Table I. Experimental Data for the Vapor Pressure of $Ru(CO)_5$[a]

T, °C	*P*, mbar	*T*, °C	*P*, mbar
−15.0[b]	10	−15.0	10
−10.2	14	−15.0	10
−4.8	20	−12.5	12
−3.6	24	−10.2	16
0.0	32	−10.0	16
4.8	41	−5.0	21
12.0	63	−5.0	23
19.3	112	−0.2	31
29.5	151	5.0	44
		10.0	58
−15.1[c]	10	10.0	61
−10.0	15	15.0	80
−7.5	19	19.6	104
0.0	31	22.8	124
		33.0	210
−30.0[c,d]	3	38.2	270
−22.5[d]	5	50.0	439
−20.0	6	9.8[e]	79
−17.5	7		

[a] ±1 mbar. [b] Measured without added CO. [c] Different experiments with approximately 1 bar of CO (at 0 °C); if the volume and the number of moles of CO remain constant, the ratio $p\{CO\}/T$, determined at low temperatures with $p\{Ru(CO)_5\} \sim 0$, is constant as well. This can be subtracted from the equation $p\{tot\}/T = p\{CO\}/T + p\{Ru(CO)_5\}/T$ and leads to the vapor pressure of the pentacarbonyl. It can be seen in Figure 1 that no systematic error was made. [d] The melting point of $Ru(CO)_5$ is reported as −22 °C.[8] The vapor pressures below this temperature are due to sublimation rather than evaporation. [e] Measured after the 50.0 °C data point; contains CO due to decomposition to $Ru_3(CO)_{12}$.

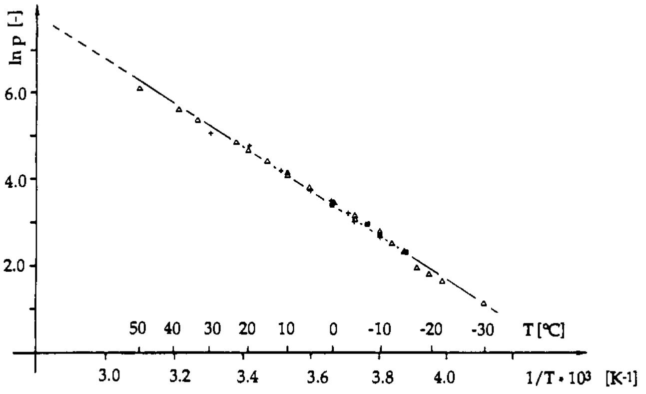

Figure 1. ln $p\{Ru(CO)_5\}$ vs $1/T$ diagram of the vapor pressure data, measured without (+) and with (■, △) approximately 1 bar of CO. (See footnote *b* of Table I.)

thermal decomposition to $Ru_3(CO)_{12}$ and CO. Therefore, the vapor pressure of pentacarbonylruthenium, $Ru(CO)_5$, was measured in a stainless steel autoclave between −30 and +50 °C (for the data, see Table I) both without and with approximately 1 bar of CO (see Table I). A plot of ln $p\{Ru(CO)_5\}$ vs $1/T$ leads to eq 1 (p in mbar, T in K). Therefrom, the enthalpy of evaporation

$$\ln p\{Ru(CO)_5\} = -5072/T + 21.95 \qquad (1)$$

$\Delta H°_{vap}$ for $Ru(CO)_5$ can be calculated as 42.2 ± 0.6 kJ/mol, and at 64 ± 6 °C, the vapor pressure is 1.0 bar (if $Ru(CO)_5$ is stabilized with CO) (Figure 1).

The accuracy of the apparatus was checked by measuring first the vapor pressure of toluene. Its enthalpy of evaporation was found to be 35 690 J/mol, and its boiling point, 110.4 °C. Both, $\Delta H°_{vap}$ and T_{bp}, are within experimental errors compared with the reported values of 35 901 and 39 198 J/mol, respectively, and 110.6 °C.[9]

The enthalpy of evaporation of $Ru(CO)_5$ is slightly higher than that reported for $Fe(CO)_5$ with 40.2[10] and 40.1 kJ/mol,[11] respectively. This trend is observed also with the hexacarbonyls of the triad Cr–Mo–W. The enthalpy of sublimation ΔH_{subl} rises from $Cr(CO)_6$ (71.6,[12] 71.4 kJ/mol[13]) to $Mo(CO)_6$ (76.9,[12] 73.8 kJ/mol[13]) and $W(CO)_6$ (78.9,[12] 76.4 kJ/mol[13]). In contrast to this behavior, a different trend for the boiling points was observed. This was found to be lower for the carbonyls of the 4d metals as compared to the 3d ones in both the present work (bp$\{Ru(CO)_5\}$ = 64 °C vs bp$\{Fe(CO)_5\}$ = 104.7[14] and 100.3 °C,[11] respectively) and the one reported for the Cr triad (bp$\{Mo(CO)_6\}$ = 138 °C vs bp$\{Cr(CO)_6\}$ = 143 °C and bp$\{W(CO)_6\}$ = 257 °C).[12] The reason for this is unclear and may come from different intermolecular forces.

Experimental Section

A 500-mL stainless steel autoclave was charged with 0.7938 g (=1.242 mmol) of $Ru_3(CO)_{12}$ (prepared according to the method of Johnson and Lewis[15]) and 160 bar of CO and heated to 160 °C.[16] After 48 h the autoclave was cooled slowly to −78 °C and the carbon monoxide released. The autoclave was then warmed to room temperature and connected with a 100-mL autoclave (fitted with a piezoresistive pressure transducer, −1.0 to +1.5 bar), which was cooled to −78 °C. Both autoclaves were evacuated with a high-vacuum pump. Thereafter, $Ru(CO)_5$ was evaporated in the first (500 mL) autoclave and trapped in the second (100 mL). Therein, the vapor pressure measurements (±0.001 bar) were carried out. The autoclave was thermostated until the pressure remained constant for at least 10 min (thermostating for a longer period showed no pressure changes) within an accuracy of ±0.1 °C. The infrared spectrum of a sample of the measured ruthenium carbonyl was recorded, and the unambiguous two bands for $Ru(CO)_5$ (2037 cm^{-1}, ϵ = 6570 ± 40 dm^3/(mol cm) and 2002 cm^{-1}, ϵ = 8100 ± 50 dm^3/(mol cm); in *n*-hexane) were observed.

Registry No. $Ru(CO)_5$, 16406-48-7.

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Reaction of Hydride with $(\eta^5\text{-}C_9H_7)Re(CO)_3$. Facile Formation of $[H_6Re_4(CO)_{12}{}^{2-}]$ and Indenide

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η^5-Cyclopentadienyl and η^5-indenyl ring slippage has been postulated as a prerequisite for substrate activation in certain catalytic processes.[1] Consistent with this notion are the rapid

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ligand substitution reactions in η^5-C_5H_5 and η^5-C_9H_7 organometallic complexes that have implicated η^3- and η^1-polyene intermediates.[2] Only recently have such species been observed and unequivocally confirmed. For example, Casey and co-workers have studied and fully characterized the complexes *fac*-(η^1-C_5H_5)$Re(CO)_3(PMe_3)_2$ and *fac*-(η^1-C_9H_7)$Re(CO)_3(PMe_3)_2$, which were obtained from the reaction of PMe_3 with (η^5-C_5H_5)$Re(CO)_3$ and (η^5-C_9H_7)$Re(CO)_3$, respectively.[3,4]

Whereas the reaction of (η^5-C_9H_7)$Re(CO)_3$ (**1**) with neutral, two-electron donor ligands has been fully explored (vide supra), the direct reaction of 1 with anionic ligands has received scant attention. In 1984, Kolobova et al. reported that 1 and [EtO^-], generated in situ from hexamethylenamine or pyridine in EtOH, gave indene and the known triply bridged dimer [$(CO)_3Re(\mu_2$-$OEt)_3Re(CO)_3^-$].[5] The same group has also shown that BuLi competitively metalates C_1 and C_2 of the indenyl ring as demonstrated by anion functionalization using CO_2/H^+ and Me_3SiCl.[6] To our knowledge these studies represent the only known reactivity reports between 1 and anionic ligands.

As part of our interest in CO reduction processes involving hydrides,[7] coupled with a recent study dealing with the reaction of the isoelectronic indenyl complex [(η^5-C_9H_7)$Fe(CO)_3^+$] with hydride,[8] we report our results on the reaction of 1 with hydrides, which demonstrate the facile formation of lithium indenide and the tetrarhenium cluster [$H_6Re_4(CO)_{12}^{2-}$].

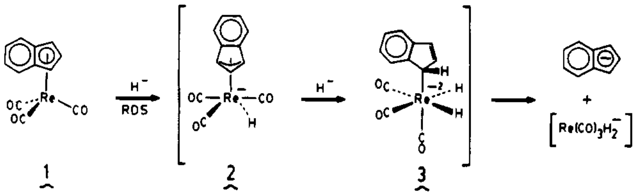
Results

The reaction between (η^5-C_9H_7)$Re(CO)_3$[9] and [Et_3BH][Li] in THF is observed to proceed rapidly at room temperature to give lithium indenide and the tetrarhenium cluster [$H_6Re_4(CO)_{12}^{2-}$].[10,11] Full solution characterization of these products along with a plausible mechanism for their formation is presented in the appropriate sections that follow.

Discussion

Treatment of a faint yellow THF solution of 1 at room temperature with 1.0 equiv of [Et_3BH][Li] (1.0 M in THF) immediately afforded a dark yellow solution containing 50% of 1 and two new carbonyl stretching bands at 1992 (s) and 1906 (vs) cm^{-1} as determined by IR analysis. Use of 2.0 equiv of [Et_3BH][Li] led to the complete consumption of 1 and a 2-fold increase in the latter ν(CO) bands. No spectroscopic intermediates were observed when the reaction was monitored by IR spectroscopy and reactions conducted below room temperature (−78 to 0 °C) proceeded too slowly and were not pursued further. The shift to lower frequency and the symmetry associated with the product's carbonyl bands are consistent with the formation of an anionic species that possesses $Re(CO)_3$ moieties with idealized C_{3v} symmetry.[12] Inspection of the literature reveals that these ν(CO) bands are in good agreement with those reported by Kaesz and co-workers for the tetrarhenium cluster [$H_6Re_4(CO)_{12}^{2-}$].[10] We note that the confacial bioctahedral complex [$(CO)_3Re(\mu_2$-$H)_3Re(CO)_3^-$] also exhibits two, strong ν(CO) bands at 1995 and 1905 cm^{-1}.[13] However, when the rhenium-containing material was isolated (as the [Ph_4P^+] salt) and examined by electronic absorption spectroscopy, only absorption bands attributed to [$H_6Re_4(CO)_{12}^{2-}$] were observed.[14] This rhenium dimer is undoubtedly involved in the formation of [$H_6Re_4(CO)_{12}^{2-}$] as noted by Kaesz[10a] and its role in this reaction is considered in our proposed mechanism (vide infra).

Scheme I



The reaction between 1 and [Et_3BH][Li] (2.0 equiv) in THF-d_8 was next examined by ^{1}H NMR spectroscopy with *p*-methoxybenzene as an internal standard in order to ascertain the fate of the idenyl ligand. ^{1}H NMR analysis revealed the complete consumption of 1 and aromatic resonances (>95% based on 1) at δ 7.26 (dd), 6.48 (t), 6.29 (dd), and 5.87 (d) along with a high-field hydride resonance at δ −17.40. The aromatic resonances agree well with those reported for lithium indenide.[15] Independently prepared lithium indenide also exhibited a ^{1}H NMR spectrum indistinguishable from that obtained from **1** and [Et_3BH][Li]. The high-field resonance is readily assigned to the edge-bridging hydrides associated with [$H_6Re_4(CO)_{12}^{2-}$].[10] On the basis of the spectroscopic results and the observed rhenium/hydride stoichiometry, the reaction between **1** and [Et_3BH][Li] is suggested to proceed as shown in eq 1.

$$4(\mathbf{1}) + 8[Et_3BH][Li] \rightarrow 4[C_9H_7][Li] + [H_6Re_4(CO)_{12}][Li]_2 + 4Et_3B + 2[Et_3B\text{-}H\text{-}BEt_3][Li] \quad (1)$$

The presence of Et_3B and lithium hexaethyldiborohydride in eq 1 was confirmed by $^{11}B\{^1H\}$ NMR analysis, which revealed a broad singlet at δ 17.50. Only a single, averaged boron resonance is observed due to the facile exchange reaction between Et_3B and the hexaethyldiborohydride anion that is known to be rapid on the NMR time scale.[16] Finally, the presence of the cubane cluster [$Re(CO)_3OH]_4$,[17] a product observed by Casey and O'Connor in the reaction of 1 with wet acetone,[3b] has been ruled out as a product in our reaction by using ^{13}C NMR spectroscopy. When a ^{13}CO-enriched sample of 1 was reduced under analogous con-

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ditions, a sharp ^{13}C resonance was observed at δ 200.1, which is incompatible with that reported for $[Re(CO)_3OH]_4$.[18]

Scheme I shows the sequences of events we believe explain the observed products. The initial step involves hydride attack at the rhenium center to give $[(\eta^3\text{-}C_9H_7)Re(CO)_3H^-]$ (2). A fast follow-up reaction of 2 with the second equivalent of hydride affords $[(\eta^1\text{-}C_9H_7)Re(CO)_3H_2^{-2}]$ (3), which releases indenide and the putative species $[Re(CO)_3H_2^-]$. Support for the indenyl $\eta^5 \rightarrow \eta^3 \rightarrow \eta^1 \rightarrow [C_9H_7][Li]$ transformations stems directly from the work of Casey.[3,4] Since no intermediates were observed, we conclude that the addition of hydride to 1 represents the rate-determining step. Proof for this was obtained by using the larger hydride reagent LS-Selectride,[19] which led to the formation of indenide and $[H_6Re_4(CO)_{12}^{2-}]$ slowly over the course of several days. Moreover, this first step has also been reported to be rate determining in the reaction of 1 with PMe_3 and PBu_3.[3,4] It is of interest to compare the ease of indenide loss in our reaction with that for $(\eta^1\text{-}C_5H_5)Re(NO)(Me)(PMe_3)_3$, which gives an ionic "$\eta^0$"-$C_5H_5$ group at elevated temperature,[4d] and the thermolysis reactions of 1 with EtOH/pyridine and acetone/H_2O, which afford indene[5] and 1-indenyl-2-propanol,[3b] respectively. Presumably the increased charge density at the rhenium center in 3 is responsible for this facile indenide displacement.

The assemblage of the tetrarhenium cluster $[H_6Re_4(CO)_{12}^{2-}]$ from $[Re(CO)_3H_2^-]$ is less straightforward but can be considered by recognizing the fact that $[Re(CO)_3H_2^-]$ is formally a d^6-ML_5 species that is isolobal with carbene.[20] Dimerization is predicted to give the 32-electron complex $[(CO)_3Re(\mu_2\text{-}H)_4Re(CO)_3^{2-}]$.[21] If this dimer is considered as a M_2L_9 confacial bioctahedral complex (i.e., $[(CO)_3Re(\mu_2\text{-}H)_3Re(CO)_3^{3-}]$ and $[H^+]$), it is predicted to be unstable in the absence of a Jahn–Teller distortion.[22] Loss of hydride would allow for the formation of the known 30-electron complex $[(CO)_3Re(\mu_2\text{-}H)_3Re(CO)_3^-]$[13,22,23] and furnish the observed hexaethyldiborohydride anion.[24] While experimentally untested, dimerization of $[(CO)_3Re(\mu_2\text{-}H)_3Re(CO)_3^-]$ under our reaction conditions would then yield the electron-precise cluster $[H_6Re_4(CO)_{12}^{2-}]$.

Experimental Section

Materials and Methods. $(\eta^5\text{-}C_9H_7)Re(CO)_3$ was prepared according to the literature.[9] The hydride reagents Super-Hydride and LS-Selectride were purchased from Aldrich as 1.0 M THF solutions and used as received. All reactions were conducted under argon with Schlenk techniques.[25] THF was distilled from sodium/benzophenone ketyl and stored under argon in Schlenk vessels. THF-d_8 was bulb-to-bulb distilled from CaH_2 on the vacuum line and immediately used. The C and H analysis was performed by Atlantic Microlab, Atlanta, GA.

The infrared spectra were recorded as previously described.[26] ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, on a Varian 300-VXR spectrometer. ^{11}B NMR spectra were recorded at 96 MHz and are referenced relative to external $BF_3{\cdot}Et_2O$, taken to have $\delta = 0$.

Reaction of $(\eta^5\text{-}C_9H_7)Re(CO)_3$ with $[Et_3BH][Li]$. To 50.0 mg (0.13 mmol) of $(\eta^5\text{-}C_9H_7)Re(CO)_3$ in a 50-mL Schlenk tube was added 10 mL of THF, followed by 0.26 mL (0.26 mmol) of a 1.0 M $[Et_3BH][Li]$ solution. The reaction was stirred for 5 min and then monitored by IR spectroscopy, which revealed the complete conversion to $[H_6Re_4(CO)_{12}^{2-}]$. Excess tetraphenylphosphonium chloride, $[Ph_4P][Cl]$, was next added and the solution was stirred overnight. After filtration, the THF solution was layered with degassed heptane, which afforded yellow crystals of $[H_6Re_4(CO)_{12}][Ph_4P]_2$. Yield: 36.2 mg (63.2%) of $[H_6Re_4(CO)_{12}][Ph_4P]_2$. IR (THF) of $[H_6Re_4(CO)_{12}][Li]_2$: ν(C) 1992 (s), 1906 (vs) cm^{-1}. IR (THF) of $[H_6Re_4(CO)_{12}][Ph_4P]_2$: 1991 (s), 1900 (s, broad) cm^{-1}. UV–vis (THF) of $[H_6Re_4(CO)_{12}][Ph_4P]_2$: ~295 (sh), 330 (sh) nm; ^1H NMR (THF-d_8) of $[H_6Re_4(CO)_{12}][Ph_4P]_2$: δ 7.26 (dd), 6.48 (t), 6.29 (dd), 5.87 (d), −5.50 (μ_2-H, hexaethyldiborohydride anion), −17.40 (μ_2-H, Re–H). $^{13}C\{^1H\}$ (^{13}CO enriched 1 in THF): δ 200.1. Anal. Calcd for $C_{60}H_{46}P_2O_{12}Re_4$: C, 40.80; H, 2.61. Found: C, 41.49, H, 3.78. Note: despite repeated recrystallizations, an acceptable microanalysis could not be obtained due to the presence of $[C_9H_7^-]$, as determined by ^1H NMR analysis.

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(18) Cf. the ^{13}C resonance (δ 196.7) for $[Re(CO)_3OH]_4$ recorded in THF-d_8. See ref 17.

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Carbonate Exchange for the Complex $UO_2(CO_3)_3^{4-}$ in Aqueous Solution As Studied by ^{13}C NMR Spectroscopy[1]

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Uranyl carbonate complexes are the most stable inorganic species of uranium(VI) and have exceptional importance in the extraction process in uranium mining[2] and in the migration of UO_2^{2+} in ground water.[3] The equilibria in the UO_2^{2+}–CO_3^{2-} system have been studied in detail, and the complexes $UO_2(CO_3)_n^{2-2n}$, where n = 1–3, and the complex $(UO_2)_3(CO_3)_6^{6-}$ have been found to dominate in aqueous solution.[4,5] A structural study has been performed,[6] but only preliminary results have been published on the ligand-exchange kinetics of $UO_2(CO_3)_3^{4-}$.[7-9] In this note, we report a ^{13}C NMR study on the dynamics of the $UO_2(CO_3)_3^{4-}$–CO_3^{2-} system in aqueous solution.

Experimental Section

Solutions. Known volumes of $UO_2(ClO_4)_2$ stock solution and a weighed quantity of ^{13}C-enriched (99%) Na_2CO_3 and/or $NaHCO_3$ (Stohler Isotope Chemicals) were mixed to prepare NMR samples. The ionic medium was 1 M $NaClO_4$. The total concentration of uranyl, c_{UO_2}, varied between 0.005 and 0.027 M, and the total carbonate concentration, c_{CO_3}, was always higher than $3c_{UO_2}$. pH was regulated by careful addition of concentrated NaOH or $HClO_4$ in order to avoid dilution and to prevent changes in c_{CO_3}. The ratio c_{CO_3}/c_{UO_2} was also checked by measuring the integrals of the NMR signals of the free (CO_3^{2-} and/or HCO_3^-) and the coordinated carbonate (cf. Figure 1). The hydrogen ion concentration was measured with a glass electrode calibrated by Irving's method.[10]

NMR Measurements. The ^{13}C NMR spectra were measured by using Bruker MSL200 and AM400 spectrometers. Typical NMR parameters (Bruker MSL200): spectral window = 1000 Hz, pulse width = 10 μs (90° pulse), pulse repetition time = 4 s. These parameters were controlled to give quantitative spectra. The chemical shifts are referred to

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