B). The ^1H NMR spectra reveal, besides the hydrogen cyclopentadienyl resonances, an upfield signal at −15.8 ppm falling in the metal bridging hydride region (Table I). These two spectroscopic characteristics are exactly similar to those exhibited by an authentic sample of the iron carbonyl cluster anion $[HFe_3(CO)_{11}]^-$. These observations and the elemental analysis are in good agreement with a structure incorporating both moieties, $[Cp'_2M(CO)]$ and $[HFe_3(CO)_{11}]$. In inert solvents such as heptane or toluene, the metallic nuclei (niobium or tantalum) and the oxygen atom of the $[Fe_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}CO)]^-$ bridging carbonyl are linked through a predominantly covalent bond. This structural feature is confirmed by the very low absorption at ca. 1550 cm^{-1} present in the IR spectrum recorded in the solid state (Figure 1C). A basic solvent as THF induces substantial dissociation, leading to an ionic structure with the companion $[Cp'_2M(CO)(THF)]^+$. The structure proposed for **4′a** and **4′b** provides an example of a bridging "O-metalated" carbyne and may be viewed as arising via the O-metalation of the bridging carbonyl of $[Fe_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}CO)]$. The presence of the carbyne ligand is proven by ^{13}C NMR spectroscopy (Table II). Beside the resonances due to the $Cp'_2M(CO)$ moieties, two signals are observed near 210 and 340 ppm. The more shielded one is broad and can be assigned to the 10 terminal carbonyls taking part in a fluxional process which occurs at room temperature. The low field resonance is attributed t othe carbyne carbon atom; when proton decoupling is not applied, this resonance shows a resolvable H–^{13}C coupling of 14.7 Hz. Analogous O-methylation reactions of clusters of the iron triad $[M_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}CO)]^-$ have been reported previously by Shriver[9] (M = Fe), Keister[10] (M = Ru, Os), Lewis[11] (M = Ru), and Mays[12] (M = Os); fur-

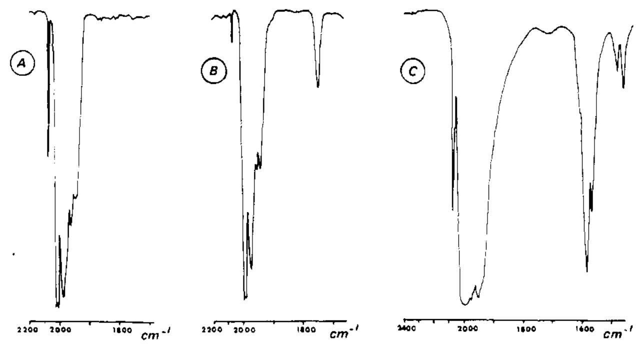
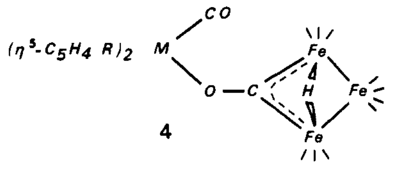


Figure 1. Infrared spectra of $Cp'_2Ta(CO)[HFe_3(CO)_{11}]$ in toluene (A), in THF (B), and in KBr (C).

Chart III



R	- H(Cp)	- CMe3 (Cp′)
M Ta	4a	4a′
M Nb	4b	4b′

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(9) Shriver, D. F.; Lehman, D.; Strope, D. *J. Am. Chem. Soc.* **1975**, *97*, 1594–1596.

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thermore, the interactions of the iron carbonylate with alkali cations have been investigated by Chen and Cheng[13] (Chart III).

Similar results are obtained with unsubstituted cyclopentadienyl compounds. However, the absence of *tert*-butyl groups on the π-bonded ligands favors the ionic structure to the detriment of a covalent association. This is particularly so in the case of **4a** as evidenced by its poor solutility in nonpolar solvents and by its CO-bridging absorption which appears at 1718 cm^{-1}.

It is noteworthy that the anion $[Fe_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}CO)]^-$ can be prepared in nearly quantitative yield by mixing the anion $[HFe(CO)_4]^-$ with $Fe_3(CO)_{12}$. This observation accounts for the formation of complexes **4** if one assumes a partial dissociation of binuclear compounds **3**:

$$(\eta^5\text{-}C_5H_4R)_2M(CO)(\mu\text{-}H)Fe(CO)_4 \rightarrow [(\eta^5\text{-}C_5H_4R)_2M(CO)]^+,\ [HFe(CO)_4]^-$$

In conclusion, the formation of binuclear complexes $(\eta^5\text{-}C_5H_4R)_2M(CO)(\mu\text{-}H)Fe(CO)_4$ can be rationalized as a simple Lewis base–acid association. The basic precursor $(\eta^5\text{-}C_5H_4R)_2M(CO)H$ is generated "in situ" from the trihydride $(\eta^5\text{-}C_5H_4R)_2MH_3$ by an "internal carbonylation" reaction. This conclusion disagrees with a previously proposed mechanism which involves the addition of an hydride ion H$^-$ to a carbonyl of $Fe(CO)_5$, followed by a speculative molecular rearrangement.[7a] In the presence of an excess of "$Fe(CO)_4$", the iron moiety of these binuclear complexes is converted to the trimetallic system $[Fe_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}CO)]$. The bonding within the μ-COM (M = Nb, Ta) can be described as a bridging carbyne O-metalated by a Lewis acid organometallic fragment. This feature is of particular interest in regard to the strategies that have been suggested for the activation of carbon monoxide toward reduction. The reduction of the carbon–oxygen bond order is achieved here both through formation of a μ-η^1 bridge and by coordination of a Lewis acid center to the oxygen atom.

Experimental Section

General Data. Infrared spectra were obtained at room temperature with a Perkin-Elmer 589 B spectrophotometer; NMR spectra were recorded on JEOL FX 100 and Brucker WM 400 spectrometers. Mass spectra were taken on Finnigan 3002 device (70 eV): only the most characteristic fragments are reported. Elemental analyses were carried out by the CNRS (Vernaison, France) and the Dornis and Kolbe (Mülheim, Germany) microanalytical service.

General Procedures. All manipulations of air-sensitive compounds were performed under purified argon and carried out by using standart Schlenk techniques. The solvents were distilled under argon from sodium and benzophenone immediately before use. Column chromatography was performed with silica gel 60 particles size 0.063–0.200 mm purchased from E. Merck AG. Trihydrides **1a**, **1′a**, **1b**, and **1′b** were prepared as previously reported by reduction of Cp_2MCl_2 or Cp'_2MCl_2 with $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ (M = Ta)[14] or with $LiAlH_4$ (M = Nb)[1a]. Compounds **2a** and **2b** were obtained by heating the trihydrides compounds **1a** and **1b**, respectively, under CO (1 atm) in boiling nonane[15] and toluene.[1d]

$(\eta^5\text{-}C_5H_4CMe_3)_2M(CO)H$ [2′a (M = Ta) and 2′b (M = Nb)]. A solution of Cp'_2MH_3 (1 mmol) in 50 mL of nonane (M = Ta) or in 40 mL of toluene (M = Nb) at reflux was treated with carbon monoxide at atmospheric pressure for 3 h. The resulting brown red solution was cooled, and the solvent was removed under reduced pressure. Sublimation of the residue (M = Ta, 150 °C at 10^{-3} torr; M = Nb, 120 °C at 10^{-3} torr) afforded purple-red crystals.

$(\eta^5\text{-}C_5H_4CMe_3)_2Ta(CO)H$ (**2′a**): 60% yield, ^{1}H NMR and IR, see Table I; ^{13}C NMR (C_6D_6) δ 32.3 (Me), 33.3 (Me_3C), 76.3, 79.5, 80.8, 81.5, 130 (Cp′), 262 (CO); mass fragments, *m/e* 452 (M, 18), 422 (M – CO – H_2, 100). Anal. Calcd for $C_{19}H_{27}OTa$: C, 50.45; H, 6.02. Found: C, 51.20; H, 5.97.

$(\eta^5\text{-}C_5H_4CMe_3)_2Nb(CO)H$ (**2′b**): 85% yield; ^{1}H NMR and IR, see Table I; ^{13}C NMR (C_6D_6) δ 32.0 (Me), 33.1 (Me_3C), 82.5, 83, 84, 84.7, 130 (Cp′), 256.5 (CO); mass fragments, *m/e* 364 (M, 15), 334 (M – CO–H_2, 100). Anal. Calcd for $C_{19}H_{27}ONb$: C, 62.64; H, 7.47. Found: C, 62.10; H, 7.15.

Reaction of $(\eta^5\text{-}C_5H_4CMe_3)_2MH_3$ (M = Ta, Nb) with $Fe_2(CO)_9$. $Fe_2(CO)_9$ (1.2 mmol) was added at room temperature with stirring to a solution of Cp'_2MH_3 (1 mmol) in toluene (30 mL). The progress of the reaction was monitored by recording infrared spectra at suitable intervals. The mixture was filtered after 5 h, when all of the $Cp'_2M(CO)H$ had disappeared. The filtrate was evaporated and the residue washed with heptane to give a dark red solid. The crude reaction product was chromatographed on silica gel at low temperature (–30 °C) with toluene as eluant. The product **3′a** (or **3′b**) eluted first, and red material remained on the column. The analytical samples were obtained by recrystallization from a toluene–heptane mixture as red-brown solids.

$(\eta^5\text{-}C_5H_4CMe_3)_2Ta(CO)(\mu\text{-}H)Fe(CO)_4$ (**3′a**): 8% yield; mass fragments, *m/e* 620 (M, 15), 592 (M – CO, 2), 480 (M – 5CO, 10), 452 ($Cp'_2Ta(CO)H$, 8), 422 ($Cp'_2Ta(CO)H\text{-}CO\text{-}H_2$ 54), 298 (Cp'_2Fe, 5), 91 (C_7H_7, 100). Anal. Calcd for $C_{23}H_{27}O_5FeTa$: C, 44.53; H, 4.39; Fe, 9.00. Found: C, 43.90; H, 4.21; Fe, 9.4.

$(\eta^5\text{-}C_5H_4CMe_3)_2Nb(CO)(\mu\text{-}H)Fe(CO)_4$ (**3′b**): 15% yield; mass fragments, *m/e* 532 (M, 2), 448 (M – 3CO, 6), 392 (M – 5 CO, 14), 364 ($Cp'_2Nb(CO)H$, 2.5), 336 (Cp'_2NbH, 6), 334 ($Cp'_2NbH\text{–}H_2$, 12), 298 (Cp'_2Fe, 3), 91 (C_7H_7, 100). Anal. Calcd for $C_{23}H_{27}O_5FeNb$: C, 51.90; H, 5.11; Fe, 10.49. Found: C, 52.25; H, 5.34; Fe, 10.75.

Reaction of $(\eta^5\text{-}C_5H_5)_2M(CO)H$ (M = Ta, Nb) with $Fe_2(CO)_9$. A solution of $(\eta^5\text{-}C_5H_5)_2M(CO)H$ (1 mmol) in toluene (30 mL) was added to a suspension of $Fe_2(CO)_9$ (1.2 mmol) in toluene (40 mL). The mixture was stirred at room temperature for 3 h and filtered. The crude solid was washed three times with heptane (30 mL) and purified by chromatography in the same manner as before. Complexes $(\eta^5\text{-}C_5H_5)_2Ta(CO)(\mu\text{-}H)Fe(CO)_4$ (**3a**) and $(\eta^5\text{-}C_5H_5)_2Nb(CO)(\mu\text{-}H)Fe(CO)_4$ (**3b**) were obtained in 45% and 55% yields, respecitvely.

Reaction of $(\eta^5\text{-}C_5H_4CMe_3)_2M(CO)H$ (M = Ta, Nb) with $Fe_2(CO)_9$. Equimolar amounts of $Cp'_2M(CO)H$ and $Fe_2(CO)_9$ in toluene (30 mL) were stirred at room temperature for 2 h. After filtration and evaporation of the solvent, a low-temperature chromatography (–30 °C; toluene as eluant) of the crude product followed by a recrystallization in toluene–heptane mixture afforded **3′a** (42% yield) or **3′b** (58% yield).

Reaction of $(\eta^5\text{-}C_5H_5)_2M(CO)H$ (M = Ta, Nb) with $Fe_3(CO)_{12}$. The reaction was carried out at room temperature by adding a toluene solution of 2 equiv of $Fe_3(CO)_{12}$ to a stirred toluene solution of the title tantalum (or niobium) complex. The reaction mixture was stirred for 7 h; the black-red precipitate was filtered and washed several times with toluene to remove the excess of $Fe_3(CO)_{12}$. The precipitate was dried under vacuum to give complex **4a** (or **4b**) as a red solid.

$(\eta^5\text{-}C_5H_5)_2Ta(CO)(\mu\text{-}H)Fe_3(CO)_{11}$ (**4a**): 35% yield. Anal. Calcd for $C_{22}H_{11}O_{12}Fe_3Ta$: C, 32.39; H, 1.36; Fe, 20.54. Found: C, 32.48; H, 1.41; Fe, 20.95.

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(η^5-$C_5H_5)_2Nb(CO)(\mu$-$H)Fe_3(CO)_{11}$ (**4b**): 30% yield (not analyzed).

Reaction of (η^5-$C_5H_4CMe_3)_2M(CO)H$ (M = Ta, Nb) with $Fe_3(CO)_{12}$. The reaction was conducted as described above. After the mixture was stirred for 4 h, the infrared spectrum of the toluene mixture showed complete conversion of **2′a** (or **2′b**). The solvent was then removed, and the crude material was chromatographed on silica gel at low temperature (–30 °C) with toluene as eluant. Complex **4′a** (or **4′b**) eluted first and was obtained as a red solid in ca. 30% yield by removal of the solvent. Recrystallization from toluene–heptane provided pure samples.

(η^5-$C_5H_4CMe_3)_2Ta(CO)(\mu$-$H)Fe_3(CO)_{11}$ (**4′a**): dark red crystals; mp 105–107 °C; mass fragments, successive loss of CO from *m/e* 704 (M – 8CO, 2), 536 (M – 2Fe – 10CO, 20), 423 (Cp'_2Ta, 85), 422 (Cp'_2Ta–H, 100). Anal. Calcd for $C_{30}H_{27}O_{12}Fe_3Ta$: C, 38.82; H, 2.93; Fe, 18.05. Found: C, 39.41; H, 3.05; Fe, 17.78.

(η^5-$C_5H_4CMe_3)_2Nb(CO)(\mu$-$H)Fe_3(CO)_{11}$ (4′b): dark red crystals; mp 120 °C; mass fragments, successive loss of CO from *m/e* 812 (M – CO, 3) and from 797 (812 – CH_3, 3), 363 (Cp'_2NbCO, 30), 335 (Cp'_2Nb, 63), 334 (Cp'_2Nb – H, 78). Anal. Calcd for $C_{30}H_{27}O_{12}Fe_3Nb$: C, 42.89; H, 3.24; Fe, 19.95. Found: C, 43.50; H, 3.51; Fe, 19.4.

Reaction of (η^5-$C_5H_4CMe_3)_2MH_3$ (M = Ta, Nb) with an Excess of $Fe_2(CO)_9$. $Fe_2(CO)_9$ (3 mmol) was added to a stirred solution of (η^5-$C_5H_4CMe_3)_2MH_3$ (1 mmol) in toluene (50 mL). After 10 h, the reaction mixture was evaporated to leave a dark brown solid. Chromatography on silica gel (at –30 °C) with toluene as eluant followed. The first material to elute was [(η^5-$C_5H_4CMe_3)Fe(CO)_2]_2$ identified by comparison of its spectroscopic data with an authentic sample synthesized from $C_5H_5CMe_3$ and $Fe(CO)_5$. Recrystallization from toluene and heptane provided a pure sample. [(η^5-$C_5H_4CMe_3)Fe(CO)_2]_2$: air-stable dark violet crystals; mp 162 °C; NMR (C_6D_6) δ 4.51 (t, 2 H), 3.87 (t, 2 H), 1.24 (s, 9 H); IR (toluene) 1990, 1944, 1777 cm^{-1}; mass fragments, *m/e* 466 (M, 35), 438 (M – CO, 18), 410 (M – 2CO, 23), 382 (M – 3CO, 38), 354 (M – 4CO, 8), 338 (M – 4CO – CH_4, 91), 205 (Cp′Fe(CO), 86), 177 (Cp′Fe, 100). Anal. Calcd for $C_{22}H_{26}FeO_4$ C, 56.58; H, 5.62; Fe, 23.96. Found: C, 56.75; H, 5.66; Fe, 24.59. This first fraction was followed by the previously described complex **4′a (or 4′b)**.

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Registry No. **1a**, 12117-02-1; 1′a, 84749-48-4; **1b**, 11105-67-2; 1′b, 84749-49-5; **2a**, 11105-69-4; **2′a**, 84749-50-8; **2b**, 11105-68-3; **2′**b, 84749-51-9; **3a**, 95765-90-5; **3′**a, 95765-91-6; **3b**, 67108-78-5; **3′**b, 95765-92-7; **4a**, 95765-93-8; **4′**a, 95765-94-9; **4b**, 95784-29-5; **4′**b, 95765-95-0; [$Cp_2Ta(CO)(THF)][Fe_3(CO)_{10}(\mu$-$H)(\mu$-$CO)]$, 95765-98-3; [$Cp_2Nb(CO)(THF)][Fe_3(CH)_{10}(\mu$-$H)(\mu$-$CO)]$, 95765-99-4; [$Cp'_2Ta(CO)(THF)][Fe_3(CO)_{10}(\mu$-$H)(\mu$-$CO)]$, 95766-01-1; [$Cp'_2Nb(CO)(THF)]Fe_3(CO)_{10}(\mu$-$H)(\mu$-$CO)]$, 95766-03-3; [$Cp'Fe(CO)_2]_2$, 95765-96-1; $Fe_2(CO)_9$, 15321-51-4; $Fe_3(CO)_{12}$, 17685-52-8; $Fe(CO)_5$, 13463-40-6; [$Fe_3(CO)_{10}(\mu$-$H)(\mu$-$CO)]^-$, 55188-22-2; [$HFe(CO)_4]^-$, 18716-80-8; $C_5H_5CMe_3$, 35059-40-6.

Solid-State Conformations of Compounds (Arene)$L_2MP(C_6H_5)_3$ and (Arene)$LL'MP(C_6H_5)_3$

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The solid-state structure of the ethane-type molecule $Cp(CO)_2MnP(C_6H_5)_3$ reveals a deviation from the staggered conformation, which can be described by an average torsion angle of 37.7° about the Mn–P bond. This deviation is caused by the propeller structure of the triphenylphosphine ligand. It brings the gauche phenyl, face exposed to Cp, closer to the Cp ring and the gauche phenyl, edge exposed to Cp, further away from the Cp ring. Additional adjustments of the phenyl rings by rotation of the $P{-}C_{ipso}$ bonds further diminish the nonbonding interactions of the Cp ring with the neighboring phenyl ortho C–H bonds. Analyses of the structures of another 11 compounds of the type (arene)$L_2MP(C_6H_5)_3$ and 17 compounds of the type (arene)$LL'MP(C_6H_5)_3$, found by a search in the Cambridge Structural Database, demonstrate that their solid-state conformations are primarily determined by similar intramolecular effects and only insignificantly influenced by crystal packing forces.

Introduction

In the Rh-catalyzed enantioselective hydrogenation of olefins, using chelating bis(phosphines) of the type diop, prophos, chiraphos, BPPFA, BPPM, and norphos, the two phenyl rings at the P atoms are differentiated with respect to axial/equatorial arrangement and face/edge exposure.[1-6] This differentiation, caused by the puckering of the chelate ring, is thought to be the primary mechanism for chirality transfer from the asymmetric centers in the chelate backbone to the Rh coordination sites, active in the enantioselective catalysis.[4-6] In this paper an alternate phenyl

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