THERMOCHEMISTRY OF MOLYBDENUM TRICARBONYL COMPLEXES OF ARENES AND CYCLIC POLYOLEFINS

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Summary

The heats of reaction of arene, cycloheptatriene, and cyclooctatetraene complexes of molybdenum tricarbonyl with pyridine yielding $(py)_3Mo(CO)_3$ have been measured by solution calorimetry. Reaction of toluene molybdenum tricarbonyl with cyclopentadiene yielding $HMo(CO)_3C_5H_5$ and with tetrahydrofuran yielding $(THF)_3Mo(CO)_3$ have also been studied thermochemically. These measurements yield accurate values for the enthalpy of arene exchange in methylene chloride solution for a number of organomolybdenum complexes. The order of stability: benzene < toluene < cyclooctatetraene < mesitylene < hexamethylbenzene < cycloheptatriene < (tris)-tetrahydrofuran < η^5-cyclopentadienylhydrido < (tris)-pyridine spans a range of 31 kcal/mol.

The enthalpy of isomerization of cycloheptatriene to toluene is reduced by 7.1 ± 1.2 kcal/mol upon coordination to molybdenum tricarbonyl, indicative of a loss of "resonance" energy for the complexed arene. The Mo–H bond strength in $HMo(CO)_3C_5H_5$ is estimated as 66 ± 8 kcal/mol. The importance of entropic factors in arene exchange is discussed.

Introduction

The thermochemistry of organometallic compounds and determination of dissociation energies for metal–ligand bonds are topics of current interest [1]. Recently we reported thermochemical investigation of the heats of iodination of arene chromium tricarbonyl complexes (eq. 1).

$$\text{areneCr(CO)}_3 + 3/2\,I_2 \xrightarrow{\text{THF}} \text{arene} + CrI_3(THF)_n + 3\,CO \tag{1}$$
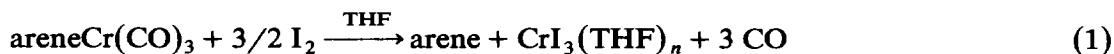
The order of stability with regard to arene exchange: benzene < toluene < cycloheptatriene < mesitylene was shown to span a range of 9.5 kcal/mol [2]. Attempts to extend this work to analogous molybdenum complexes led to irreproducible calorimetric results due to formation and slow decomposition of molybdenum

carbonyl iodide intermediates [3a]. Ligand substitution reactions for these complexes are known to proceed more readily for molybdenum than for either chromium or tungsten [4]:

$$areneMo(CO)_3 + 3 L \rightarrow L_3Mo(CO)_3 + arene \tag{2}$$

(L = PR$_3$, MeCN, amine, etc.)

Reaction with pyridine does not appear to have been reported [5]. It is rapid and quantitative at room temperature. Utilizing this reaction we report results of thermochemical measurements for a series of arenes and cyclic polyolefins.

In order to gain information about the thermochemistry of the Mo–ether linkage, we have studied the equilibrium shown in eq. 3:

$$areneMo(CO)_3 + 3 \text{ THF} \underset{}{\overset{\text{THF}}{\rightleftharpoons}} (THF)_3Mo(CO)_3 + arene \tag{3}$$

This reaction was first reported by Muetterties, Bleeke, and Sievert [6]. Arene complexes are of considerable importance in organometallic chemistry [7], and are often prepared or used in ether solvent [8]. Despite a favorable enthalpy for reaction 3, (due to the relatively strong Mo–ether bond) a large negative entropy of reaction offsets this. Variable temperature IR and NMR results in the range 25–81°C show the qualitative shift in equilibrium 3 towards formation of the arene complex with increasing temperature. Quantitative values calculated for the enthalpy of reaction are in agreement with direct calorimetric measurement. The increased kinetic reactivity of molybdenum compared to chromium allows the equilibrium in eq. 3 to be established at room temperature where it is still relatively favorable. Analogous solvation of arenechromium tricarbonyls by THF does not occur, presumably since the elevated temperatures needed to reach equilibrium disfavor the reaction.

The increased lability of the molybdenum complexes is illustrated by reaction with cyclopentadiene, shown in eq. 4:

$$tolueneMo(CO)_3 + C_5H_6 \xrightarrow{\text{THF}} HMo(CO)_3Cp + toluene \tag{4}$$
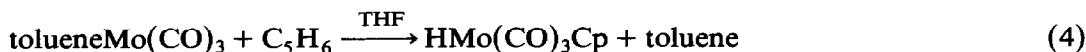
This reaction has not been reported [9]. In the presence of excess cyclopentadiene it is rapid and quantitative at room temperature. The direct measurement of the enthalpy of this reaction is of thermochemical interest. There are few "clean" reactions which can be used to cleave the cyclopentadienyl group. The facile oxidative addition of CpH allows estimation of the Mo–H bond strength, and provides entry into the thermochemistry of the Mo(CO)$_3$Cp group, currently under investigation in our laboratory [3b].

Coordination of arenes is well known to alter their electronic nature [8]. Theoretical arguments have been made that the "aromatic" character in arenes decreases upon coordination [10a]. Based on an analysis of structural data, the loss of aromaticity in bis-benzene-chromium has been estimated as on the order of 14 kcal/mol [10b]. The theoretical interpretation of the meaning of aromaticity in the organometallic chemistry is difficult [11]. We report results which indicate the difference in resonance energy between cycloheptatriene and toluene is reduced by about 7 kcal/mol upon coordination to molybdenum tricarbonyl. This represents the first experimental measurement of the extent to which coordination to a metal can affect the thermodynamics of organic isomerizations.

Experimental

Materials

Organomolybdenum complexes were prepared according to the references shown, or slight modifications thereof: benzeneMo(CO)$_3$ [12], tolueneMo(CO)$_3$ [13], mesityleneMo(CO)$_3$ [14], hexamethylbenzeneMo(CO)$_3$ [15], cycloheptatriene-Mo(CO)$_3$ [16], cyclooctatetraeneMo(CO)$_3$ [17], tris-pyridineMo(CO)$_3$ [18], HMo(CO)$_3$Cp [16], ClMo(CO)$_3$(Cp) [16]. The complexes were purified initially by either recrystallization or high vacuum sublimation followed by a second (or third) recrystallization from methylene chloride/heptane. Only materials of high crystalline quality, with no trace of impurities in either the IR or NMR spectrum were used in thermochemical measurements. All manipulations were carried out using standard Schlenk tube techniques under an atmosphere of prepurified argon, or in a vacuum/atmospheres glove box (equipped with 40 scfm purification train) containing less than 1 ppm O$_2$/H$_2$O. Half the dual length glove box is used for synthetic manipulations, the other half houses the calorimeter described later.

The solvents benzene, toluene, and tetrahydrofuran were distilled from sodium benzophenone ketyl under an argon atmosphere into flame dried glassware. Methylene chloride was distilled from P$_2$O$_5$. Pyridine was refluxed and distilled from anhydrous BaO under an argon atmosphere. After it became clear that water present in the pyridine did not interfere with any of the reactions, it was simply degassed by repeated evacuation and filling with argon. Cycloheptatriene was fractionally distilled under argon; cyclopentadiene was freshly cracked just prior to use. Cyclooctatetraene (Aldrich, 98%) was used without further purification.

Infrared spectra were recorded on a Perkin–Elmer 599 or 267 spectrophotometer in 0.1 mm KBr solution cells. NMR spectra were run on a Varian FT-80A spectrometer.

Calorimetric measurements

The most important quantity in the measurements is the stoichiometry of the reaction. All reactions were first run in Schlenk tubes, and verified to be quantitative under conditions similar to the actual calorimetric procedure. These conditions are described later. The calorimetric measurements were made using a Guild solution calorimeter (model 400) installed in an argon filled inert atmosphere box (vacuum/atmospheres) with purification train. Additional heat exchangers were added to the purification train to control the temperature within the glove box. The dewar vessel of the calorimeter was placed in an air thermostatted insulated container inside the glove box. Electrical feed throughs (Conax) connected the reaction vessel and the rest of the calorimeter. Sealed glass ampoules of the crystalline organometallic complex (= 0.2 g) were broken on a glass anvil to initiate the reaction with the solvent/solution (= 200 ml). Electrical calibrations done before and after the reaction were compared directly to the heat of reaction. The entire system was standardized on two separate occasions using the "tris" reaction. The value we obtain, -246 ± 3 J/g based on twelve separate measurements is in good agreement with the literature value -245.76 ± 0.26 J/g [19].

Reaction of areneMo(CO)$_3$ complexes with pyridine

In a typical reaction, 0.2 g of the areneMo(CO)$_3$ complex was loaded into a

Schlenk tube fitted with a stopcock protected rubber septum. Pyridine (100 ml) was added to the flask, and it was shaken. Immediately upon dissolution the yellow arene complex yielded an orange solution characteristic of $(py)_3Mo(CO)_3$. An infrared spectrum run after 5 min showed only bands at 1905 and 1775 cm^{-1} in the carbonyl region, in agreement with the spectrum of an authentic sample of $(py)_3Mo(CO)_3$. The solution remained clear, with no sign of decomposition. While they were not used in the calorimetric experiments, the reaction of $(THF)_3Mo(CO)_3$ and $HMo(CO)_3Cp$ with pyridine were also tested and found to be quantitative as determined by infrared spectroscopy.

Reaction of tolueneMo(CO)₃ with tetrahydrofuran

This reaction has been reported, but not in detail [6]. Dissolution of 0.16 g of tolueneMo(CO)$_3$ in about 50 ml of dry THF in a manner strictly analogous to that described above for pyridine led to a clear yellow solution. The infrared spectrum after 10 min showed bands at 1920 and 1780 cm^{-1} characteristic of $(THF)_3Mo(CO)_3$ and only traces of the tolueneMo(CO)$_3$ bands at 1965 and 1887 cm^{-1}. Under these conditions, we estimate approximately 1–2% unreacted starting material. We have measured the equilibrium constant by NMR (see below). Under the calorimetric conditions (0.20 g in 200 ml THF), the reactions go to greater than 99.5% completion.

Reaction of tolueneMo(CO)₃ with cyclopentadiene in tetrahydrofuran

In a Schlenk tube, under an atmosphere of argon, a solution made of 36 ml dry THF and 12 ml freshly cracked cyclopentadiene was added to 0.2 g of tolueneMo(CO)$_3$. The yellow complex dissolved to give a faint pink solution with infrared bands at 2015 and 1935 cm^{-1}, in agreement with those run for an authentic sample of $HMo(CO)_3Cp$ [16]. Addition of 1 ml of CCl_4 resulted in immediate formation of a red color characteristic of $ClMo(CO)_3Cp$ and infrared bands in agreement with those from an authentic sample [16]. In the calorimetric experiments, approximately 0.2 g of crystalline tolueneMo(CO)$_3$ was added to a mixture of 50 ml freshly cracked cyclopentadiene in 150 ml THF.

Competition experiments

The qualitative nature of the ligand exchange equilibrium was checked for a number of the complexes. In each case, the order of stability was in agreement with thermochemical predictions. The competition experiments were approached from both sides of the equilibrium, to insure that kinetic factors were not controlling. A typical procedure is described below.

A standard solution of tolueneMo(CO)$_3$ (0.08 M) in toluene was prepared. Acetone or THF was added as a catalyst in a 1/1 ratio. Five ml of this solution was withdrawn and added to a separate flask, followed by addition of 5 ml of cycloheptatriene. Six separate samples (approx. 1 ml) were withdrawn by syringe and sealed off in ampoules under vacuum. The ampoules were wrapped in aluminum foil, and placed in a water bath thermostatted to 25°C. Ampoules were opened and the IR spectra run at intervals until there was no further apparent change in the spectra. In a parallel experiment, the procedure was reversed, starting from cycloheptatrieneMo(CO)$_3$ in cycloheptatriene solution, and adding toluene.

The competition experiments showed that cycloheptatrieneMo(CO)$_3$ was more

stable than the corresponding complexes of benzene, toluene (o,m,p), xylene, mesitylene, hexamethylbenzene, and cyclooctatetraene. Reaction of the cycloheptatriene complex with cyclopentadiene, however, resulted in quantitative conversion to $HMo(CO)_3Cp$.

NMR study of reaction of tolueneMo(CO)$_3$ and THF

A special Schlenk tube was prepared which contained a sidearm leading to a frit and joined to a 10 mm NMR tube. The entire apparatus was flame dried under vacuum. After cooling, 0.27 g of tolueneMo(CO)$_3$ was weighed into the flask. Addition of 5 ml of THF-d_8 led to a dark green concentrated solution. This was forced through the frit under argon pressure, and then sealed off under vacuum. A small residue of solid remained on the frit, but the amount appeared negligible compared to the starting material.

The variable temperature study was conducted using a Varian FT-80A. A variable temperature controller was used to maintain probe temperatures between 34.5 and 81.0°C. Relative proportions of the complexes were calculated by integration of the methyl signal of free and complexed toluene. The temperature controller was calibrated by direct insertion of a standardized thermometer into the probe at each temperature. At the beginning of the experiment, a small amount of decomposition product was evident in the NMR tube, probably due to impurities in the THF. At the conclusion of the variable temperature experiment there appeared to be slightly more decomposition, but a second run at 34.5°C was identical to the first sample run. One week later, a ^{13}C spectrum of the sample run at 34.5°C was both qualitatively and quantitatively in agreement with the proton results.

Variable temperature IR study of the reaction of tolueneMo(CO)$_3$ with THF

The reaction was studied in a water jacketed Schlenk tube connected with teflon valves and fittings (Hamilton Syringe, Reno, Nevada) to the IR cell. The temperature of the IR cell was controlled as described below. Eight five-inch sections of 3/8 inch copper tubing were wired tightly to the metal cell holder. The metal pipes were interconnected with rubber tubing, and water from a constant temperature bath was pumped through the Schlenk tube and then through the pipes surrounding the infrared cell. Before clamping the IR cell in the spectrophotometer, it was wrapped with aluminum foil and then with glass cloth so that only the salt plate windows were exposed. An asbestos board was used to block the IR beam and further insulate the cell except during the measurement. Aliquots of the solution were withdrawn from the Schlenk tube and the IR cell was filled by use of a gas tight syringe fitted with a three-way valve. Over the temperature range 25–50°C, the only carbonyl bands in the infrared spectrum were due to $(THF)_3Mo(CO)_3$ at 1920 and 1780 cm^{-1}, and tolueneMo(CO)$_3$ at 1965 and 1887 cm^{-1}. There were no signs of formation of $Mo(CO)_6$ in the infrared spectrum ($Mo(CO)_6$ would not show up in the NMR spectrum). The changes with temperature of the infrared spectrum with temperature paralleled those in the NMR study. Quantitative estimates based on absorbances of the species agreed within 20% with the NMR and calorimetric data. Due to the high uncertainty in the temperature in the infrared beam, no attempt was made to refine these values.

Results and discussion

The goal of this research was to obtain reliable values for the enthalpy of the arene exchange reaction [6,7] (eq. 5).

$$Arene^1Mo(CO)_3 + Arene^2 \rightarrow Arene^2Mo(CO)_3 + Arene^1 \tag{5}$$

Information about the enthalpy of this reaction in the gas phase is of most utility in making theoretical calculations, but it is difficult to obtain reliable heats of sublimation for the organometallic compounds. We report data based on solution studies. The enthalpy of reaction in solution probably reflects that in the gas phase [1a], and in any case it is also important. Equilibrium measurements for arene exchange in methylene chloride solution are available [6], and we chose this solvent for initial study.

The bulk of this work is based on reaction of the crystalline organomolybdenum complex with pyridine to yield a pyridine solution of the (tris)-pyridine complex.

$$areneMo(CO)_{3(c)} + 3\,py \xrightarrow{py} arene(py) + (py)_3Mo(CO)_3(py) \tag{6}$$
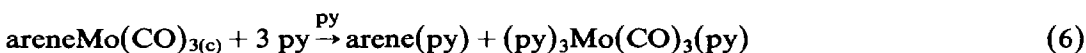
Conversion of this measurement to the enthalpy of arene exchange in methylene chloride solution is done using the thermochemical cycle shown in Scheme 1, which yields eq. 7 (where $C^1 = Complex^1$, $A^1 = Arene^1$, etc.):

$$\Delta H(C^1 + A^2 \rightarrow C^2 + A^1)\,(\text{Exchange})$$

$$= \Delta H(C^1)(\text{React. py}) - \Delta H(C^2)(\text{React. py}) + \Delta H(C^2)(\text{Soln.CH}_2\text{Cl}_2) - \Delta H(C^1)(\text{Soln.CH}_2\text{Cl}_2)$$

$$+ \Delta H(A^2)(\text{Soln.py}) - \Delta H(A^1)(\text{Soln.py}) + \Delta H(A^1)(\text{Soln.CH}_2\text{Cl}_2) - \Delta H(A^2)(\text{Soln.CH}_2\text{Cl}_2) \tag{7}$$

The first two terms (the respective heats of reaction with pyridine) dominate this expression. The difference between the heats of solution of the complexes in methylene chloride (the third and fourth terms) seldom exceeds 1 kcal/mol (see Table 1). Literature data [11] indicate that for the organic liquids studied the last four terms either cancel or can be expected to cancel within 0.3 kcal/mol. For solid hexamethylbenzene, a residual term of 0.8 ± 0.3 kcal/mol was determined by us (see footnote to Table 1). This is in keeping with other work with organochromium
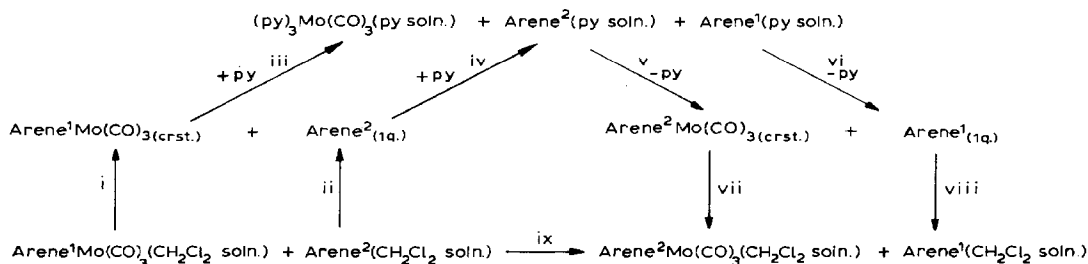
Scheme 1. Thermochemical cycle for calculation of enthalpies of arene exchange in methylene chloride. i: $-\Delta H(C^1)(\text{soln.CH}_2\text{Cl}_2)$; ii: $-\Delta H(A^2)(\text{soln.CH}_2\text{Cl}_2)$; iii: $\Delta H(C^1)(\text{react.py})$; iv: $\Delta H(A^2)(\text{soln.py})$; v: $-\Delta H(C^2)(\text{react.py})$; vi: $-\Delta H(A^1)(\text{soln.py})$; vii: $\Delta H(C^2)(\text{soln.CH}_2\text{Cl}_2)$; viii. $\Delta H(A^1)(\text{soln.CH}_2\text{Cl}_2)$; ix: $\Delta H(C^1 + A^2\ C^2 + A^1)(\text{exchange})$.

complexes where calculated enthalpies of arene exchange showed little solvent dependence [3b].

Experimental data for heats of reaction with pyridine and heats of solution in methylene chloride are collected in Table 1. This data is used to calculate the relative stability with regard to ligand exchange; benzeneMo(CO)$_3$ is taken as reference. The position of (THF)$_3$Mo(CO)$_3$ and HMo(CO)$_3$Cp are based on direct measurements discussed later. Using the recent bond strength estimate Mo−mesitylene = 63.7 kcal/mol [1c] we assign bond strength estimates for these complexes based on the assumption that the solution phase reactions reflect gas phase enthalpies. The experimental errors listed in Table 1 are the standard deviation on typically eight separate determinations. We take the calculated enthalpies of arene exchange to be uniformly reliable to ±1.2 kcal/mol. Qualitative exchange studies, and quantitative determination of the temperature variation of the equilibrium constant for the THF-toluene exchange give added support to the data in Table 1.

Arene complexes

As shown in Table 1 there is a regular increase in thermodynamic stability upon increasing methyl substitution. This is in keeping with many observations in synthetic organometallic chemistry, and earlier results for chromium [2]. Compared to chromium, however, there is less distinction between arenes, despite the fact that the overall bond strength is presumably greater for molybdenum [1c]. For example, substitution of mesitylene for benzene, exothermic by 9.5 kcal/mol for chromium, is only exothermic by 3.5 kcal/mol for molybdenum. On the other hand, the situation is reversed with regard to cycloheptatriene. Thus substitution of benzene by cycloheptatriene, exothermic by 6.3 kcal/mol for chromium, is exothermic by 9.1 kcal/mol for molybdenum.

The agreement between the enthalpy of arene exchange for methyl substituted benzenes and the free energy calculated from available data [6] is fair and implies little entropy change for the reaction. There is spectroscopic evidence which indicates there should be a small entropic effect favoring the less substituted benzenes. Variable temperature ^{13}C NMR results have been interpreted in terms of the conformational changes shown in eq. 8:


(8)
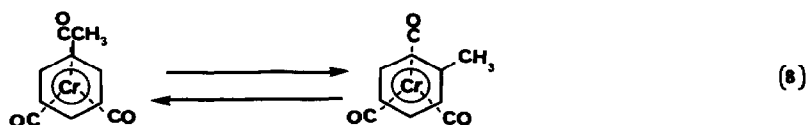
($\Delta H° = +0.85$ kcal/mol; $\Delta S° = +2.0$ cal/mol K)

The entropy change of 2 cal/mol deg was attributed to hindered rotation of the methyl group when it is eclipsed with the carbonyl [21]. Thus substitution of benzene for toluene, shown in eq. 9 should have a favorable entropy change, since rotation of the methyl group of free toluene is unhindered [22].

(9)
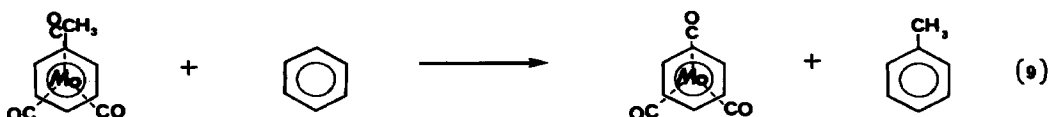
TABLE 1

EXPERIMENTAL AND CALCULATED DATA (kcal/mol) FOR MOLYBDENUM TRICARBONYL COMPLEXES

Ligand	Complex	ΔH(react.py)	ΔH(soln.CH$_2$Cl$_2$)	ΔH°(exchange)	ΔG°(exchange)	M–L[a]
	BenzeneMo(CO)$_3$	−25.7(0.4)	+4.7(0.4)	0	0	63.2
	TolueneMo(CO)$_3$	−24.1(0.7)	+4.3(0.1)	−2.0	−0.7[b]	65.2
	COTMo(CO)$_3$	−22.9(1.0)	+5.0(0.4)	−2.5	–	65.7
	MesMo(CO)$_3$	−21.2(0.6)	+5.7(0.1)	−3.5	−2.8[b]	66.7
	HmbMo(CO)$_3$	−21.0(0.8)	+4.5(0.3)	−5.7[c]	−4.8[b]	68.9

ChptMo(CO)₃	−17.3(0.9)	+4.0(0.2)	−9.1	—	72.3
(THF)₃Mo(CO)₃	—	—	−11.3[d]	+1.6[d]	24.8[e]
HMo(CO)₃Cp	—	—	−12.8[f]	—	93 Mo–Cp[g] 66 Mo–H
(py)₃Mo(CO)₃	+3.1(0.1)	+2.6(0.4)	−30.9	—	31.4[e]
Mo(CO)₆	—	—	—	—	36[h]

[a] Based on value of Mo–mesitylene bond strength of 66.7 kcal/mol [1c]. We consider the absolute values reliable to ±5 kcal/mol. Relative values in solution are reliable to ±1.2 kcal/mol; experimental errors shown in parenthesis refer to standard deviation from the mean on typically eight separate determinations. [b] Calculated from value listed in ref. 6 for the equilibrium constant. [c] Calculated from the thermochemical cycle shown in Scheme 1, using ΔH(soln.) of hexamethylbenzene in methylene chloride and pyridine as +4.7(0.3) and 5.5(0.3) respectively. [d] Estimated from direct measurement of heat of reaction of tolueneMo(CO)₃ with THF; see discussion. The free energy change relative to benzene is based on equilibrium data for toluene assuming similar entropy change; see discussion. [e] Refers to a single two electron M–L bond for L = THF, pyridine, CO; as opposed to the six electron bond in the arene complexes. [f] Based on direct measurement of reaction of tolueneMo(CO)₃ and cyclopentadiene, see discussion. [g] The sum of the Mo–Cp and Mo–H bonds is 159 kcal/mol. The partitioning of this is somewhat arbitrary; see discussion. [h] Based on data for Mo(CO)₆ listed in ref. 1c.

The free energy changes are uniformly smaller in magnitude than the enthalpy changes, supportive of a small entropy effect of this kind. The experimental errors in the present study are too high to analyze this further. It is clear that coordination to a metal (or surface) will reduce the rotational and vibrational entropy of the arene, and that this will likely differ depending on the arene. A more detailed study of this problem is planned.

Cycloheptatriene and cyclooctatetraene

In the previous section we mentioned the increased stability of the cycloheptatriene complex of molybdenum tricarbonyl. Based on high temperature thermal decomposition studies [1c] the metal–cycloheptatriene bond is held to be weaker than the metal–arene bond for the Group VI metals [4]. This is not the case. In addition to our calorimetric results, competition studies such as that shown in eq. 10, approached from both sides of the equilibrium, show that cycloheptatriene will displace any of the ligands above it in Table 1:

(10)
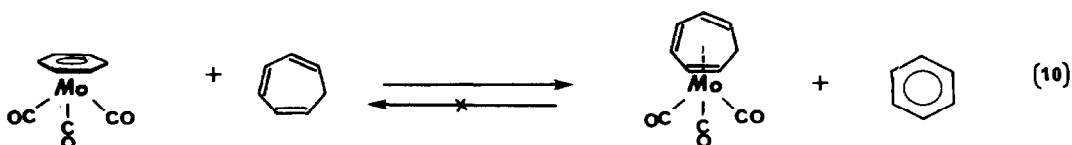
Due to its increased kinetic lability relative to chromium, the chemistry of the molybdenum complexes is more strongly governed by thermodynamic factors. For example, cyclopentadiene readily displaces cycloheptatriene as predicted from thermochemical results.

Despite the strength of the cycloheptatriene–molybdenum bond, isomerization to tolueneMo(CO)$_3$ is thermodynamically favored. This is illustrated by adding equations 11 and 12. (Eq. 11: $\Delta H = -31.74$ kcal/mol [11b]; eq. 12: $\Delta H = +7.1$ kcal/mol; eq. 13: $\Delta H = -24.6$ kcal/mol).


(11)

(12)

(13)
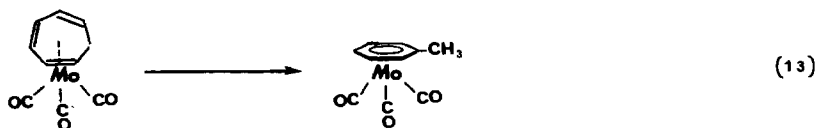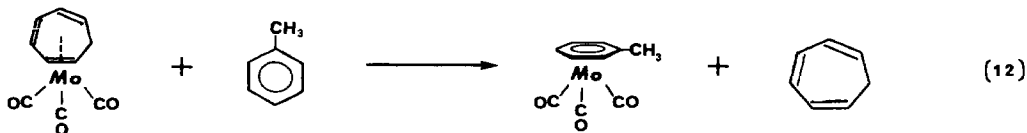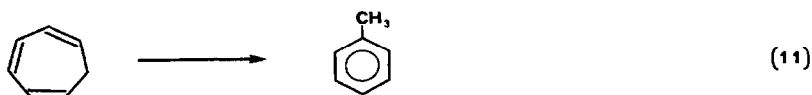
The 32 kcal/mol given off when cycloheptatriene isomerizes to toluene is associated with the "resonance energy" of the arene [11] and is the driving force for

reaction 13. The 7 kcal/mol preference of the molybdenum tricarbonyl group for cycloheptatriene reduces the energy of this conversion, which has not been observed experimentally. A series of reactions leading to net conversion to methyl-benzoateCr(CO)$_3$ from the corresponding cycloheptatriene has been reported [18]. While the "resonance" energy of the coordinated toluene may be reduced, it could also be argued that the relatively unstable cycloheptatriene molecule gains stability through coordination [11]. Clearly the 7 kcal/mol the metal contributes is not enough to overcome the 32 kcal/mol favoring toluene over cycloheptatriene, but it is a significant effect. Rearrangements of organic compounds on transition metals is an important aspect of catalysis. Thermochemical study of related isomerizations which are not so strongly disfavored (i.e. rearrangements of dienes) is underway in our laboratory.

In view of the relative stability of the Mo–cycloheptatriene bond, the position of cyclooctatetraene was surprising. It seems most likely that this reflects steric differences between the two ligands. It may be that constraining cyclooctatetraene to the configuration in the complex induces more strain than for cycloheptatriene. Crystal structures have been reported for both complexes [24] as have analyses of the strain energies in the free ligands [25]. While this explanation (steric effects) appears plausible to us, we can not rule out the contribution of electronic effects.

Cyclopentadiene

The increased stability of coordinated olefins as opposed to arenes sparked our interest in cyclopentadiene. The fact that tolueneMo(CO)$_3$ dissolves in THF forming (THF)$_3$Mo(CO)$_3$ [6], and that HMo(CO)$_3$Cp is made in THF [16] implied that the cyclopentadiene complex should be more stable unless there was some kinetic barrier involved. Therefore reaction of tolueneMo(CO)$_3$ with cyclopentadiene was investigated synthetically and found to be suitable for calorimetric study (eq. 14).

$$(14)$$
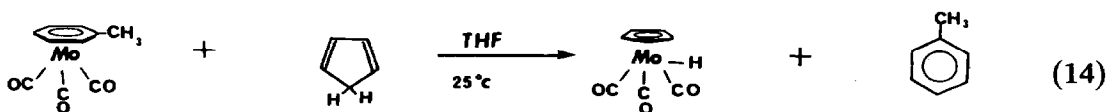
This is a convenient synthesis of HMo(CO)$_3$Cp, and could be of synthetic utility. The enthalpy of this reaction (-7.8 ± 0.5 kcal/mol) was measured directly. The enthalpy of solution of tolueneMo(CO)$_3$ in THF can not be determined since it reacts with THF (see below). We take it to be $+3.0 \pm 0.5$ kcal/mol based on the enthalpy of solution of tolueneCr(CO)$_3$ ($+2.75 \pm 0.2$ kcal/mol) and cycloheptatrieneMo(CO)$_3$ ($+3.09 \pm 0.2$ kcal/mol) which we determined. Thus the enthalpy of reaction 14 in THF solution is -10.8 ± 1.0 kcal/mol. This places HMo(CO)$_3$Cp 10.8 kcal/mol lower than tolueneMo(CO)$_3$ and hence -12.8 ± 1.0 kcal/mol relative to benzene in Table 1.

This data allows estimation of the Mo–H bond strength. Reaction 14 can be imagined to proceed in three steps (eq. 15, 16 and 17). The enthalpy of the first step (reaction 15) has been determined as $+82.9 \pm 2.2$ kcal/mol in the gas phase [26]. The second step involves replacement of coordinated benzene by the cyclopentadienyl radical, followed by combination of the CpMo(CO)$_3$ radical with the H radical in the third step. Since the sum of these reactions is eq. 14 (with benzene

(15)

(16)

(17)

replacing toluene), assuming the heats of sublimation cancel, then:

$$95.7 \pm 3.2 \text{ kcal/mol} = D(\text{Mo–C}_5\text{H}_5) - D(\text{Mo–C}_6\text{H}_6) + D(\text{Mo–H}) \tag{18}$$

It is not straightforward to separate the energy differences. We take the term $D(\text{Mo–C}_5\text{H}_5) - D(\text{Mo–C}_6\text{H}_6)$ to equal 30 ± 5 kcal/mol based on literature data [27]. This leads to $D(\text{Mo–H}) = 66 \pm 8$ kcal/mol. We have deliberately assigned a somewhat high error limit here, and hope to refine this value by combining other thermochemical and electrochemical data.

Tetrahydrofuran, pyridine, and carbon monoxide

These are the first ligands discussed where a sizable entropy contribution can be expected. For example in reaction 19 it is straightforward to estimate $\Delta S = -32$ cal/mol deg by an entropy cycle [28]. An entropy term of this size (in the order of 10 kcal/mol at room temperature) has real significance and explains why cyclohep-

$$\text{tolueneMo(CO)}_3 + 3 \text{ THF} \rightarrow (\text{THF})_3\text{Mo(CO)}_3 + \text{toluene} \tag{19}$$
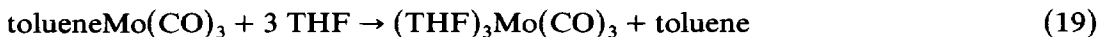
tatrieneMo(CO)$_3$ does not react with THF despite the favorable enthalpy change. The entropy term should be similar for pyridine and carbon monoxide, but due to the much larger enthalpy terms (see Table 1) they still lead to favorable free energies of formation (at least at room temperature). A consequence of the entropy term is that raising the temperature should shift the equilibrium in eq. 19 to formation of the arene complex. This is exactly what happens. Data from a variable temperature NMR study are given in Table 2. The reversible changes in the methyl region of a

TABLE 2

EQUILIBRIUM DATA AS A FUNCTION OF TEMPERATURE FOR THE REACTION:
tolueneMo(CO)$_3$ + 3 THF $\rightleftarrows$ (THF)$_3$Mo(CO)$_3$ + toluene

Temperature (°C)	Toluene [a]	TolueneMo(CO)$_3$ [a]	K_{eq} [b]
34.5	0.188	0.012	16×10^{-4}
55.5	0.172	0.028	5.9×10^{-4}
67.5	0.161	0.039	3.7×10^{-4}
81.0	0.149	0.051	2.4×10^{-4}

[a] Concentrations (mol/liter) determined by integration of free and complexed toluene methyl group resonances in 0.2 M solution of tolueneMo(CO)$_3$ in THF-d_8.

[b] $K_{eq} = \dfrac{[(\text{THF})_3\text{Mo(CO)}_3][\text{toluene}]}{[\text{tolueneMo(CO)}_3][\text{THF}]^3}$; the concentration of THF was taken to be 12.14 M uniformly, based on its density.
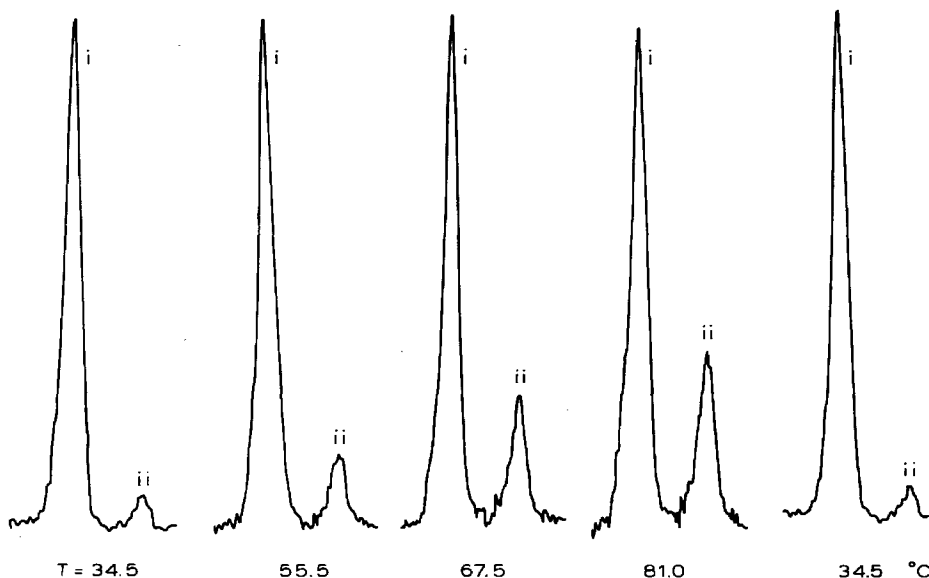
Fig. 1. Variable temperature NMR of methyl region in equilibrium study of the reaction: tolueneMo(CO)$_3$ + 3 THF → (THF)$_3$Mo(CO)$_3$ + toluene. (i: toluene, ii: tolueneMo(CO)$_3$).

0.2 M tolueneMo(CO)$_3$ solution in THF-d_8 are shown in Fig. 1. This data can be used to calculate $H = -8.8 \pm 0.4$ kcal/mol and $S = -41.5 \pm 1.2$ cal/mol deg. The enthalpy term is in good agreement with the calorimetric value of -9.3 ± 1.2 kcal/mol. The entropy term is in rough agreement with the estimate of -32 cal/mol deg. Qualitative (and semiquantitative) determinations over a more limited range by infrared spectroscopy are also in agreement. Since there are other equilibria which can occur [29], we use the equilibrium data as a check on our calorimetric measurements.

For THF and pyridine, we estimate individual bond strengths of 24.8, and 31.4 kcal/mol. Included for comparison in Table 1 is the estimate of 36 kcal/mol for the Mo–CO bond strength in Mo(CO)$_6$ [1c]. This value gives us confidence in our rough bond strength assignments. The position of carbon monoxide seems in accord with qualitative understanding of the chemistry of these complexes. Further thermochemical studies on these and related compounds are in progress.

Acknowledgements

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