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SYNTHESIS AND THERMOCHEMISTRY OF $HMo(CO)_3C_5Me_5$; COMPARISON OF CYCLOPENTADIENYL AND PENTAMETHYLCYCLOPENTADIENYL LIGANDS

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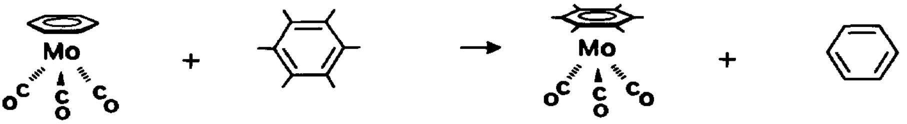
Summary

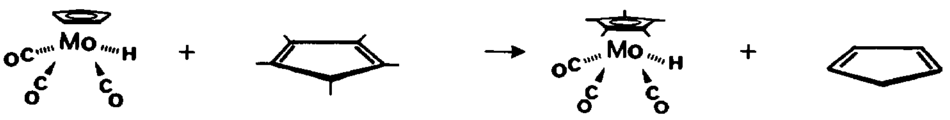
Toluenemolybdenum tricarbonyl reacts quantitatively with pentamethylcyclopentadiene in THF at room temperature yielding $HMo(CO)_3C_5Me_5$. The heat given off in this reaction has been measured by solution calorimetry and indicates there is little difference in the $Mo–C_5H_5$ and $Mo–C_5Me_5$ bond strengths. Thermochemical measurements of the reaction of $HMo(CO)_3C_5R_5$ ($R = H, CH_3$) with pyridine yielding $(py)_3Mo(CO)_3$ confirm this result. In THF solution, $HMo(CO)_3C_5Me_5$ is a weaker acid than $HMo(CO)_3C_5H_5$, $\Delta pK_a \geqslant 3$. The heat of hydrogenation of $(Mo(CO)_3C_5R_5)_2$ to yield two mol of $HMo(CO)_3C_5R_5$ is more favorable by about 2 kcal/mol for $R = CH_3$ compared to $R = H$, probably due to steric repulsion in $(Mo(CO)_3C_5Me_5)_2$.

The metal complexes of pentamethylcyclopentadiene have been shown to display considerably different chemistry than the corresponding cyclopentadiene complexes for several metals [1–3]. There is no data available to indicate whether the apparent stability of the pentamethylcyclopentadienyl complexes is kinetic or thermodynamic in nature. Recent thermochemical measurements in our laboratory have shown an increasing thermodynamic stability for methyl substituted arene complexes of chromium [4] and molybdenum [5]. Thus substitution of hexamethylbenzene for benzene is exothermic by 5.7 kcal/mol for the molybdenum tricarbonyl complex shown in eq. 1.

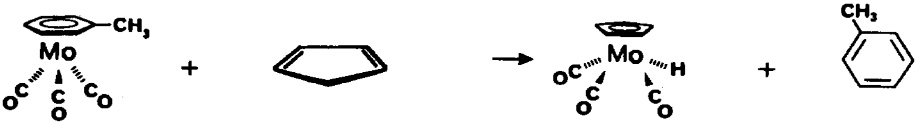


(1)

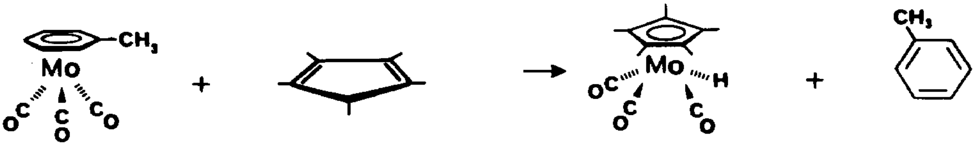
This work was begun to see if a comparable effect occurs when pentamethylcyclopentadiene substitutes for cyclopentadiene as shown in eq. 2.


(2)

As part of a study of molybdenum tricarbonyl complexes of arenes and cyclic polyolefins [5] we recently reported a thermochemical study of reaction 3.


(3)

This reaction had not been previously reported. While it represents a convenient in situ generation of $HMo(CO)_3C_5H_5$ from the readily available (toluene)$Mo(CO)_3$ [6], there is no clear-cut advantage to this synthesis over the established one [7]. Since pentamethylcyclopentadiene is less readily available than cyclopentadiene, reaction 4 offers a convenient route to $HMo(CO)_3C_5Me_5$.


(4)

Reaction 4 is rapid and quantitative at room temperature as determined spectroscopically. The yellow crystalline hydride can be isolated in 95% yield by high vacuum sublimation at 60°C. It is fully characterized by its IR and NMR spectra as well as its chemical reactions discussed below. The only literature reference to this compound that we have found is mention that it can be obtained by acidification of $LiMo(CO)_3C_5Me_5$ [8,20].

Reaction 4 provides a good entry to the chemistry of $HMo(CO)_3C_5Me_5$ [9]; it also allows the first thermochemical evaluation of pentamethylcyclopentadiene as a ligand. Subtracting eq. 3 from eq. 4 yields eq. 2 directly since all other terms cancel. We have previously measured the enthalpy of reaction 3 at 25°C using an isoperibol calorimeter [5]. The value we obtained (-7.8 ± 0.5 kcal/mol) is in reasonable agreement with our new measurements made at 30°C using a Setaram C-80 Calvet calorimeter (-7.3 ± 0.6 kcal/mol). The enthalpy of reaction 4 (-5.5 ± 0.2 kcal/mol) was also measured at 30°C in the Calvet calorimeter. The difference between these two measurements indicates that in THF solution substitution of pentamethylcyclopentadiene for cyclopentadiene in eq. 2 is actually endothermic by 1.8 kcal/mol. Attempts to measure the equilibrium constant for eq. 2 at room temperature failed; at higher temperatures stoichiometric hydrogenation of the diene yielding $[M(CO)_3C_5R_5]_2$ occurred [10].

As an independent check of the direct thermochemical measurements described above we have investigated the reaction of both hydrides with pyridine. At room temperature this reaction is slow, but at 50°C it proceeds quantitatively as shown in eq. 5 below.

$$HMo(CO)_3C_5R_5 + 3py \xrightarrow{py,\ 50°C} (py)_3Mo(CO)_3 + C_5R_5H \quad (5)$$

The enthalpies of this reaction are -16.7 ± 0.7 and -16.2 ± 0.3 kcal/mol for $HMo(CO)_3C_5H_5$ and $HMo(CO)_3C_5Me_5$, respectively. We have not corrected these values for heat capacity and heat of solution differences; however they are clearly in accord with a small difference in the $Mo{-}C_5H_5$ and $Mo{-}C_5Me_5$ bond strengths.

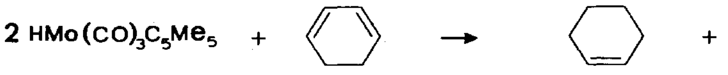
This result was unexpected. Increasing methyl substitution results in definite increases in the metal–arene bond strength. This is not the case (at least for these complexes) with the metal–cyclopentadienyl bond. It should be noted that alkyl substitution was found to decrease the stability of olefin complexes of nickel(0), and that electron-withdrawing substituents increased the stability. The conclusion was reached by Tolman [11] that donation from metal *d*-orbitals to the antibonding orbitals of the olefins was critical in determining stability of the metal–olefin bond. In this regard the cyclopentadienyl–metal bond appears to parallel more closely the behavior of the olefin complexes. Theoretical calculations have further delineated the differences between the metal–cyclopentadienyl and metal–arene bonds [12].

Jordan and Norton have recently reported [13] a study on the acidities of the Group VI hydrides $HM(CO)_3C_5H_5$. The p*K*a's in acetonitrile were 13.3, 13.6, and 16.1 for Cr, Mo, and W respectively. In order to determine the relative acidities of $HMo(CO)_3C_5H_5$ and $HMo(CO)_3C_5Me_5$, we have studied the equilibrium shown in eq. 6.

$$Mo(CO)_3C_5H_5^- + HMo(CO)_3C_5Me_5 \xrightarrow{THF} Mo(CO)_3C_5Me_5^- + HMo(CO)_3C_5H_5 \quad (6)$$

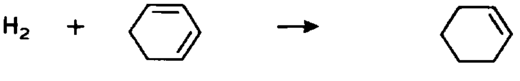
The equilibrium was approached from both sides and lies to the left for eq. 6, $K_{eq} \leq 10^{-3}$ as determined spectroscopically. It is clear that methyl substitution dramatically decreases the acidity of the hydride, and that $\Delta pK_a \geqslant 3$ in tetrahydrofuran solution. A more detailed investigation of the comparative acidities and electrochemistry for these hydrides is planned.

Finally we have determined the heat of hydrogenation of $(Mo(CO)_3C_5Me_5)_2$. Reaction of $HMo(CO)_3C_5Me_5$ with cyclohexadiene in heptane is quantitative at 50°C as shown in eq. 7.



(7)

The dimeric product seperates as bright red-orange crystals, and has been previously characterized [14]. The heat of hydrogenation of cyclohexadiene, shown in eq. 8 is well known [15].



(8)

Subtracting eq. 7 from eq. (8) yields eq. 9 directly:

$$(Mo(CO)_3C_5R_5)_2(s) + H_2(g) \rightarrow 2H\text{-}Mo(CO)_3C_5R_5(s) \qquad (9)$$

We have previously measured the enthalpy of reaction of $HMo(CO)_3C_5H_5$ with cyclohexadiene, -33.8 ± 0.8 kcal/mol leading to an enthalpy of reaction 9 for R = H of $+7.3 \pm 0.8$ kcal/mol (16). The enthalpy of reaction of $HMo(CO)_3C_5Me_5$ with cyclohexadiene according to eq. 7 is -32.0 ± 0.6 kcal/mol, leading to an enthalpy of reaction 9 for $R = CH_3$ of $+5.5 \pm 0.6$ kcal/mol. Thus hydrogenation of the pentamethylcyclopentadienyl dimeric complex is more favorable by 1.8 kcal/mol. This refers to hydrogenation of the solid dimeric complex to yield the solid hydride; however preliminary work indicates that the heats of solution for the complexes are comparable in toluene and dichloromethane. While the difference (1.8 kcal/mol) is close to the limits of experimental error, it is in the expected direction. Steric crowding by the bulky pentamethylcyclopentadienyl groups should destabilize the dimer leading to a more favorable heat of hydrogenation. There are a number of observations in synthetic chemistry to support this [2,3,14,17]. In addition, the position of the σ to σ^* transition, indicative of the metal–metal bond strength [18], also suggests a weaker Mo–Mo bond in the pentamethylcyclopentadienyl complex. Further thermochemical studies on these and related compounds are in progress.

Experimental

General

All manipulations involving organometallic compounds were performed using standard Schlenk tube techniques under an argon atmosphere or in a vacuum/atmospheres glove box. Tetrahydrofuran was stored over calcium hydride and freshly distilled from sodium benzophenone into flame dried glassware. Pentamethylcyclopentadiene was purchased from Strem Chemical and distilled under reduced pressure prior to use. Infrared spectra were determined on a Perkin–Elmer 267 spectrometer. Ultraviolet spectra were run on a Cary-15 and NMR spectra on a Varian FT-80A spectrometer.

Synthesis of $HMo(CO)_3C_5Me_5$

To a Schlenk tube containing 5.0 g toluene$Mo(CO)_3$, 25 ml of a 50% solution of C_5Me_5H in THF was added. The reaction mixture was shaken and then allowed to stand for an hour at room temperature. The Schlenk tube was then connected via rubber tubing to a clean trap (held at $-78°C$) which connected to a high vacuum line. Volatile material was removed at room temperature. Excess C_5Me_5H/THF can be reused and is collected at the end of the experiment from the trap. The solid residue is transferred under argon to a sublimation vessel. Slow sublimation at 60°C and 10^{-5} mmHg onto a water cooled probe yields 5.5 g (95%) of pale yellow crystalline $HMo(CO)_3C_5Me_5$. The hydride appears to be less sensitive to air oxidation than $HMo(CO)_3C_5H_5$, but it is best handled and stored under inert atmosphere. The NMR spectrum in C_6D_6 shows the expected singlets for the methyl group (δ 1.5 ppm) and hydride (δ -2.9 ppm) in 15/1 ratio. The infrared spectrum shows bands at 2015 and 1936 cm^{-1} in the carbonyl region (heptane solution). The Mo–H vibration at 1763 cm^{-1} (CS_2 solution) compares with the value of 1790 cm^{-1} for $HMo(CO)_3C_5H_5$ [19].

Reaction of $HMo(CO)_3C_5Me_5$ with 1,3-cyclohexadiene

In a Schlenk tube 5.0 ml of a 50% solution of 1,3-cyclohexadiene in THF was added to 1.0 g of $HMo(CO)_3C_5Me_5$. The reaction mixture was heated to 50°C in a water bath for 1 h. During this time bright red-orange needles precipitated on the sides of the reaction flask. The yield of $[Mo(CO)_3C_5Me_5]_2$ was quantitative as determined by IR spectroscopy. The product was identified by its IR [14] and UV-VIS [18] spectrum which agreed with the literature.

Reaction of $HMo(CO)_3C_5Me_5$ with cyclopentadiene and with pyridine

In procedures analogous to those described above $HMo(CO)_3C_5Me_5$ was treated with C_5H_6 in THF and with pyridine. Reaction with cyclopentadiene did not occur in 24 h at room temperature. At 50°C, slow conversion to $[Mo(CO)_3C_5Me_5]_2$ was observed. Reaction with neat pyridine at room temperature, analogous to the reaction of $HMo(CO)_3C_5H_5$ (13) produces the anion $^-Mo(CO)_3C_5Me_5$ and slow production of $(py)_3Mo(CO)_3$ [5]. At 50°C both $HMo(CO)_3C_5Me_5$ and $HMo(CO)_3C_5H_5$ produce $(py)_3Mo(CO)_3$ quantiatively within 30 min.

Determination of relative acidities for $HMo(CO)_3C_5R_5$

In the glove box stock solutions of the hydrides, $HMo(CO)_3C_5H_5$ and $HMo(CO)_3C_5Me_5$, were prepared in THF. Stock solutions of the anions $NaMo(CO)_3C_5H_5$ and $NaMo(CO)_3C_5Me_5$ were prepared by reaction of the parent hydrides with NaH in THF using a procedure similar to that described by Jordan and Norton [13]. The highest frequency bands of the hydrides at 2027 $[HMo(CO)_3C_5H_5]$ and 2015 $[HMo(CO)_3C_5Me_5]$ were well resolved as determined in separate experiments mixing the two hydrides. The lowest frequency bands due to the anions at 1760 $[NaMo(CO)_3C_5H_5]$ and 1730 $[NaMo(CO)_3C_5Me_5]$ could also be resolved. This allowed quantitative determination of the species present within 10%. Aliquots of the solutions were mixed in a number of experiments. In all cases $HMo(CO)_3C_5H_5$ was completely deprotonated by $NaMo(CO)_3C_5Me_5$. In a similar fashion $NaMo(CO)_3C_5H_5$ was not protonated by even 100 fold excess of $HMo(CO)_3C_5Me_5$. Reasonable estimates of the limits of detection indicate $K_{eq} \leq 10^{-3}$ for reaction 6. Due to the air sensitive nature of the solution it was not feasible to work with extremely dilute solutions of either reactant.

Calorimetric determination of heats of reaction

Heats of reactions were determined using a Setaram C-80 Calvet calorimeter, purchased from ASTRA scientific. The calorimeter has been described previously [16]. All reported values are the average of five to eight separate determinations, and assigned error limits are the average deviation from the mean. A typical procedure is described below.

The mixing vessels were cleaned, dried at 150°C in an oven for 3 h and then taken into the glove box with the reactants. A sample of recrystallized toluene$Mo(CO)_3$ (approx. 0.2 g) was weighed into the lower vessel, closed and sealed with 1.5 ml of mercury. Then 4 ml of a 50% solution of C_5Me_5H in THF were added and the sample vessel sealed using a teflon gasket. In a similar fashion the reference cell was filled with the exception that the lower chamber was left empty. The two vessels were taken out of the glove box and loaded into the calorimeter and allowed to equilibrate (approx. 2 h). At the end of this time the reaction was initiated by inverting the calorimeter. When the signal had returned to base-line the cells were taken back into the glove box, opened, and the IR spectrum of the product run to verify quantitative conversion to $HMo(CO)_3C_5Me_5$.

Acknowledgement

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References

1 J.K. Hoyano, A.D. Master, and W.A.G. Graham, J. Amer. Chem. Soc., 105 (1983) 7190.
2 P.M. Maitlis, Acc. Chem. Res., 11 (1978) 301.
3 R.B. King, Coord. Chem. Rev., 20 (1976) 155.
4 C.D. Hoff, J. Organomet. Chem., 246 (1983) C53.
5 C.D. Hoff, J. Organomet. Chem., 282 (1985) 201.
6 B. Nicholls and M.C. Whitting, J. Chem. Soc., (1959) 551.
7 R.P. King, Organometallic Synthesis Volume 1, Academic Press, New York, 1965.
8 R.B. King and M.B. Bisnette, J. Organomet. Chem., 8 (1967) 287.
9 S.P. Nolan, J.T. Landrum, and C.D. Hoff, work in progress.
10 A. Miyake and H. Kondo, Angew. Chem. Int. Ed. Engl., 7 (1968) 880.
11 C.A. Tolman, J. Am. Chem. Soc., 96 (1974) 2780.
12 B.E. Burstein and R.F. Fenske, Inorg. Chem., 18 (1979) 760.
13 R.F. Jordan and J.R. Norton, J. Am. Chem. Soc., 104 (1982) 1255.
14 R.B. King. M.Z. Igbal, and A.D. King, Jr., J. Organomet. Chem., 171 (1979) 53.
15 J.D. Cox and G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, New York, 1970.
16 J.T. Landrum and C.D. Hoff, J. Organomet. Chem., 282 (1985) 215.
17 D.S. Ginley, C.R. Bock, and M.S. Wrighton, Inorg. Chim. Acta., 23 (1974) 85.
18 G.L. Geoffroy and M.S. Wrighton, Organometallic Photochemistry, Academic Press, New York, 1979, p. 61.
19 A. Davison, J.A. McCleverty, and G. Wilkinson, J. Chem. Soc., (1963) 1133.
20 *Note added in proof:* Details of preparation of $HMo(CO)_3C_5Me_5$ in 44% yield have appeared; M. Rakowski-DuBois, D.L. BuBois, M.C. VanderVeer, and R.C. Haltiwanger, Inorg. Chem., 20 (1981) 3064.