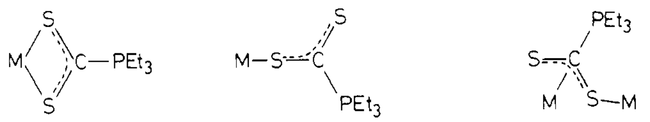
Chart I



the basis of steric requirements due to the larger coordination number and of the different oxidation number of the metal.

Conclusions

The triethylphosphine–carbon disulfide adduct $Et_3P{\cdot}CS_2$ is a very versatile ligand. Indeed this zwitterion can act as a monodentate or bidentate σ donor by means of its electron-rich sulfur atoms, but it can be also π bonded to a metal through the conjugated CS_2 pseudoallylic system, as a four-electron donor (Chart I).

The formation of the complexes **1**–**5**, in which the zwitterion acts as a monodentate ligand, by displacement of the weakly coordinated THF ligand from carbonyl derivatives, is not unexpected. In fact Z has undoubtely nucleophilic character, undergoing alkylation with a variety of electrophiles such as CH_3I to give the phosphonium salt $[Et_3PCSSCH_3]I$.

Concerning the formation of the unexpected complex **6**, on the basis of the reactivity pattern summarized in Scheme I, it is possible to propose a reaction mechanism involving the initial formation of the mononuclear compound **2**. The CS_2 group of the coordinated zwitterion in **2** can, in fact, displace two CO groups from another $[Mo(CO)_5(S_2CPEt_3)]$ molecule by the four-electron donor pseudoallylic CS_2 group. The successive displacement of another CO molecule by triethylphosphine suggests a remarkable back-donation in the metal–pseudoallylic group linkage.

As it is shown in the Experimental Section, at least in two cases the triethylphosphine ligand in compound **6** comes from the cleavage of the P–CS_2 bond in a zwitterion molecule. Such a cleavage is not completely unexpected in reactions carried out at high temperature: it has been previously observed in the reaction of Z with Co(II) aquocations and the triphospine 1,1,1-tris((diphenylphosphino)methyl)ethane,[26] but it is rather surprising in the reaction of Z with $[Mo(CO)_3(C_7H_8)]$ which is carried out under mild conditions. On the other hand the reaction of tertiary phosphines and carbon disulfide is somewhat reversible, expecially when higher trialkylphosphines are employed.[27]

Acknowledgment. Thanks are expressed to Mr. F. Cecconi and Mr. G. Scapacci for technical assistance and to Mr. F. Nuzzi and Mr. G. Vignozzi for microanalyses.

Registry No. **1**, 80975-88-8; **2**, 80975-89-9; **3**, 80975-90-2; **4**, 80975-91-3; **5**, 80975-93-5; **6**, 80137-00-4; $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(THF)]BF_4$, 63313-71-3; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$, 12079-65-1; $[Mo(C_7H_8)(CO)_3]$, 12125-77-8; $Et_3P{\cdot}CS_2$, 997-47-7.

Supplementary Material Available: Listings of structure factor amplitudes for compounds 1 and 6 (16 pages). Ordering information is given on any current masthead page.

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Synthesis and Reactions of Dicarbonyl(η-cyclopentadienyl)dihydridorhenium(III)

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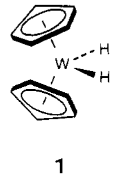
The title compound $(\eta\text{-}C_5H_5)Re(CO)_2H_2$ (**2**), a thermally stable colorless crystalline solid melting at 36–37 °C, was prepared in 49% yield by UV irradiation of $(\eta\text{-}C_5H_5)Re(CO)_3$ with Et_2SiH_2 and treatment of the intermediate hydridosilylrhenium compound with silica gel in $CHCl_3$. Ethanolic KOH deprotonates **2** forming $[(\eta\text{-}C_5H_5)Re(CO)_2]^{2-}$ which was isolated as its tetraethylammonium salt. Derivatives prepared from **2** or its dianion are $(\eta\text{-}C_5H_5)Re(CO)_2(SnCl_3)H$ (**4**), $(\eta\text{-}C_5H_5)Re(CO)_2(SnMe_3)_2$ (**5**), $(\eta\text{-}C_5H_5)Re(CO)_2Me_2$ (**7**), and $(\eta\text{-}C_5H_5)Re(CO)_2(1\text{-}2\text{-}\eta^2\text{-}C_7H_8)$ (**6**). IR intensities of carbonyl stretching bands indicate trans stereochemistry for **2**, **4**, **5**, and **7**. An unusual reaction of the dianion with acetyl chloride forms $(\eta\text{-}C_5H_5)Re(CO)_2(\eta^2\text{-vinyl acetate})$ (**8**).

Introduction

The interest and importance of molecular hydrides of transition metals is attested by several major reviews of the subject over the past 25 years.[1] Much current work involves hydrido cluster complexes,[1e] but numerous gaps remain in our knowledge of mononuclear hydrides, especially mononuclear polyhydrides. Thus, a number of organometallic hydrides which could reasonably be expected to exist on the basis of 18-electron formalism have not been prepared.

The dihydrides **1** and **3** are well-known, and many aspects of their chemistry have been explored.[1] We now report the synthesis and some reactions of the novel dihydride **2**, which constitutes the middle member of an isoelectronic series formed by successive replacement η-



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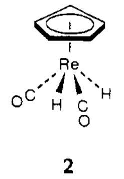

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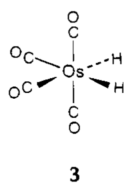

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C_5H_5 groups[2a] with pairs of carbonyls as the electronic requirement of the metal decreases. Another interesting aspect of **2** is that it is a member of the relatively small group of mononuclear polyhydrides known at present that do not contain phosphorus ligands.

Results and Discussion

Synthesis of (η-C_5H_5)Re(CO)$_2$H$_2$ (2). The new hydride was first observed in trace amounts during product workup from photochemical reactions of silanes with (η-C_5H_5)Re(CO)$_3$.[2b] We have now established that **2** may be prepared in reasonable (49%) yield by the sequence of eq 1 and that a hydridosilylrhenium intermediate is involved.

$$(\eta\text{-}C_5H_5)Re(CO)_3 \xrightarrow[\text{heptane}]{Et_2SiH_2,\ h\nu} (\eta\text{-}C_5H_5)Re(CO)_2(SiEt_2H)H$$

$$(\eta\text{-}C_5H_5)Re(CO)_2(SiEt_2H)H \xrightarrow[CHCl_3]{\text{silicic acid}} \underset{\mathbf{2}}{(\eta\text{-}C_5H_5)Re(CO)_2H_2} \quad (1)$$

Pure **2** was separated from unreacted starting materials by careful chromatography on silicic acid using heptane. Because of convenience and availability, the silane generally used in the synthesis was Et_2SiH_2; some other silanes such as Me_2SiH_2 and $PhCH_2SiH_3$ resulted in similar yields. However, use of the same procedure with Ph_3SiH, Et_3SiH, Me_3SiH, or Ph_2SiH_2 led to much lower yields of **2**; the main product isolated was the hydridosilylrhenium compound, e.g., (η-C_5H_5)Re(CO)$_2$(SiPh$_3$)H.[2b] The crucial factor here appears to be the susceptibility of the rhenium–silicon bond to cleavage by the silicic acid–chloroform medium, and this is influenced by the substituents.

Silicic acid conversion of a rhenium–silicon to a rhenium–hydrogen bond was presumably involved in the synthesis of $H_2Re_2(CO)_8$ from $Ph_2SiH_2Re_2(CO)_8$.[3] A likely route for the conversion would involve the –OH groups of silicic acid, as suggested in eq 2; this process resembles the known reaction of $Me_3SiMn(CO)_5$ with water or methanol.[4]

$$Re{-}SiR_3 + HO{-}Si{\equiv} \rightarrow Re{-}H + R_3Si{-}O{-}Si{\equiv} \quad (2)$$

We have also obtained the dihydride **2** by reduction of (η-C_5H_5)Re(CO)$_2$Br$_2$[5] with either $NaBH_4$ or (i-C_4H_9)$_2$AlH, but yields are in the 10–15% range at best. These reductions are not straightforward, and there is considerable decomposition during the reaction.

Properties of (η-C_5H_5)Re(CO)$_2$H$_2$ (2). When very pure, **2** is a colorless crystalline solid (mp 36–37 °C) which can be handled for several hours in air, either in the solid state or in solution, without noticeable decomposition. It sublimes readily (room temperature (0.005mmHg)) and has high solubility in common organic solvents, including paraffin hydrocarbons. Compound **2** is thermally very stable, and no reaction or decomposition occurred when it was refluxed in various hydrocarbon solvents with boiling points up to 140 °C. In this respect it differs from the isoelectronic $H_2Os(CO)_4$ (**3**) which forms polynuclear carbonyl hydrides with loss of H_2 and CO under those conditions.[6,7]

Table I. Spectroscopic Properties of (η-C_5H_5)Re(CO)$_2$H$_2$ (2)

infrared[a]	ν(CO), cm^{-1}	2022 (m)	1954 (s)
Raman[b]	ν(Re–H), cm^{-1}	1996	1969
	ν(Re–D),[c] cm^{-1}	1411	1398
NMR[d]	^{1}H, δ	5.28 (s, 5 H)	–9.26 (s, 2 H)
	^{13}C, δ	82.65[e]	194.09

[a] In n-heptane. [b] Solid state, see Figure 1. [c] For (η-C_5H_5)Re(CO)$_2$D$_2$. [d] C_6D_6 solution. [e] C_5H_5 carbons.

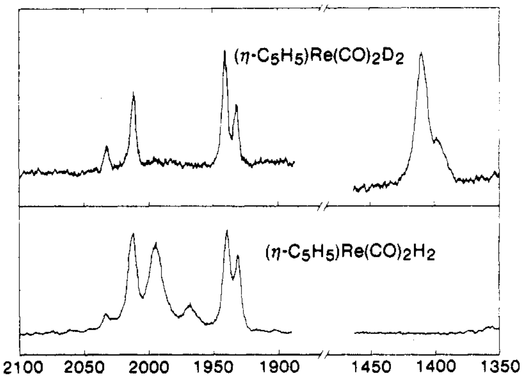
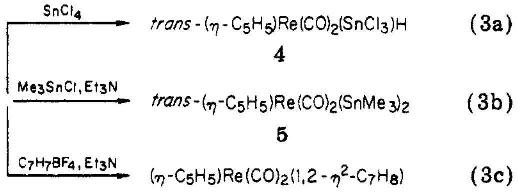


Figure 1. Raman spectra of solid-state samples of (η-C_5H_5)Re(CO)$_2$H$_2$ (**2**) and its deuterated form.

IR and NMR spectroscopic data for **2** are summarized in Table I. The lower frequency (asymmetric) carbonyl stretching vibration in the infrared spectrum is more intense than the higher frequency band, indicative of the trans geometry shown in **2**.[2b,8] No infrared bands due to ν(Re–H) are observable in the infrared even at higher concentration, but two ν(Re–H) bands appear in the Raman spectrum, appropriately shifted in the dideuteride (η-C_5H_5)Re(CO)$_2$D$_2$ (see Figure 1). The two Re–H stretching bands are clearly the symmetric and asymmetric combinations and occur in the region expected for terminal hydrides.[1d]

The ^{1}H NMR spectrum (Table I) shows the Re–H signal at δ –9.86. The mass spectrum of **2** shows the molecular ion, and competitive loss of CO and H as would be expected for terminally bonded hydrides.[9] There is a tendency for hydrogens to be lost in pairs; for example, the intensity ratio for the ions $C_5H_5Re(CO)_2^+$, $C_5H_5Re(CO)_2H^+$, and $C_5H_5Re(CO)_2H_2^+$ is 12:1:7, as determined by a fitting program similar to one described.[10]

Reactions of (η-C_5H_5)Re(CO)$_2$H$_2$ (2). The dihydride undergoes several reactions with electrophiles as summarized in eq 3. The reaction of **2** with $SnCl_4$ is similar to that of $H_2Os(CO)_4$.[6,11] We have recently prepared



$$\mathbf{2} \xrightarrow{SnCl_4} \underset{\mathbf{4}}{trans\text{-}(\eta\text{-}C_5H_5)Re(CO)_2(SnCl_3)H} \quad (3a)$$

$$\mathbf{2} \xrightarrow{Me_3SnCl,\ Et_3N} \underset{\mathbf{5}}{trans\text{-}(\eta\text{-}C_5H_5)Re(CO)_2(SnMe_3)_2} \quad (3b)$$

$$\mathbf{2} \xrightarrow{C_7H_7BF_4,\ Et_3N} \underset{\mathbf{6}}{(\eta\text{-}C_5H_5)Re(CO)_2(1,2\text{-}\eta^2\text{-}C_7H_8)} \quad (3c)$$

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(2) (a) We use the prefix η without superscript to imply that all the atoms in a ring or chain, or all the multiply bonded ligand atoms, are bound to the central atom. This is in accordance with recommendations of the International Union of Pure and Applied Chemistry: *Pure Appl. Chem.*, 1971, *28*, 1. (b) Dong, D. F.; Hoyano, J. K.; Graham, W. A. G. *Can. J. Chem.*, **1981**, *59*, 1455.

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Table II. Infrared Carbonyl Stretching Frequencies

compd	ν(CO), cm^{-1}
$(\eta\text{-}C_5H_5)Re(CO)_2(SnCl_3)H^b$ (4)	2040 (m), 1982 (s)
$(\eta\text{-}C_5H_5)Re(CO)_2(SnMe_3)_2$ (5)	1948 (m), 1895 (s)
$(\eta\text{-}C_5H_5)Re(CO)_2(C_7H_8)$ (6)	1969 (s), 1902 (s)
$[Et_4N]_2[(\eta\text{-}C_5H_5)Re(CO)_2]^c$	1849 (s), 1775 (s)
$(\eta\text{-}C_5H_5)Re(CO)_2Me_2$ (7)	2009 (m), 1940 (s)
$(\eta\text{-}C_5H_5)Re(CO)_2(C_4H_6O_2)^d$ (8)	1986 (s), 1915 (s)

[a] In heptane solution unless otherwise indicated; w = weak, m = medium, s = strong. [b] Dichloromethane solution. [c] Tetrahydrofuran solution. [d] Acetate carbonyl band at 1748 (m) cm^{-1}.

trans-$(\eta\text{-}C_5H_5)Re(CO)_2(SnCl_3)H$ (4) by an alternative route involving protonation of the $[(\eta\text{-}C_5H_5)Re(CO)_2SnCl_3]^-$ anion.[2b]

In the reaction with Me_3SnCl (eq 3b) a base was required to carry the reaction to completion. Although we were unable to isolate the presumed intermediate $(\eta\text{-}C_5H_5)Re(CO)_2(SnMe_3)H$, it was detected spectroscopically during the course of the reaction. When the reaction of 2 with 1 mol of Me_3SnCl was monitored by IR, new product bands first appeared at 1988 (m) and 1925 (s) cm^{-1}, which we attribute to the monohydride intermediate. These bands soon disappeared with the development of bands due to 5 and 2. This suggests that a facile disproportionation (eq 4) occurs.

$$(\eta\text{-}C_5H_5)Re(CO)_2(SnMe_3)H \rightarrow 2 + 5 \quad (4)$$

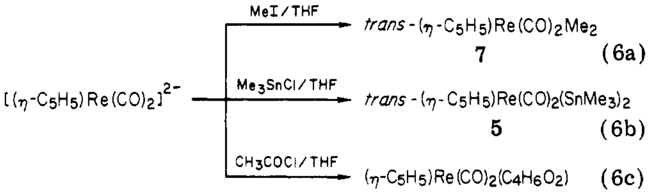
The reaction of 2 with tropylium ($C_7H_7^+$) cation was of interest in view of the behavior of monohydrides toward this strong electrophile and hydride abstractor.[12,13] Reaction of 2 and $[C_7H_7][BF_4]$ either did not occur or was very slow but proceeded more rapidly when triethylamine was added (eq 3c) forming 6, a 1,2-η^2 complex of 1,3,5-cycloheptatriene. Convincing evidence for this coordination mode of cycloheptatriene is provided by the seven different ^{13}C NMR signals for this ring; the two observed ^{13}CO signals confirm the unsymmetrical coordination. The only other well-defined neutral $\eta^2\text{-}C_7H_8$ complex is $(\eta\text{-}C_5H_5)Mn(CO)_2(1\text{-}2\text{-}\eta^2\text{-}C_7H_8)$, formed by reaction of C_7H_8 with photochemically generated $(\eta\text{-}C_5H_5)Mn(CO)_2THF$.[14] We have also prepared 6 photochemically. The detailed course of the reaction of eq 3c is not known, but we consider that likely intermediates are $[(\eta\text{-}C_5H_5)Re(CO)_2(H)(1\text{-}2\text{-}\eta^2\text{-}C_7H_8)]^+$, formed by hydride abstraction and coordination of the resulting C_7H_8,[12] or the tautomeric $[(\eta\text{-}C_5H_5)Re(CO)_2(\eta^3\text{-}C_7H_9)]^+$.

$[(\eta\text{-}C_5H_5)Re(CO)_2]^{2-}$ and Its Reactions. While triethylamine displaced the equilibrium of eq 3b, it was ineffective even in excess when similar reactions of 2 with alkyl halides were attempted. Spectroscopic studies showed that 2 was not sufficiently acidic to be deprotonated by Et_3N to an observable extent. We therefore set out to deprotonate 2 with stronger bases in the hope that the resulting anion would be useful synthetically.

After a number of attempts using various bases and solvents, ethanolic KOH was found to deprotonate 2 conveniently forming a dianion, which could be obtained as an analytically pure yellow solid with large counterions such as Et_4N^+ or $(Ph_3P)_2N^+$ (eq 5). Elemental analysis

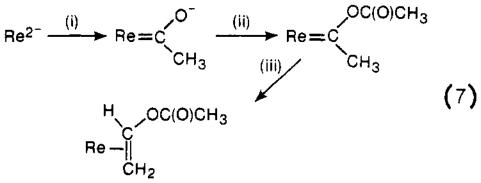
$$2 \xrightarrow[\text{ethanol}]{\text{KOH}} [(\eta\text{-}C_5H_5)Re(CO)_2]^{2-} \xrightarrow{Et_4NBr} [Et_4N]_2[(\eta\text{-}C_5H_5)Re(CO)_2] \quad (5)$$

is consistent with formulation as a dianion, as is the IR spectrum; carbonyl stretching bands (Table II) occur at 1849 and 1775 cm^{-1}, some 160 cm^{-1} lower than in 2. Reactions so far investigated also support the dianion formulation and are shown in eq 6.



The dimethylrhenium derivative 7 from eq 6a forms stable, pale yellow crystals. Nesmeyanov et al.[15] have previously prepared 7 from $(\eta\text{-}C_5H_5)Re(CO)_2Br_2$ and CH_3MgI. The bis(trimethyltin) derivative 5 is identical with the compound obtained in eq 3b.

Compound 8, formed from acetyl chloride in eq 6c, is formulated as an η^2-vinyl acetate complex. A reasonable reaction sequence leading to 8 is shown in eq 7, where Re



represents the $(\eta\text{-}C_5H_5)Re(CO)_2$ moiety. Initial formation of an acylate anion would be followed by attack of a second mole of acetyl chloride on the acylate oxygen to form the acetoxycarbene complex. The latter, upon shift of hydrogen to the carbene carbon and coordination of the double bond produced, would yield 8. There is precedent for step ii,[16] and a process that may be similar to step iii has been studied. Thus, Fischer et al.[17] observed that tertiary nitrogen bases reacted with $(OC)_5Cr{=}C(OCH_3)CR_2H$ forming $(OC)_5CrNR_3$ and the vinyl ether $CH_3O(H)C{=}CR_2$. Although it was suggested that the carbene fragment underwent the hydrogen shift after displacement,[17] the possibility of a shift on the complexed ligand with subsequent displacement of the olefin cannot be excluded. In the reaction leading to 8, just what basic species (if any) is involved is unclear; if it is tetrahydrofuran (the solvent), a product having coordinated olefin would be expected regardless of the details of the shift.

Carbonyl stretching frequencies for the derivatives of 2 are summarized in Table II. In all species where cis and trans isomers are possible, the trans isomer only is present in the solutions on the basis of relative band intensities.

Both $[NO][PF_6]$ and $[C_7H_7][BF_4]$ react very rapidly with the $[(\eta\text{-}C_5H_5)Re(CO)_2]^{2-}$ anion in THF at room temperature to produce the dihydride 2 in good yield. We presume that these reactions proceed by oxidation of the anion forming metal-centered radicals which then abstract hydrogen atoms from the solvent. This would imply a Re–H bond strength greater than that of the α-C–H bond in THF, which is given as 92 kcal mol^{-1}.[18]

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Conclusions

The number of known dicarbonyl(η-cyclopentadienyl)rhenium(III) derivatives is not large. These consist of (η-C_5H_5)Re$(CO)_2Br_2$,[19] (η-C_5H_5)Re$(CO)_2$(X)Me (X = Br, I),[20,21] (η-C_5H_5)Re$(CO)_2$(X)H,[20] (η-C_5H_5)Re$(CO)_2Me_2$,[20] (η-C_5H_5)Re$(CO)_2$(I)HgCl,[20] (η-C_5H_5)Re$(CO)_2$(Br)HgBr,[20] (η-C_5H_5)Re$(CO)_2$(CH_2Ph)H,[22] and ten derivatives of the formula (η-C_5H_5)Re$(CO)_2$(ER_3)R′, where ER_3 is a silyl, germyl, or tin ligand and R′ is H, Me, or $SnMe_3$.[2b]

We have now prepared the dihydride **2**, the simplest member of this class, as a stable and readily accessible compound that provides a valuable synthetic starting point. As noted above, **2** is closely related through the 18-electron rule to $H_2Os(CO)_4$ (**3**), and in the same way $[(\eta\text{-}C_5H_5)Re(CO)_2]^{2-}$ is an analogue of the useful anion $[Os(CO)_4]^{2-}$. We are currently attempting to extend this method to the synthesis of other new mononuclear polyhydrides. It is of interest that two phosphine derivatives of **2**, (η-C_5H_5)Re$(PR_3)_2H_2$, have recently been prepared by a quite different route starting with $H_7Re(PR_3)_2$.[23]

Experimental Section

All reactions were carried out under an atmosphere of nitrogen mainly by the use of Schlenk-type apparatus. Solvents were dried by standard procedures (if necessary) and deaerated just prior to use. The reagents used were commercial reagent gradient quality or were prepared according to published procedures. The (η-C_5H_5)Re$(CO)_3$ was prepared in nearly quantitative yield from C_5H_5Tl and BrRe$(CO)_5$.[19a]

Melting points were taken in capillaries and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 337 grating spectrometer and in expanded form on a Hewlett-Packard 7127A recorder; spectra were calibrated with gaseous carbon monoxide. ^{1}H NMR measurements were made on Varian HA-100, Varian HA-100/Digilab FT system, and Bruker WH-200 instruments. The proton-decoupled ^{13}C NMR measurements were obtained on the Bruker HFX-90/Nicolet 1085 system in the FT mode. Mass spectra were obtained on an AEI-MS-12 instrument operating at 15–70-eV ionizing voltage. Microanalyses were carried out by the microanalytical laboratory of this department.

Preparation of (η-C_5H_5)Re$(CO)_2H_2$ (2). A solution of (η-C_5H_5)Re$(CO)_3$ (2.00 g, 5.97 mmol) and Et_2SiH_2 (5.0 g, 57 mmol) in 250 mL of cyclohexane was irradiated by using a 450-W UV source through a water-cooled quartz jacket for 10 h. IR indicated approximately a 1:1 mixture of (η-C_5H_5)Re$(CO)_3$ and (η-C_5H_5)Re$(CO)_2$($SiEt_2H$)H.[24] After removal of the solvent under vacuum, the residual oil was stirred for 3 h with 10 g of silicic acid and 50 mL of chloroform. This mixture was filtered, and an additional 50 mL of chloroform was used to ensure all product was removed from the silicic acid; IR of the combined filtrates indicated that (η-C_5H_5)Re$(CO)_3$ and **2** were the only carbonyl compounds present. The chloroform was evaporated, leaving a reddish oil, which was then carefully chromatographed on a 50-g silicic acid column made up and eluted with heptane. The fractions were monitored by IR in the carbonyl stretching region and showed a separation of the two compounds with **2** eluted first. The fractions containing product were evaporated, and the residue was sublimed at 30 °C (0.005 mm) to afford colorless crystals of (η-C_5H_5)Re$(CO)_2H_2$ (0.90 g, 49%), mp 36–37 °C.

Anal. Calcd for $C_7H_7O_2Re$: C, 27.18; H, 2.28. Found: C, 26.95; H, 2.19.

Preparation of (η-C_5H_5)Re$(CO)_2D_2$. To a sample of (η-C_5H_5)Re$(CO)_2H_2$ (100 mg) dissolved in 20 mL of heptane was added D_2O (2 mL), florisil (0.20 g which had been pretreated with D_2O), and Et_3N (0.50 mL). This reaction mixture was stirred vigorously for 24 h. The heptane layer was decanted and then evaporated under vacuum. The residue was sublimed at 30 °C to afford colorless crystals of the product (60 mg); the mass spectrum indicated that deuteration was more than 90% complete.

Preparation of (η-C_5H_5)Re$(CO)_2$($SnCl_3$)H (4). A solution of **2** (0.20 g, 0.65 mmol) in heptane (25 mL) was treated with $SnCl_4$ (0.30 g, 1.15 mmol) and then stirred for 1 h. The resulting pale yellow solid precipitate was filtered, washed with heptane (2 × 10 mL), and then dried under vacuum. This solid was crystallized from heptane–dichloromethane to yield pale yellow crystals of the product (0.18 g, 52%), mp 130 °C dec.

Anal. Calcd for $C_7H_6Cl_3O_2Sn$: C, 15.76; H, 1.13. Found: C, 15.88; H, 1.20.

Preparation of (η-C_5H_5)Re$(CO)_2$$(SnMe_3)_2$ (5). A solution of **2** (0.15 g, 0.50 mmol) and Me_3SnCl (0.18 g, 0.90 mmol) in heptane (25 mL) was treated with 0.10 mL of Et_3N. There was an immediate precipitate of Et_3NHCl; the mixture was stirred for 2 h. The precipitate was filtered off, and then the heptane filtrate was evaporated under vacuum. The residue was sublimed at 30 °C for 5 h to remove any remaining **2**, after which sublimation at 70 °C (0.005 mm) afforded white crystals of the product (200 mg, 62%): mp 105–106 °C; ^{1}H NMR ($CDCl_3$) δ 5.03 (s, 5 H), 0.42 (s, 18 H, $J(^{117}Sn\text{–}CH_3)$ = 46.4 Hz, $J(^{119}Sn\text{–}CH_3)$ = 48.6 Hz); mass spectrum, molecular ion observed and peaks corresponding to competitive CO and CH_3 loss.

Anal. Calcd for $C_{13}H_{23}O_2ReSn_2$: C, 24.59; H, 3.65. Found: C, 24.95; H, 3.78.

Preparation of (η-C_5H_5)Re$(CO)_2C_7H_8$ (6). A solution of **2** (0.155 g, 0.50 mmol) in tetrahydrofuran (20 mL) was treated with $C_7H_7BF_4$ (0.15 g, 0.84 mmol) and Et_3N (0.25 mL), and the resulting mixture was stirred for 30 h. The solvent and volatiles were removed under vacuum, and the remainder was dissolved in heptane (25 mL) and filtered through a short florisil column. The column was first washed with 50 mL of heptane, followed by 75 mL of dichloromethane; the latter fraction contained the product. After the dichloromethane was removed under vacuum, the white solid residue was recrystallized from heptane to yield white crystals of the product (120 mg, 60%): ^{1}H NMR ($CDCl_3$) δ 6.77 (q, 1 H), 6.0 (m, 3 H), 5.26 (s, 5 H, C_5H_5), 3.83 (q, 1 H), 3.18 (m, 2 H), 2.08 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 203.9 (carbonyl), 202.4 (carbonyl), 138.0, 134.2, 128.2, 125.3, 85.9 (C_5H_5), 78.4, 77.0, 76.5; mass spectrum, parent ion and loss of two carbonyls observed; $C_7H_7^+$ is the most intense ion.

Anal. Calcd for $C_{14}H_{13}O_2Re$: C, 42.10; H, 3.28. Found: C, 42.51; H, 3.41.

Deprotonation of (η-C_5H_5)Re$(CO)_2H_2$. A sample of **2** (0.31 g, 1.00 mmol) was added to 10 mL of a 0.4 M KOH solution in ethanol. The resulting mixture was stirred for 4 h to produce an orange solution. Then a solution of Et_4NBr (0.45 g, 2.14 mmol) in 5 mL of ethanol was added, and stirring produced a small amount of a yellow precipitate. This mixture was concentrated (vacuum) to about half volume, resulting in more of the precipitate. The yellow solid was filtered off, washed with cold ethanol (2 × 3 mL), and dried to yield the crude anion (0.30 g, 53%). Analytical samples were obtained by recrystallization from tetrahydrofuran, in which it was slightly soluble. Similar results were obtained by using $(Ph_3P)_2NCl$ instead of Et_4NBr.

Anal. Calcd for $C_{23}H_{45}N_2O_2Re$: C, 48.65; H, 7.99; N, 4.93. Found: C, 49.10; H, 8.20; N, 5.10.

Preparation of (η-C_5H_5)Re$(CO)_2$$(CH_3)_2$ (7). The tetraethylammonium salt of the anion prepared above (0.20 g, 0.35 mmol) was stirred with 0.15 mL of methyl iodide in 20 mL of tetrahydrofuran for 1 h. The solvent was removed under vacuum and the residue extracted with 30 mL of benzene. Evaporation of the benzene gave a yellow solid, which was sublimed at 45 °C (0.005 mm) to afford pale yellow solid product (65 mg, 55%): mp 150–155 °C; ^{1}H NMR ($CDCl_3$) δ 5.05 (s, 5 H, cyclopentadienyl protons), 0.77 (s, 6 H, methyl protons); mass spectrum, molecular ion and loss of two carbonyls observed along with competitive loss of methyl groups.

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[24] Continued irradiation beyond this point led to some decomposition and complications during product recovery. An approximately 50% conversion of (η-C_5H_5)Re$(CO)_3$ may be near the optimum, since unconsumed starting material is so easily recovered.

Anal. Calcd for $C_9H_{11}O_2Re$: C, 32.04; H, 3.29. Found: C, 32.32; H, 3.31.

Preparation of (η-C_5H_5)Re(CO)$_2$($C_4H_6O_2$) (8). The tetraethylammonium salt of the anion prepared above (0.15 g, 0.26 mmol) was stirred with acetyl chloride (50 mg, 0.64 mmol) in 10 mL of tetrahydrofuran for 10 h. Solvent was removed (vacuum), and the residue was extracted with heptane (30 mL); IR spectrum showed product plus some (η-C_5H_5)Re(CO)$_3$ and 2. This heptane extract was placed on a 50-g florisil column. Elution with 100 mL of a 1:1 mixture of dichloromethane and heptane removed the two carbonyl impurities, and then 75 mL of pure dichloromethane eluted the product. Evaporation of the solvent and sublimation of the residue under vacuum resulted in a pale yellow solid product (50 mg, 50%): mp 38-41 °C; ^{1}H NMR ($CDCl_3$) δ 6.49 (dd, 1 H), 5.30 (s, 5 H, cyclopentadienyl), 2.28 (dd, 1 H), 2.13 (dd, 1 H), 2.03 (s, 3 H); mass spectrum, M^+, $(M - CO)^+$, $(M - 2CO)^+$, $(C_4H_6O_2)^+$.

Anal. Calcd for $C_{11}H_{11}O_4Re$: C, 33.59; H, 2.80. Found: C, 33.70; H, 2.95.

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Registry No. 2, 80952-45-0; **4**, 79061-68-0; **5**, 80925-98-0; **6**, 80925-99-1; **7**, 80952-46-1; **8**, 80926-00-7; $[Et_4N]_2[(\eta$-$C_5H_5)Re(CO)_2]$, 80926-02-9; Et_2SiH_2, 542-91-6; $SnCl_4$, 7646-78-8; Me_3SnCl, 1066-45-1; acetyl chloride, 75-36-5.

Reductive Carbonylation of $Mn(CO)_5(CH_3)$ and (η^5-C_5H_5)$Fe(CO)_2(CH_3)$ To Produce Hydrocarbons and Oxygen-Containing Products

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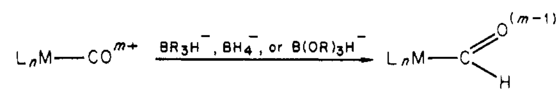
Under a CO atmosphere $Mn(CO)_5(CH_3)$ reacts with diborane to produce alkanes and olefins up to C_4. The yield drops greatly from C_2 through C_4 products, suggesting a chain growth mechanism. Addition of BF_3 to the reaction mixture alters the product distribution by increasing the yield of the longer chain and more saturated hydrocarbons. The reaction of (η^5-C_5H_5)$Fe(CO)_2(CH_3)$ with CO and diborane requires the presence of BF_3 to produce C_2 and higher products, and the function of BF_3 is to promote CO migratory insertion. Isotopic labeling experiments confirm diborane as a source of hydrogen in the products and also demonstrate that carbon atoms in the hydrocarbon products are derived from CO. These general observations are consistent with a repetitive series of migratory insertion and reduction steps, but the presence of unsaturated hydrocarbons and oxygen-containing organics as well as the isotopic composition of the hydrocarbons indicate a complex set of intermediate steps.

Introduction

Since the initial report in 1939,[1] the reduction of organic carbonyl groups by boron and aluminum hydrides has received widespread application.[2] The varying strengths and selectivities of these reagents allow considerable control over the specific reaction. More recently these inorganic hydrides have found application as well in organometallic systems.[3-15] The course of the reactions differs slightly in the organic and organometallic systems. In a typical organic procedure the initial reduction is followed by a hydrolysis step to produce an alcohol, while in the organometallic systems hydrolysis is not always required to produce a boron-free product.

As seen in the following examples, the extent of reaction varies from transfer of a single hydride (eq 1) to more complex reactions involving several equivalents of hydride (eq 2). A borohydride reagent, BH_4^-, BR_3H^-, or $B(OR)_3H^-$,



$$L_nM{-}CO^{m+} \xrightarrow{BR_3H^-,\ BH_4^-,\ \text{or}\ B(OR)_3H^-} L_nM{-}C(=O)H^{(m-1)+} \quad (1)$$

m = 0, 1

$$[(\eta^5\text{-}C_5H_5)(NO)(CO)_2Re]^+ \xrightarrow{BH_4^-} (\eta^5\text{-}C_5H_5)(NO)(CO)Re(CH_3) \quad (2)$$

can attack and transfer a single hydride to the electrophilic

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