this is further evidence for only a very small concentration of the η^1-intermediate species during the fluxional processes; otherwise, it would reduce substantially this ring-current effect.

Epilogue

The most interesting result to emanate from this study is the isolation of the desired mixed bis(alkyl) complexes. They do not appear to be particularly unstable in any manner, nor do they show any propensity to undergo disproportionation to symmetric bis(alkyl) complexes. Hence, it can be concluded that the previous attempts to synthesize complexes such as $CpW(NO)(CH_2Ph)(CH_2SiMe_3)$ must have failed due to the synthetic route chosen to prepare them rather than because of the inherent instability of the products. The other bis(alkyl) complexes prepared previously in this research group exhibit a marked reduction in their thermal stability when the metal is changed from tungsten to molybdenum. However, the benzyl-containing compounds are uniformly stable regardless of the metal center involved. This last observation is in accord with the view that it is the extra electron density donated from the benzyl ligand that permits the metal center to attain the favored 18-valence-electron configuration that is the preeminent factor in determining the relative stability of these complexes.

Given the existence of these complexes, it is hoped that a wider ranging investigation of the remarkable transformations observed for the $CpW(NO)(CH_2SiMe_3)_2$ complex[4] can now be extended to encompass these benzyl complexes. For instance, since these new complexes allow variation in their alkyl groups in a systematic manner, this feature could be utilized to probe relative alkyl ligand reactivities. The $Cp'M(NO)(CH_2Ar)X$ species also contain a chiral metal center since the four different ligands are arrayed in a pseudotetrahedral manner about the metal center. Therefore, as well as being possible starting materials for futher reactivity studies, these complexes hold out the promise that detailed mechanistic investigations of any transformations observed could be carried out on their optically active forms. Such reactivity studies are currently in progress.

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Supplementary Material Available: Tables of final anisotropic thermal parameters, bond lengths involving hydrogen atoms, bond angles involving hydrogen atoms, and torsion angles for $Cp^*Mo(NO)(CH_2Ph)Cl$ and $Cp^*Mo(NO)(CH_2Ph)(CH_2SiMe_3)$ (10 pages); listings of observed and calculated structure factors (49 pages). Ordering information is given on any current masthead page.

Solution Calorimetric, Equilibrium, and Synthetic Studies of Oxidative Addition/Reductive Elimination of C_5R_5H (R = H, Me, Indenyl) to/from the Complexes $M(CO)_3(RCN)_3/(\eta^5\text{-}C_5R_5)M(CO)_3H$ (M = Cr, Mo, W)

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Equilibrium data are reported for the reaction $CpMo(CO)_3H + 3MeCN \rightleftharpoons Mo(CO)_3(MeCN)_3 + CpH$. Over the temperature range 43–82 °C, $\Delta H = -11.2$ kcal/mol, $\Delta S = -51.3$ cal/(mol °C). Calorimetric data for the enthalpies of displacement of C_5R_5H by nitriles are reported: Cr, R = Me, −0.7 ± 0.7 kcal/mol, M = W, R = H, −5.6 ± 0.7, R = Me, −5.4 ± 0.7 kcal/mol. The enthalpy of reaction of $Na^+(indenyl)^-$ with (*p*-xylene)$Mo(CO)_3$ forming $Na^+Mo(CO)_3(indenyl)^-$ is −17.3 ± 0.2 kcal/mol, approximately 10 kcal/mol less than the corresponding reaction of $Na^+C_5H_5^-$. The heat of reaction of (indenyl)$W(CO)_3H$ with EtCN forming $W(CO)_3(EtCN)_3$, −20.0 ± 0.8 kcal/mol, is approximately 14 kcal/mol more exothermic than the corresponding reaction of the cyclopentadienyl complex, also in keeping with a reduced M–indenyl ground-state bond energy. Synthetic strategies to the $(C_5R_5)M(CO)_3H$ complexes are summarized.

Introduction

The complexes $CpM(CO)_3H$ (M = Cr, Mo, W) have been widely studied in the 35 years since their discovery by E. O. Fischer.[1] While reports on the unsubstituted cyclopentadienyl hydrides are well-known, data on the substituted complexes are scattered throughout the literature. King and Fronzaglia[2] reported the preparation of $Cp^*W(CO)_3H$ according to eq 1 in 1966. This was one of the

$$W(CO)_3(NCR)_3 + Cp^*H \rightarrow Cp^*W(CO)_3H + 3RCN \quad (1)$$

first Cp* complexes to be synthesized but has been vir-

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(2) King, R. B.; Fronzaglia, A. *Inorg. Chem.* **1966**, *5*, 1837.

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tually unrecognized. In a following paper by King,[3] an analogous preparation of the molybdenum congener was first reported, although only in a footnote with no detail or characterization. Only relatively recently have these Cp*H complexes been "rediscovered" and studied whereupon several preparations have sprouted up with little or no cross-referencing.[4]

In the case of the corresponding (indenyl)M(CO)$_3$H complexes, only one literature reference to their preparation could be found, and only for M = W[5] (in fact, this was only discovered by a computer search after this work was completed). It is well-known that indenyl complexes are more reactive than the corresponding cyclopentadienyl or pentamethylcyclopentadienyl complexes. The "indenyl effect" has been widely studied kinetically.[6] For example, the associative substitution reaction shown in eq 2 occurs approximately 10^8 times more rapidly for the indenyl than for the cyclopentadienyl complex.[7] This increased reactivity could be due to either reduced "ground-state" η^5-indenyl–M bond strength or to increased stability of the η^3-indenyl–M "excited-state" complex. Increased reactivity is generally attributed to increased stability of the η^3-indenyl complex compared to the corresponding η^3-cyclopentadienyl complex. In spite of the large number of synthetic and mechanistic works on indenyl complexes, there is no available thermodynamic data to evaluate the ground-state M–indenyl bond strength. Calorimetric data on the enthalpy of addition of CO to [Mo(CO)$_2$(indenyl)]$_2$ has been reported[8a] but gives no insight into the Mo–indenyl bond strength.

$$(\eta^5\text{-}C_9H_7)Rh(CO)_2 + PPh_3 \xrightarrow{\text{slow}} (\eta^3\text{-}C_9H_7)Rh(CO)_2(PPh_3) \xrightarrow{\text{fast}} (\eta^5\text{-}C_9H_7)Rh(CO)(PPh_3) \quad (2)$$

In this paper, we report equilibrium and calorimetric studies of the unexpectedly facile oxidative addition/reductive elimination equilibria of substituted cyclopentadienyl ring complexes of the group 6 metals. Improved synthetic routes to Cp*M(CO)$_3$H (M = Mo, W), [CpCr(CO)$_3$]$_2$, and CpCr(CO)$_3$H are also described.

Experimental Section

All manipulations were performed under an argon atmosphere by using standard Schlenk tube or glovebox techniques. Metal carbonyls and Cp*H were obtained from Strem Chemicals. Solvents were carefully purified and distilled prior to use. Calorimetric measurements were made by using the Setaram C-60 Calvet calorimeter using procedures similar those described in detail elsewhere.[8] CpMo(CO)$_3$H and (indenyl)W(CO)$_3$H were prepared by literature methods.[5,9] Infrared spectra were obtained by using either a Perkin-Elmer 1850 FTIR or 521 spectrophotometer; NMR studies were performed on a Varian EM-390.

Preparation of Cp*Mo(CO)$_3$H. Mo(CO)$_6$ (6.0 g, 22.7 mmol) and 60 mL of propionitrile (acetonitrile could also be used here) were refluxed overnight in a 250-mL flask to give Mo(CO)$_3$(NCEt)$_3$[10] (ν_{CO} = 1920, 1797 cm^{-1} in EtCN). Solvent was removed in vacuo, and Cp*H (5 g, 36.7 mmol) in 200 mL of toluene was added to the residue. The mixture was stirred for 2 h and then warmed to 50–60 °C for 15 min or until all solid dissolved (the rate-determining factor was found to be solubilization of Mo(CO)$_3$(NCEt)$_3$, which could be slower for the MeCN analogue). The resulting solution, which became red, symptomatic of traces of [Cp*Mo(CO)$_3$]$_2$, was stripped of all liquid volatiles by pumping in vacuo (heating the flask in a 70–80 °C water bath was required to complete the process). The residue, consisting primarily of Cp*Mo(CO)$_3$H, was placed into a sublimation apparatus and covered with a layer of cheesecloth to prevent fly-up of solid onto the probe. The apparatus was covered with Al foil to prevent photolytic decomposition and heated to 55 °C overnight under high vacuum. The yield of yellow or slightly pink-tinged sublimate was 6.33 g (88% based on Mo(CO)$_6$). The above synthesis also gave excellent yields starting with isolated Mo(CO)$_3$(NCR)$_3$ [for R = Me, the reaction with Cp*H (in benzene) was somewhat less facile (lower solubility) and the yield was 60%].

Preparation of Cp*W(CO)$_3$H. The synthesis can be carried out analogous to the one above except that the reactions are slower and use of EtCN or even PrCN is highly recommended both to facilitate CO displacement and to increase the solubility of W(CO)$_3$(NCR)$_3$.[11] Although we did not attempt a "one-pot" preparation, several reactions of isolated W(CO)$_3$(NCR)$_3$ with Cp*H in toluene were carried out and gave good yields (70–75%). Reaction of W(CO)$_3$(NCPr)$_3$ (7.53 g, 15.8 mmol), Cp*H (4 g, 4.7 mL, 29.5 mmol), and toluene (200 mL) under the same conditions as the Mo case gave, upon sublimation of the product at 75 °C, a yield of 4.63 g (73%). The use of W(CO)$_3$(NCEt)$_3$ (15.61 g, 34.6 mmol), Cp*H (7.7 g, 9.0 mL, 56 mmol), and toluene (200 mL) was much slower and probably would have been facilitated if more toluene or possibly another solvent (e.g., THF) was used. After 3 h at 60–70 °C and further stirring at 25 °C overnight, the reaction was not quite complete, and 2.5 g of solid (2.1 g of unreacted W(CO)$_3$(NCEt)$_3$ and 0.4 g of insoluble impurity) had to be removed by filtration prior to solvent removal. The yield of yellow sublimed product was still very good, however (9.87 g, 71% based on 15.61 g of W(CO)$_3$(NCEt)$_3$ or 84% based on 13.11 g). The complex is much more air- and light-stable than its Cp or Mo congeners, not darkening significantly even after overnight exposure. Long-term storage under nitrogen away from light is still recommended, however. IR of Cp*W(CO)$_3$H:ν_{CO} 2008, 1919 cm^{-1} (Nujol mull). ^{1}H NMR: δ in toluene-d_8 1.78 (Cp*), −6.47 (hydride).

Reactions of CpM(CO)$_3$H and Cp*M(CO)$_3$H with Coordinating Solvents. Acetonitrile. NMR spectroscopy of solutions of Cp*Mo(CO)$_3$H in CD$_3$CN showed gradual formation of Cp*H concomitant with a decrease in intensity of resonances due to the hydride. The reaction was complete in 2 h at probe temperature (33 °C). Infrared spectroscopy of an aliquot of the solution demonstrated clean formation of Mo(CO)$_3$(NCCD$_3$)$_3$. The reaction with the Cp congener gave equilibrium behavior (see below). The tungsten analogues did not react with MeCN, even upon heating to 55 °C for several hours.

DMSO. The NMR tube reaction of Cp*Mo(CO)$_3$H in DMSO-d_6 as above was quite fast. The approximate half-life for formation of Cp*H as determined by integration was 5 min, and the reaction was complete in 20 min. The hydride resonance at ca. −5 ppm was broad and weak throughout the course of reaction. The Cp analogue reacted somewhat more slowly: mostly complete after 20 min, but still incomplete after 30 min (an equilibrium may gradually be attained here also). Some minor side reaction

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[11] (η^6-naphthalene)Cr(CO)$_3$ is readily prepared by refluxing an equimolar mixture of Cr(CO)$_6$ and naphthalene in dibutyl ether to which a small amount of THF has been added, a common technique for the formation of (arene)Cr(CO)$_3$ complexes: Mahaffy, C. A.; Pauson, P. L. *Inorg. Synth.* **1979**, *19*, 154.

Table I. Equilibrium Data as a Function of Temperature for the Reaction $CpMo(CO)_3H + 3CD_3CN = Mo(CO)_3(CD_3CN)_3 + CpH$

temp, °C	[CpH][a]	[CpMo(CO)$_3$H][a]	K_{eq}[b]
43	0.511	0.139	3.44×10^{-4}
59	0.421	0.229	1.42×10^{-4}
69	0.367	0.283	8.70×10^{-5}
73.5	0.341	0.309	6.88×10^{-5}
82	0.303	0.347	4.85×10^{-5}

[a] Concentrations (mol/L) determined by integration of free and coordinated Cp resonances in a 0.65 M solution of $CpMo(CO)_3H$ in CD_3CN. [b] $K_{eq} = [CpH]^2/[CpMo(CO)_3H][CD_3CN]^3$; the concentration of CD_3CN was calculated to be 17.6 M based on its density (0.844 g/mL) and taken to be constant.

to form red $[Cp^*Mo(CO)_3]_2$ was noted.

Pyridine. The rate of reaction of $Cp^*Mo(CO)_3H$ was similar to that for DMSO.

THF. No evidence for reaction in THF-d_8 was found even after 2 days at 25 °C.

Reaction of $Cp^*Mo(CO)_3H$ with Phosphorus-Donor Ligands. Formation of $Cp^*Mo(CO)_2[P(OPh)_3]H$. A benzene solution containing excess $P(OPh)_3$ reacted to give CO substitution and no evidence for Cp^*H displacement. The reaction was ~70% complete in an hour and complete overnight at 25 °C to give $Cp^*Mo(CO)_2[P(OPh)_3]H$, which displayed ^1H NMR signals at 1.78 (Cp^*) and −5.76 ppm (doublet, J_{PH} = 77 Hz, hydride) in benzene. No reaction occurred at all for the bulkier PCy_3 ligand.

NMR Study of the Equilibrium $CpMo(CO)_3H + 3CD_3CN = Mo(CO)_3(CD_3CN)_3 + CpH$. A solution of $CpMo(CO)_3H$ (0.163 g, 0.662 mmol) in CD_3CN (solution volume was 1.02 mL; concentration was calculated to be 0.65 M) was made up in an NMR tube and allowed to reach equilibrium at probe temperature (33 °C) for ~3 h. The ^1H spectrum showed resonances due to both coordinated Cp and free CpH. Instrumental integration of these signals allowed calculation of the equilibrium constant at a series of temperatures (see Results and Discussion section). The sample temperature was initially raised to 69 °C (as determined by MeOH calibration), and equilibrium was reestablished in 35 min. The temperature was increased to 82 °C (30 min between each increase) and then decreased to 69 °C again to check whether the same CpMo/CpH ratio was reattained. The ratio was 0.436, compared to 0.435 obtained on increasing the temperature to 69 °C, indicating true dynamic equilibrium behavior and excellent reproducibility in the data. The temperature was then lowered in two stages to 43 °C, with 40–50 min required to reattain equilibrium; the data are summarized in Table I.

A kinetic study of the approach to equilibrium was conducted by monitoring the reaction of 0.1062 g (0.432 mmol) of hydride in 1.00 mL of CD_3CN (0.45 M) over a 6-h period in an NMR tube kept in the spectrometer probe at 37.5 °C. Integration showed that after 20 min displacement of CpH was 40% complete and after 40 min 66% complete (see Figure 1). Equilibrium was essentially attained in 2.5 h at 88.6% completion ($[CpMo(CO)_3H]/[\text{total Cp}] = 0.114$); the value after 6 h was 89.0%. A plot of log $(C - C_\infty)$ vs T gave a straight line, where $C = [CpMo(CO)_3H]/[\text{total Cp}]$ and $C_\infty = 0.11$.

Preparation of $[CpCr(CO)_3]_2$ and $CpCr(CO)_3H$. To a 500-mL Schlenk tube, 17 g of (naphthalene)$Cr(CO)_3$,[11] 200 mL of freshly distilled THF, and 25 mL of freshly cracked CpH were added. The flask was evacuated and heated in a water bath to 50 °C for 3 h. During this time, the color of the solution changed from red to dark green. The contents of the flask were evacuated to dryness and washed several times with warm heptane under argon to remove naphthalene. The flask was taken into the glovebox and the crude solid—useful for most preparative purposes as it is—was collected—12.1 g, 94%. Recrystallization of this solid was normally done in batches. To a clean Schlenk tube, 1.8 g of the crude solid was dissolved in about 500 mL of freshly distilled CH_2Cl_2. The solvent was evaporated to about 50 mL, yielding 1.5–1.6 g (85%) of highly pure crystalline material. Evaporation of the remaining 50 mL of solution yielded material that was recycled for future recrystallization.

Conversion of the pure dimer $[CpCr(CO)_3]_2$ to the hydride was readily effected in a pressure bomb. A 1-L sample cylinder was taken into the glovebox and loaded with 300–400 mL of THF and 2–3 g of $[CpCr(CO)_3]_2$. The valve to the cylinder was closed, and it was taken to a pressure manifold and filled with 300 psi H_2. The vessel was shaken occasionally and allowed to stand for several hours. Excess hydrogen was vented into the hood, and the entire vessel was taken into the glovebox. The valve fitting was removed but it was important to not decant the solution immediately since the solvent was supersaturated with H_2 gas. The contents of the flask were shaken, and the solution was cautiously transferred to a clean Schlenk tube. The solution was typically colorless, and the infrared spectrum showed that conversion to hydride was quantitative. Storage of such solutions for several months in the glovebox has not lead to significant decomposition. It should be kept in mind that small quantities of H_2 gas are released to the glovebox atmosphere, and if this interferes with other work, the bomb should be evacuated and filled with argon prior to bringing it into the glovebox.

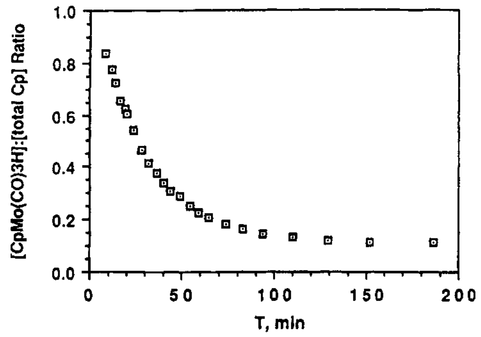

Figure 1. Rate of approach to the equilibrium, $CpMo(CO)_3H + 3CD_3CN = Mo(CO)_3(CD_3CN)_3 + CpH$, at 37.5 °C as measured by ratios of integrated Cp-ring NMR resonances due to $CpMo(CO)_3H$ and total Cp (coordinated plus free CpH). Initial concentration of $CpMo(CO)_3H$, 0.45 M; final measured value of ratio, 0.110 after 6 h.

Results and Discussion

Synthesis of $Cp^*W(CO)_3H$ and $Cp^*Mo(CO)_3H$. From all appearances, the existence of $Cp^*W(CO)_3H$ has been nearly overlooked in the literature, which is surprising because the Cp congeners of all the group 6 metals have been heavily studied and, unlike typical hydrides, are easily prepared in high yield and are quite stable. One possible explanation is that the yield of King and Fronzaglia's[2] preparation was poor (12%). Their novel synthetic strategy, reaction of $W(CO)_3(NCMe)_3$ with Cp^*H (methylcyclohexane reflux, 21 h), was later modified by Keppie and Lappert,[9b] who used THF as the solvent to prepare the Cp congeners. The solubility of the nitrile precursor complex is a critical factor in its reactivity, as we have also found in reactions of $W(CO)_3(NCEt)_3$ with olefins to form, for example, $W(CO)_3$(cycloheptatriene).[10] The yields of the latter in large-scale reactions were much higher starting with the more soluble R = Et and Pr congeners than those previously reported for R = Me.[2] As we now show here, application of these higher homologues to the synthesis of $Cp^*W(CO)_3H$ also gives vastly improved yields (70–75%):

$$W(CO)_3(NCR)_3 + Cp^*H \xrightarrow[25-70\ ^\circ C]{2-3\ h} Cp^*W(CO)_3H + 3RCN \quad (3)$$

$$R = Et, Pr$$

A convenient solvent, toluene, can be employed without need for drying or purification (noncoordinating or weakly coordinating solvents must be used; THF might give a faster reaction but normally must first be purified). Few chemical and spectroscopic properties were reported for $Cp^*W(CO)_3H$ in King's original paper which dealt more with olefinic and other complexes. We find that it is the most stable of the $(\eta^5\text{-}C_5R_5)M(CO)_3H$ series: even after weeks of exposure to air and light, the only evidence of decomposition was surface discoloration from yellow to orange. Infrared ν_{CO} bands occur at 2008 and 1919 cm^{-1} (Nujol mull, lit.[2] 2015 and 1928 cm^{-1} in cyclohexane solution) and proton NMR resonances at 1.78(Cp*) and −6.47 ppm (hydride) in toluene-d_8 (lit.[2] −6.85 ppm in CS_2).

$Cp^*Mo(CO)_3H$ was also prepared in excellent yield (88%) (in a reaction analogous to that shown in eq 3) by using a single-flask reaction in which $Mo(CO)_3(EtCN)_3$ formed from reaction of $Mo(CO)_6$ and EtCN was treated with Cp*H/toluene directly upon removal of unreacted EtCN in vacuo. This in situ procedure is also applicable to the W analogue, but care must be taken to ensure that the less facile formation of $W(CO)_3(NCR)_3$ is complete. Thermally activated displacement of the third carbonyl group from $W(CO)_6$ is unpredictably sluggish (up to 6 days for R = Et). We have made many unsuccessful attempts to hasten CO loss using either promoters (Me_3NO,[12] $CoCl_2$,[13] or Et_4NCl) or other higher boiling coordinating solvents instead of nitriles. Dioxane failed to react faster than nitriles (if at all), DMSO apparently oxidized the metal, and diglyme–benzene gave decomposition (despite the fact that $Mo(CO)_3$(diglyme) is stable[14]).

Synthesis of $[CpCr(CO)_3]_2$ and $CpCr(CO)_3H$. The chromium complexes are the most difficult to prepare and store due to their lability. A one-flask preparation of $[CpCr(CO)_3]_2$ is described. Reaction of (naphthalene)$Cr(CO)_3$ with excess C_5H_6 can be used to prepare the green dimeric complex in 93% yield:

$$2(\text{naphthalene})Cr(CO)_3 + 3C_5H_6 \xrightarrow[50\ ^\circ C]{THF} [(C_5H_5)Cr(CO)_3]_2 + C_5H_8 + 2(\text{naphthalene}) \quad (4)$$

Quantitative conversion of THF solutions of the dimer to the hydride, according to eq 5, can be achieved at 300 psi H_2 in about 3 h at room temperature. Procedures for these conversions are described in the Experimental Section since we have found them to be the easiest routes to high yields of these complexes.

$$[(C_5R_5)Cr(CO)_3]_2 + H_2 \xrightarrow[20\ atm]{THF} 2(C_5R_5)Cr(CO)_3H \quad (5)$$

Reactions of $CpMo(CO)_3H$ and $Cp^*Mo(CO)_3H$ with Coordinating Solvents and Phosphorus Donors. Three reaction channels are available for reaction of these hydrides with basic donor ligands:

$$CpM(CO)_3H + L \rightarrow [CpM(CO)_3]^-[LH]^+ \quad (6)$$

$$CpM(CO)_3H + L \rightarrow CpM(CO)_2(L)(H) + CO \quad (7)$$

$$CpM(CO)_3H + 3L \rightarrow M(CO)_3(L)_3 + CpH \quad (8)$$

In fact, each of these reactions under appropriate conditions is an equilibrium process. Which reaction occurs is determined by the nature of the base ligand and experimental conditions. Deprotonation, as shown in eq 6, occurs primarily with basic nitrogen donor ligands and has been extensively studied by Norton and co-workers.[15] Displacement of CO occurs primarily with ligands whose M–L bond strength is close to that of CO—typically isonitriles, phosphines, and phosphites. The enthalpies of reaction of the molybdenum hydride with phosphines and phosphites have been measured.[16] The solvent-induced "reductive elimination" of CpH, eq 8, like the reverse "oxidative addition" is not a well-known process in organometallic chemistry, having been previously observed for $CpMo(CO)_3H$[15a] and recently for $[CpRu(CO)(PPh_3)(H_2)]^+$.[15c]

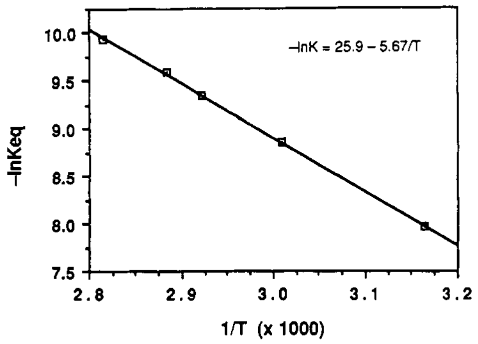

Figure 2. van't Hoff plot for the equilibrium, $CpMo(CO)_3H + 3CD_3CN = Mo(CO)_3(CD_3CN)_3 + CpH$.

As determined by NMR and IR monitoring, reductive elimination of Cp*H from $Cp^*Mo(CO)_3H$ was complete in CD_3CN at room temperature within 2 h. For the corresponding Cp complex, an *equilibrium* was established, as described below. In addition to nitriles, other ligands are capable of displacing CpH under appropriate conditions. For L = DMSO and pyridine, reactions were faster than for the nitriles, on the order of 20 min. Displacement by THF does not occur, except for the weakly bound indenyl hydrides as discussed later. These observations are in keeping with thermodynamic measurements of M–L bond strengths as discussed later. Due to possible displacement and "noninnocent" behavior of CpH in these complexes, caution is indicated in using acetonitrile, DMSO, and similar donor solvents for organometallic reactions and spectroscopic, electrochemical, or other measurements.

As previously found for the Cp analogue,[17] $Cp^*Mo(CO)_3H$ readily reacted with $P(OPh)_3$ in benzene (25 °C, 2 h) to give CO substitution as shown in eq 9. No evidence

$$Cp^*Mo(CO)_3H + P(OPh)_3 \rightarrow Cp^*Mo(CO)_2(P(OPh)_3)H + CO \quad (9)$$

of Cp*H displacement was seen by NMR; the doublet hydride signal (−5.76 ppm) was shifted to about 1 ppm lower than for the Cp analogue. The bulky phosphine PCy_3 did not react, probably due to steric effects. It has been reported that PPh_3 and other phosphines will substitute for CO in *acetonitrile* solution on a similar time scale to solvent displacement of CpH.[16] The high product yields (70–80%) indicate that solvolytic displacement from substituted hydrides is inhibited. It may also indicate that the intermediate in CpH displacement is effectively intercepted by the phosphorus donor.

NMR Thermochemical Study of the Equilibrium $CpMo(CO)_3H + 3CD_3CN = Mo(CO)_3(CD_3CN)_3 + CpH$. A kinetic-type experiment demonstrated that, upon dissolving $CpMo(CO)_3H$ in CD_3CN at 37.5 °C, equilibrium was steadily attained within 2.5 h at close to 89% reaction completion (Figure 1). After an initial equilibration time of 3 h, a proton NMR spectrum of 0.65 M $CpMo(CO)_3H$ in CD_3CN at 33 °C displayed signals due to displaced CpH

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and coordinated Cp in a ratio of 4.38:1 by integration. When the sample was warmed stepwise in the probe, the left side of the equilibrium was favored, with the above ratio becoming 1:1 near 80 °C. Assuming [Mo(CO)$_3$(CD$_3$CN)$_3$] = [CpH], [CpMo(CO)$_3$H] + [CpH] = 0.65 M, and [CD$_3$CN] = 17.6 M, the equilibrium constant K_{eq} was calculated from the concentrations determined by NMR integration (Table I). A van't Hoff plot of $-\ln K_{eq}$ vs $1/T$ gave an excellent fit to a straight line (Figure 2) from which the enthalpy of reaction was calculated to be $\Delta H^\circ = -11.2 \pm 0.5$ kcal/mol. The entropy of reaction was calculated from the intercept to be -51.3 ± 2.0 cal/(mol °C).

The value for the enthalpy of reaction can be estimated from earlier solution calorimetric data on reactions 10 and 11. The enthalpies of these reactions, in THF solution,

$$\mathrm{(C_6H_6)Mo(CO)_3 + 3CH_3CN \rightarrow Mo(CO)_3(CH_3CN)_3 + C_6H_6} \quad (10)$$

$$\mathrm{(C_6H_6)Mo(CO)_3 + CpH \rightarrow CpMo(CO)_3H + C_6H_6} \quad (11)$$

were reported as -21.8 ± 1.0 and -12.8 ± 1.0 kcal/mol, respectively.[8b] This leads to a calculated enthalpy of displacement of CpH by CH$_3$CN of -9.0 ± 2.0 kcal/mol. The two values overlap within experimental error, and considering the different nature of the solvent system (pure CD$_3$CN vs THF), these values are in good agreement.

The entropy of reaction can be compared to that determined earlier, also by NMR techniques[8c] for eq 12. The

$$\mathrm{(toluene)Mo(CO)_3 + 3THF \rightleftharpoons Mo(CO)_3(THF)_3 + toluene} \quad (12)$$

value for ΔS, -41.5 cal/(mol °C), is smaller in absolute value than reported here (-51.3 cal/(mol °C)). In both reactions, however, there is a large entropic component to the reaction favoring formation of the arene or cyclopentadienyl system. A practical consequence to this is that low temperature favors formation of the solvent-substituted product; raising the temperatures tends to favor formation of the arene or cyclopentadienyl complex. These experimental entropies of reaction may be useful in estimating thermodynamic parameters for related reactions. Mechanisms for elimination of CpH from [CpRu(CO)(PPh$_3$)(H$_2$)]$^+$ have been discussed and could involve solvent-induced "ring slippage" pathways.[15c]

Calorimetric Determination of the Enthalpy of the Reaction H–M(CO)$_3$C$_5$R$_5$ + 3RCN → (RCN)$_3$M(CO)$_3$ + C$_5$R$_5$H (M = Cr, W). (i) Chromium. While the molybdenum complexes establish an equilibrium with RCN as described above, the corresponding chromium and tungsten nitrile complexes react quantitatively with cyclopentadienes. This difference in behavior sparked our interest to determine if kinetic or thermodynamic factors were involved. The enthalpy of reaction in the chromium system was investigated by utilizing reactions of the naphthalene complex:

$$\mathrm{(naphthalene)Cr(CO)_3(s) + 3CH_3CN(soln) \xrightarrow[30\,^\circ C]{THF} Cr(CO)_3(CH_3CN)_3(soln) + naphthalene(soln)} \quad (13)$$

$$\Delta H = -12.2 \pm 0.3 \text{ kcal/mol}$$

Reaction with pentamethylcyclopentadiene is quantitative as shown in

$$\mathrm{(naphthalene)Cr(CO)_3(s) + C_5Me_5H(soln) \xrightarrow[30\,^\circ C]{THF} (C_5Me_5)Cr(CO)_3H(soln) + naphthalene(soln)} \quad (14)$$

$$\Delta H = -11.5 \pm 0.4 \text{ kcal/mol}$$

The difference between these two reactions indicates that oxidative addition is nearly thermoneutral for chromium:

$$\mathrm{Cr(CO)_3(MeCN)_3 + C_5Me_5H \xrightarrow[30^\circ C]{THF} (C_5Me_5)Cr(CO)_3H + 3MeCN} \quad (15)$$

$$\Delta H = 0.7 \pm 0.7 \text{ kcal/mol}$$

The driving force for reaction 15 is the entropy of reaction (discussed above) favoring the right side of the equation. Direct measurement of the enthalpy of reaction 15 yielded a value of 1 ± 2 kcal/mol. Due to the instability of Cr(CO)$_3$(MeCN)$_3$, the results based on the naphthalene complex are more accurate.

Attempts to measure the enthalpy of reaction of (naphthalene)Cr(CO)$_3$ with C$_5$H$_6$ analogous to reaction 14 were not successful since the hydride formed goes on to react with cyclopentadiene (as reported in the literature[18]) and is shown in reaction 16. Estimates of the enthalpy

$$\mathrm{2CpCr(CO)_3H + C_5H_6 \rightarrow [CpCr(CO)_3]_2 + C_5H_8} \quad (16)$$

of reaction for C$_5$H$_6$ could be made based on estimates of the extent of hydrogenation of cyclopentadiene. These estimates[19] indicated little difference in the heat of binding of C$_5$H$_6$ and C$_5$Me$_5$H, as was reported earlier for Mo[8b] and shown below for W.

(ii) Tungsten. Reaction of W(CO)$_3$(EtCN)$_3$ with excess C$_5$H$_6$ in THF is quantitative as shown in eq 17. No hydrogenation of cyclopentadiene (as in eq 16 for chromium) occurs under these conditions for tungsten.

$$\mathrm{W(CO)_3(EtCN)_3(s) + C_5H_6(soln) \xrightarrow[30\,^\circ C]{THF} (C_5H_5)W(CO)_3H(soln) + 3EtCN(soln)} \quad (17)$$

$$\Delta H = 9.9 \pm 0.3 \text{ kcal/mol}$$

Reaction with pentamethylcyclopentadiene is also quantitative as shown in eq 18. The enthalpy of solution of W(CO)$_3$(EtCN)$_3$ in

$$\mathrm{W(CO)_3(EtCN)_3(s) + C_5Me_5H(soln) \xrightarrow[30\,^\circ C]{THF} (C_5Me_5)W(CO)_3H(soln) + 3EtCN(soln)} \quad (18)$$

$$\Delta H = 9.7 \pm 0.2 \text{ kcal/mol}$$

pure THF gave an anomalously high endothermic value in the range of 7–8 kcal/mol due to additional endothermic formation of the THF-substituted complex as shown in eq 19. Addition of excess nitrile eliminates the formation

$$\mathrm{W(CO)_3(EtCN)_3 + THF \rightarrow W(CO)_3(EtCN)_2(THF) + EtCN} \quad (19)$$

of any mixed complexes, and the enthalpy of solution was measured to be $\Delta H = 4.3 \pm 0.1$ kcal/mol in 10% EtCN/THF. Subtracting out this heat of solution yields enthalpies of reaction in solution for eqs 17 and 18 of 5.6 ± 0.4 and 5.4 ± 0.3 kcal/mol, respectively. As was observed above for chromium and earlier for molybdenum, the enthalpies of oxidative addition of C$_5$H$_6$ and C$_5$Me$_5$H are similar.

Calorimetric Measurement of the M–Indenyl vs M–Cyclopentadienyl Bond Strengths in Na$^+$Mo(CO)$_3$(indenyl) and H–W(CO)$_3$(indenyl). We have reported earlier[8b] the enthalpy of reaction of Na$^+$C$_5$H$_5^-$ with (toluene)Mo(CO)$_3$:

$$\mathrm{(toluene)Mo(CO)_3(s) + Na^+C_5H_5^-(soln) \xrightarrow[25\,^\circ C]{THF} Na^+Mo(CO)_3(C_5H_5)^- + toluene(soln)} \quad (20)$$

$$\Delta H = -30.1 \pm 0.4 \text{ kcal/mol}$$

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This measurement was made by using isoperibol calorimetry, and we repeated this measurement for the *p*-xylene complex as shown in eq 21 using Calvet calorimetry.

$$(p\text{-xylene})Mo(CO)_3(s) + Na^+C_5H_5^-(soln) \xrightarrow[30\ ^\circ C]{THF} Na^+Mo(CO)_3(C_5H_5)^-(soln) + p\text{-xylene}(soln) \quad (21)$$

$$\Delta H = -27.6 \pm 0.6\ \text{kcal/mol}$$

These two values are in reasonable agreement considering that the *p*-xylene complex is slightly more stable than the toluene complex.[8] In addition, it is known that these complexes in solution occur as a mixture of "free" ions and "contact ion pairs".[20] Thus, the heats of these ionic reactions may be somewhat temperature and concentration dependent. Examination of the role of ion pairs in these energetics is beyond the scope of this paper. The measurement in reaction 21 was repeated so that comparison to indenyl complex ions could be made under identical conditions:

$$(p\text{-xylene})Mo(CO)_3(s) + Na^+C_9H_7^-(soln) \xrightarrow[30\ ^\circ C]{THF} Na^+Mo(CO)_3(C_9H_7)^-(soln) + p\text{-xylene}(soln) \quad (22)$$

$$\Delta H = -17.3 \pm 0.2\ \text{kcal/mol}$$

These results indicate that complexation of the indenyl anion is approximately 10 kcal/mol thermodynamically less favorable than for the cyclopentadienyl anion (all species in solution):

$$Na^+Mo(CO)_3(\text{indenyl})^- + Na^+C_5H_5^- \xrightarrow[30\ ^\circ C]{THF} Na^+Mo(CO)_3(C_5H_5)^- + Na^+(\text{indenyl})^- \quad (23)$$

$$\Delta H = -10.3 \pm 0.9\ \text{kcal/mol}$$

These results do not deal with the role of ion pair or solvation energies. The infrared spectra indicate roughly the same amount of free and contact ion pairs for the organometallic anions.[19,20] [This is not surprising since the ion pairs exist between the counterion and the carbonyl oxygen—the position of the infrared bands are very similar for both species.]

This result was surprising to us in view of the fact that the indenyl anion is a stronger base than the cyclopentadienyl anion with regard to protonation—pK_a = 20.1 vs a value of 18 for CpH.[21] It might have been anticipated on this basis that the indenyl anion might be a better donor to the metal as well as to a proton. The poor ability of the indenyl ligand to bind to metals is also reflected in the covalent hydrides discussed below.

The indenyl complex dissolves in pure propionitrile to react quantitatively as shown in eq 24. The half-life of this reaction is about 1 h under these conditions. This is in stark contrast to the CpH system, where $CpW(CO)_3H$ undergoes no solvation and in fact is formed quantitatively as shown in eq 17 in the reverse of the solvolysis reaction. Attempts to measure the heat of solution of the indenyl hydride in THF led to slow formation of a solution with infrared bands at 1910 and 1760 cm^{-1}, indicating that coordination of indene is weak enough that even THF can displace it, forming $W(CO)_3(THF)_3$.[22] The enthalpy of solution was measured in toluene, 4.7 ± 0.1 kcal/mol, and is probably similar in THF and propionitrile. This indicates that cleavage of the indenyl complex by propionitrile in solution is exothermic by about 20 kcal/mol. This compares to the corresponding reaction of cyclopentadiene (the reverse of reaction 17), which is exothermic by only 5.6 kcal/mol with all species in solution. Combining these two results, the enthalpy of substitution of the indenyl ligand (with all species in solution) is exothermic by 14.4 kcal/mol:

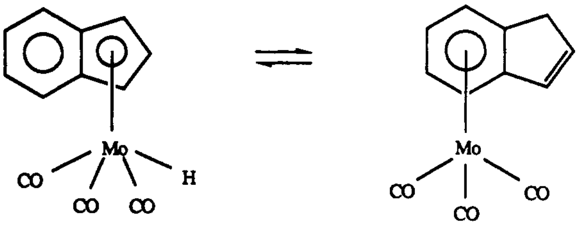
$$(\text{indenyl})W(CO)_3H(s) + 3EtCN(soln) \xrightarrow[30\ ^\circ C]{EtCN} W(CO)_3(EtCN)_3(soln) + \text{indene}(soln) \quad (24)$$

$$\Delta H = -15.3 \pm 0.8\ \text{kcal/mol}$$

$$(\text{indenyl})W(CO)_3H + C_5H_6 \rightarrow (C_5H_5)W(CO)_3H + C_9H_8 \quad (25)$$

In addition to measuring the differences in η^5-indenyl and η^5-cyclopentadienyl bond strength, the enthalpy of reaction 25 will include terms for differences in H–indenyl and H–cyclopentadienyl bond strengths: 79 ± 3 and 81 ± 3 kcal/mol, respectively.[21] Differences in M–H bond strengths for substituted cyclopentadienyl hydrides appear to show only a small dependence on substitution at Cp for the M–H bond strength.[19]

Several attempts to prepare the complexes (indenyl)M(CO)$_3$H for M = Cr, Mo have led only to isolation of (η^6-indene)M(CO)$_3$.[5,19] These observations indicate that the tautomerization reaction shown in eq 26 favors formation of the arene complex for the first- and second-row metals. Nevertheless, it can be estimated that the indenyl hydride complexes are much less stable than the cyclopentadienyl hydride complexes. The enthalpy of reaction 11 shows that the η^6-arene complex is 12.8 ± 1 kcal/mol less stable with regard to ligand substitution than the cyclopentadienyl hydride complex. Since the entropy of the tautomerization reaction shown in eq 26 is probably small, the enthalpy of reaction 26 is either small or positive. That would appear to indicate that for molybdenum the indenyl hydride is at least 13 kcal/mol less stable than the cyclopentadienyl hydride complex with regard to ligand substitution—in keeping with the results found for W as shown in eq 25.



(26)

From these results, both the indenyl anionic and indenyl hydrido complexes are less stable by 10–15 kcal/mol than the corresponding cyclopentadienyl complexes. These results can be compared to the approximately 10^8 kinetic enhancement observed in reactions of indenyl complexes. This corresponds at room temperature to a free-energy difference of about 12 kcal/mol. It seems most likely to us that the most significant contribution of the "indenyl effect" may in fact be ground-state thermodynamic differences. We have observed similar results for a related polycyclic aromatic system—(η^6-arene)Cr(CO)$_3$—in which naphthalene is bound some 6 kcal/mol weaker than benzene.[19]

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Conclusion

There are few solution-phase studies of M–cyclopentadienyl bond strengths.[8] In contrast, a number of studies have been made on complexes with cyclopentadienyl ligands in which this ligand is essentially a spectator. Calorimetric data in this and an earlier paper indicate that cyclopentadiene and pentamethylcyclopentadiene have similar heats of binding in these complexes. This is in contrast to binding of arene ligands where the methyl-substituted complexes are more stable.[8] On the other hand, complexes of the indenyl ligand have been shown to be 10–15 kcal/mol less stable. It seems likely that this contributes to the "indenyl effect", which probably includes a large ground-state destabilization of these complexes.

Surprisingly facile solvolytic reductive elimination of CpH and related ligands occurs for all three group 6 metals when it is thermodynamically allowed. The entropy of this reaction has been measured for the molybdenum complex in acetonitrile. Its value, −51.3 cal/(mol °C), can be used to predict which ligands are capable of forcing reductive elimination. Additional studies of ligand-substitution-induced oxidative addition and reductive elimination are in progress.

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Reactions of Molecular Hydrogen Complexes $[RuH(\eta^2\text{-}H_2)P_4]BF_4$ with Alkynes: Preparation and Crystal Structure of the $[Ru\{\eta^3\text{-}(p\text{-tolyl})C_3CH(p\text{-tolyl})\}\{PhP(OEt)_2\}_4]BPh_4$ Derivative[1]

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Complexes $[RuH(\eta^2\text{-}H_2)P_4]BF_4$ [P = $PhP(OEt)_2$, $P(OEt)_3$, $P(OMe)_3$] react with terminal alkynes HC≡CR (R = Ph, *p*-tolyl, CMe_3, $SiMe_3$) to yield alkenes $H_2C{=}CHR$ and $[Ru(\eta^3\text{-}RC_3CHR)P_4]^+$ derivatives. Selective hydrogenation of the alkyne to alkene by the η^2-H_2 ruthenium catalyst precursor in mild conditions was also observed. The structure of the compound $[Ru\{\eta^3\text{-}(p\text{-tolyl})C_3CH(p\text{-tolyl})\}\{PhP(OEt_2\}_4]BPh_4$ was determined crystallographically: space group $P2_1$, a = 12.497 (5) Å, b = 24.407 (8) Å, c = 12.763 (5) Å, β = 96.89 (2)°, Z = 2; final R = 0.057 and R_w = 0.074. The ruthenium atom has a pseudooctahedral coordination with four phosphite groups and the η^3-RC_3CHR ligand. The $[Ru(\eta^3\text{-}RC_3CHR)P_4]^+$ derivatives react with acetylacetone to afford $[Ru(acac)P_4]^+$ cations and organic compounds (*Z*)-R(H)C=C(H)C≡CR. The reaction of other alkynes [$MeO_2CC{\equiv}CCO_2Me$, RC≡CR (R = Me, Ph)] toward the $[RuH(\eta^2\text{-}H_2)P_4]BF_4$ complexes was also investigated and the synthesis of the vinyl derivatives $[Ru\{C(CO_2Me){=}C(H)CO_2Me\}\{PhP(OEt)_2\}_4]PF_6$ achieved. Characterization of the complexes by IR and ^1H and $^{31}P\{^1H\}$ NMR spectra is also discussed.

Introduction

The reaction of transition-metal hydrides with 1-alkynes represents an important process in organometallic chemistry,[2] and in recent years, a number of studies[3-5] have been reported in this field. Besides simple insertion of the alkyne into the M–H bond to give alkenyl derivatives,[3,4] oxidative additions to the central metal of the C–H group affording alkynyl complexes can also take place,[5] as well as subsequent reaction of these derivatives with alkyne.[6] The factors governing the course of the reaction, i.e. experimental conditions, the nature of the M–H bond, and the alkyne substituent, were extensively investigated and in part rationalized; however, the nature of the resulting product is still poorly predictable owing to the delicate balance of factors that affect this reaction.

Table I. Catalytic Hydrogenation[a] of Alkynes by the Catalyst Precursor $[RuH(\eta^2\text{-}H_2)\{PhP(OEt)_2\}_4]BF_4$ at 25 °C

substrate	time	product	conv, %
HC≡CPh	3 min	$H_2C{=}C(H)Ph$	30
$HC{\equiv}CCMe_3$	20 min	$H_2C{=}C(H)CMe_3$	25
$HC{\equiv}CSiMe_3$	60 min	$H_2C{=}C(H)SiMe_3$	30
HC≡CPh[b]	6 min	$H_2C{=}C(H)Ph$	50
$MeO_2C{\equiv}CCO_2Me$	24 h	*cis*- and *trans*-(MeO_2C)-HC=$CHCO_2Me$[c]	5
MeC≡CPh	36 h	*cis*-Me(H)C=C(H)Ph	10

[a] Reaction conditions: H_2 pressure, 1 atm; alkyne, 4 mmol; catalyst, 0.04 mmol; solvent (CH_2Cl_2 or CD_2Cl_2), 3 mL. [b] Using $[RuH(\eta^2\text{-}H_2)\{P(OMe)_3\}_4]BF_4$ as catalyst. [c] cis and trans isomers in about 6:4 ratio.

Despite the number of studies on metal hydrides, very few data are available[7] on the reactivity with alkynes of molecular hydrogen complexes containing the $MH(\eta^2\text{-}H_2)$ fragment, although the presence of both H^- and H_2 ligands can give insight both on the interaction of acetylenes with nonclassical hydrides and on possible catalytic hydrogen-

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