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THE HEATS OF HYDROGENATION OF THE METAL–METAL BONDED COMPLEXES $[M(CO)_3C_5H_5]_2$ (M = Cr, Mo, W)

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Summary

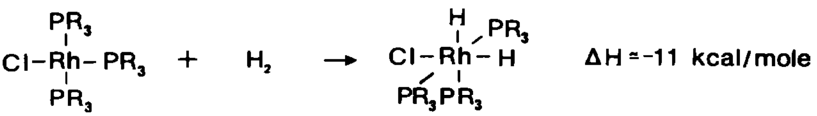
Direct measurement of the enthalpy of decomposition of $HCr(CO)_3C_5H_5$ to $[Cr(CO)_3C_5H_5]_2$ and H_2 was made by differential scanning calorimetry. The heat of hydrogenation of 1,3-cyclohexadiene by $HM(CO)_3C_5H_5$ for M = Cr, Mo, and W was measured by solution calorimetry. The enthalpies of iodination of $[M(CO)_3C_5H_5]_2$ and $HM(CO)_3C_5H_5$ were measured for M = Mo and W. These data have been used to calculate the heats of hydrogenation for each of the metal–metal bonded dimers, $[M(CO)_3C_5H_5]_2$ (M = Cr, Mo, and W).

$$C_5H_5(CO)_3M{-}M(CO)_3C_5H_5(s) + H_2(g) \rightarrow 2HM(CO)_3C_5H_5(s)$$

Addition of hydrogen has been found to be exothermic for M = Cr, W (−3.3 kcal/mol and −1.5 kcal/mole, respectively) but endothermic for M = Mo (+6.3 kcal/mol). These results are consistent with the trend of increasing M–H bond strengths upon descending Group VI. Addition of H_2 to $[Cr(CO)_3C_5H_5]_2$ is favored by the unusually weak chromium–chromium bond.

Introduction

Addition of hydrogen to transition metals is a key step in a number of catalytic cycles [1], yet there is little thermodynamic data regarding this important reaction. Oxidative addition of hydrogen has been studied for the mononuclear complexes shown in eq. 1 [2] and 2 [3]:



$$ClRh(PR_3)_3 + H_2 \rightarrow ClRh(H)_2(PR_3)_3 \quad \Delta H = -11 \text{ kcal/mole} \qquad (1)$$

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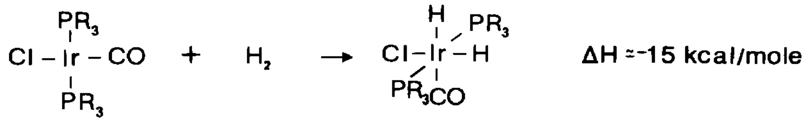


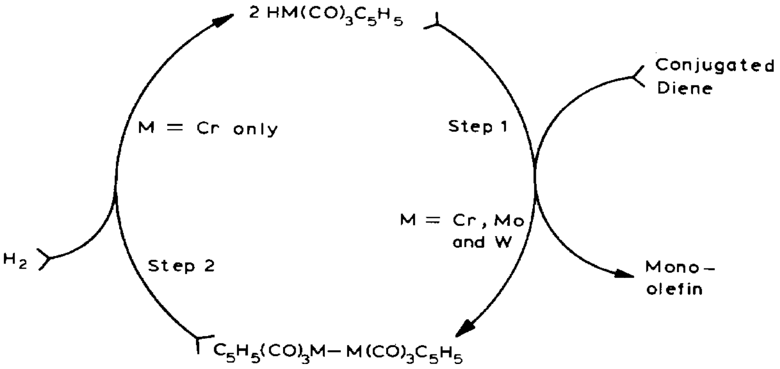
$$Cl-Ir(PR_3)_2-CO + H_2 \rightarrow Cl-Ir(H)_2(PR_3)_2CO \quad \Delta H \simeq -15\ \text{kcal/mole} \quad (2)$$

These reactions are exothermic. They do not, however, involve cleavage of a metal–metal bond as is generally the case for addition of hydrogen to dinuclear complexes or clusters. The only dinuclear complex for which the heat of hydrogenation is known is dicobalt octacarbonyl [4]:

$$Co_2(CO)_8 + H_2 \rightleftharpoons 2HCo(CO)_4 \quad (3)$$

This reaction is endothermic. Temperature variation of the equilibrium constant for eqn. 3 was used by Ungvary to calculate ΔH +3.2 kcal/mole and ΔS +4.4 e.u.. These values were later challenged by Alemdaroglu, Perninger and Oltay who obtained ΔH +6.6 kcal/mol and ΔS +14.6 e.u. [5]. Independent work by Bor and Tannenbaum [6] confirmed the earlier values of Ungvary [4].

Such data are important since addition of hydrogen to a dinuclear complex can distinguish between stoichiometric and catalytic reduction. For example, all three of the hydrides studied in this report hydrogenate conjugated dienes stoichiometrically as shown in Scheme 1 [7].



SCHEME 1

Step 1 proceeds to completion for each of the Group VI metals with the relative rates Cr > Mo > W [7]. Step 2, the regeneration of the hydride, is essential to complete the catalytic cycle and occurs readily only for chromium. The goal of this research was the measurement of the enthalpy of step 2 for the metals Cr, Mo and W in order to determine whether the barrier to hydrogenation of the molybdenum and tungsten complexes is kinetic or thermodynamic in nature.

Results

Heats of iodination of $HM(CO)_3C_5H_5$ and $[M(CO)_3C_5H_5]_2$ for M = Mo and W

The reactions of the $HM(CO)_3C_5H_5$ and $[M(CO)_3C_5H_5]_2$ with iodine, eq. 4 and 5, are well known [8,9]. They are rapid and quantitative at room temperature yielding $IM(CO)_3C_5H_5$.

$$[M(CO)_3C_5H_5]_2(s) + I_2(soln) \xrightarrow{CH_2Cl_2} 2IM(CO)_3C_5H_5(soln) \qquad (4)$$

$$2HM(CO)_3C_5H_5(s) + I_2(soln) \xrightarrow{CH_2Cl_2} 2IM(CO)_3C_5H_5(soln) + 2HI(soln) \qquad (5)$$

At higher temperatures or for long reaction times the complex $I_3M(CO)_2C_5H_5$ is formed [10]. The latter product is not observed under the conditions of our measurements.

In order to complete the thermochemical cycle yielding the heat of hydrogenation of the metal dimers, the enthalpy of reaction 6 is required.

$$H_2(g) + I_2(soln) \xrightarrow{CH_2Cl_2} 2HI(soln) \qquad (6)$$

The enthalpy of formation of HI gas (+6.35 kcal/mole) [11] must be corrected for the enthalpy of solution of I_2 and HI in dichloromethane. Our measurements of these values, $\Delta H^{\text{soln } I_2}_{CH_2Cl_2} = +5.7 \pm 0.3$ kcal/mol and $\Delta H^{\text{soln HI}}_{CH_2Cl_2} = -3.0 \pm 0.6$ kcal/mol enable us to calculate the enthalpy of reaction 6 as $+1.0 \pm 0.87$ kcal/mol.

The sum of reactions 4 and 6 minus twice reaction 5 leads directly to eq. 7:

$$C_5H_5(CO)_3M{-}M(CO)_3C_5H_5(s) + H_2(g) \rightarrow 2HM(CO)_3C_5H_5(s) \qquad (7)$$

$$\Delta H_{\substack{\text{Hydrogenation}\\ \text{of M-M}}} = \Delta H_{\substack{\text{Iodination}\\ \text{of M-M}}} - 2\Delta H_{\substack{\text{Iodination}\\ \text{of M-H}}} + 1.0 \text{ kcal/mol}$$

Experimental data for the enthalpy of iodination and calculated enthalpies of hydrogenation are collected in Table 1.

Heats of hydrogenation of 1,3-cyclohexadiene

The instability of $ICr(CO)_3C_5H_5$ [9] precludes determination of the heat of hydrogenation of $[Cr(CO)_3C_5H_5]_2$ by the method outlined above. The selective

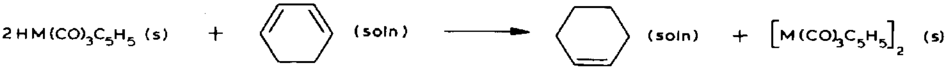
TABLE 1

ENTHALPIES OF IODINATION, REACTION WITH 1,3-CYCLOHEXADIENE, AND HYDROGENATION (kcal/mol)

	Metal		
	Chromium	Molybdenum	Tungsten
$\Delta H^{\text{Iodination}}_{M-M}$	–	-31.8 ± 1.0	-35.0 ± 0.9
$\Delta H^{\text{Iodination}}_{M-H}$	–	-18.0 ± 0.6	-16.1 ± 0.9
$\Delta H^{\text{diene-hydride}}_{\text{reaction}}$	-23.5 ± 0.9	$-33.8 + 0.8$	-33.1 ± 0.8
$\Delta H^{\text{Hydrogenation}}_{M-M+H_2 \rightarrow 2HM}$	-3.0 ± 0.9 [a]	7.3 ± 0.8 [a]	-1.2 ± 0.8 [a]
	-3.6 ± 1.0 [b]	5.2 ± 1.9 [c]	-1.8 ± 1.8 [c]
M–M bond strength	12.7 [d]	32.5 [e]	55.9 [g]
M–H bond strength	60 [d]	65 66 [f]	80.7

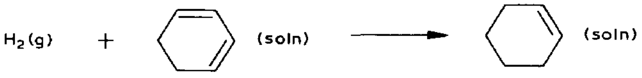
[a] Based on reaction with 1,3-cyclohexadiene, see text for full details. [b] Based on direct measurement of thermal decompostion of $HCr(CO)_3C_5H_5$. [c] Based on enthalpies of iodination, see text for full details. [d] Rough estimate based on using an average of 60 kcal/mol for the Cr–H bond strength. [e] Ref. 17. [f] Ref. 20. [g] Ref. 18.

hydrogenation of dienes by $HM(CO)_3C_5H_5$, reported by Miyaka and Kondo [7], provides the key step in the thermochemical cycle for the chromium system. 1,3-Cyclohexadiene is hydrogenated to cyclohexane in 100% yield by $HM(CO)_3C_5H_5$:



(8)

(M = Cr (30°C) , M = Mo (50°C) , M = W (80°C))



(9)

(ΔH −26.46 kcal/mol)

The heat of hydrogenation of cyclohexadiene, eq. 9 is well known [12]. Subtracting eq. 8 from eq. 9 provides a second method for obtaining heats of hydrogenation (eq. 10).

$$C_5H_5(CO)_3M\text{-}M(CO)_3C_5H_5(s) + H_2(g) \rightarrow 2HM(CO)_3C_5H_5(s) \qquad (10)$$

$$(M = Cr, Mo, W)$$

$$\Delta H_{\substack{\text{Hydrogenation}\\ \text{of M-M}}} = \Delta H_{\substack{\text{reaction}\\ \text{diene} + H_2}} - \Delta H_{\substack{\text{reaction}\\ \text{2MH} + \text{diene}}}$$

Due to the decreasing reactivity Cr > Mo > W, elevated temperatures were necessary to study the Mo and W reactions. The heats of hydrogenation were obtained in a Calvet twin cell calorimeter. The reference cell contained the metal–metal dimer and a solution of 1,3-cyclohexadiene in heptane. The sample cell contained the metal-hydride and a solution of the diene in heptane. This eliminates all enthalpies of solution (see experimental section).

In order to correct the values measured for molybdenum (50°C) and tungsten (80°C) back to room temperature, the difference in heat capacity between the dimer versus two moles of the hydride was measured. In the case of molybdenum in the range of 30–50°C this proved to be zero. The tungsten hydride melts at 67°C with an enthalpy of melting of $+3.93 \pm 0.2$ kcal/mol; aside from this there is no significant difference in the heat capacities of the hydride and dimer. Experimental data for the hydrogenation of 1,3-cyclohexadiene are included in Table 1, as well as the calculated heats of hydrogenation of the metal–metal dimers (including in the case of tungsten the 7.9 kcal for the melting of two mol of hydride). The values agree within experimental error with values determined by iodination.

Differential scanning calorimetry of the hydrides

Recognizing the known lability of the chromium hydride, the difficulties attendent to its preparation in pure form and its tendency to lose hydrogen, an independent verification of this measurement was sought. Direct measurement of the thermal decomposition of the hydride to the dimeric complex and hydrogen was made in the temperature range 30–130°C. The integrated data yielded a result of −3.6 kcal/mol for the hydrogenation of the dimer (the reverse reaction of the actual measurement). This was in surprisingly good agreement with the diene result of −3.0 ± 0.9 kcal/mol.

A similar attempt to measure the decomposition of the molybdenum hydride was unsuccessful. Heated to 135°C we saw no signs of decomposition and observed the enthalpy of melting as the sole thermal process. This was surprising in view of the reported thermal instability of the molybdenum hydride [13]. During sublimation we have observed decomposition of the hydride above 80°C. The samples used for calorimetric measurements were highly pure materials free of any dimer which might serve as a catalyst for decomposition in a manner similar to that known to occur for $HCo(CO)_4$ and $Co_2(CO)_8$ [14]. Also the samples were heated under an argon atmosphere in the dark. The tungsten hydride shows similar stability.

Discussion

The only previous determinations of the heat of hydrogenation to transition metal complexes have been made by measurement of the temperature variation of the equilibrium constant [2–4]. It is not always possible to find systems which establish equilibrium rapidly and cleanly enough to allow this approach. We describe here the first calorimetric determinations of the heat of hydrogenation of dinuclear metal complexes. For each of the complexes $[M(CO)_3C_5H_5]_2$ the heat of hydrogenation, eq. 10, has been determined by two independent thermochemical methods. This approach should be of wide applicability and we are currently extending it to other dinuclear and polynuclear complexes.

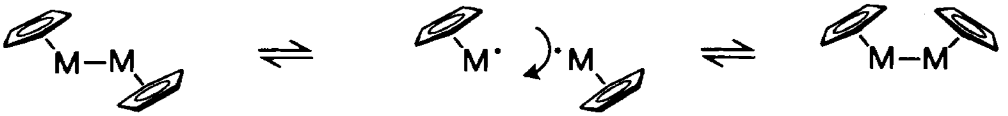
The heats of hydrogenation for the Group VI dimers, averaged between the two methods, (see Table 1) are −3.3, +6.3 and −1.5 kcal/mol, respectively for the Cr, Mo and W dimers. These results refer to hydrogenation of the solid dimer to yield the solid hydride. Initial work indicates that solution effects largely cancel for the hydrogenation reaction. However, in view of the importance of such reactions, a detailed investigation of solvent effects is in progress.

The heats of hydrogenation span a range of 10 kcal/mol, with the surprising result that the molybdenum hydride is least stable with regard to loss of H_2. The thermal lability of the chromium hydride is well known, as is its tendency to lose hydrogen. The chromium dimer is, however, the only member of the Group VI dimers which readily adds hydrogen, originally reported to occur under rather forcing conditions [15], but more recently shown to proceed at least fractionally at 20°C and 1 atm hydrogen [7a,16].

It is generally agreed that both metal–metal and metal–hydride bonds increase in strength upon descending the periodic table. The strength of the molybdenum–molybdenum bond has been estimated as 32.5 kcal/mol based on kinetic measurements [17] and the tungsten–tungsten bond has been determined as 55.9 kcal/mol by electron impact [18]. The chromium dimer is of special interest. It has a metal–metal bond longer than its molybdenum and tungsten analogs [19]. This has been interpreted in terms of steric repulsion between the ligands on the adjacent metals. The dimer is believed to exist in equilibrium with a small concentration of the radical monomer as shown in eq. 11, and determined by NMR and ESR spectroscopy.

$$[Cr(CO)_3C_5H_5]_2 \rightarrow 2\,{}^{\cdot}Cr(CO)_3C_5H_5 \qquad (11)$$

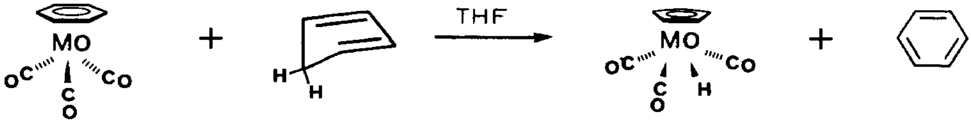
These observations point to an extremely weak Cr–Cr bond. Using the average value for first row transition metal hydride bonds of 60 kcal/mol, our data leads to an estimate of the Cr–Cr bond strength in the order of 12.7 kcal/mol. This value seems low, however, a higher value of the chromium–chromium bond strength requires an even higher Cr–H bond strength. The Mo–H bond has been estimated to be 65 kcal/mol, vide infra, and it seems unlikely that the Cr–H bond is stronger. The activation energy for interconversion of the *anti* and *gauche* isomers of $[Cr(CO)_3C_5H_5]_2$ is 13.7 kcal/mol [19]. One possible mechanism, dissociation–recombination of ${}^{\cdot}Cr(CO)_3C_5H_5$ radicals as shown in eq. 12, would require a very weak chromium–chromium bond.



(12)

It should be pointed out that the related complex $[Cr(CO)_2(P(OMe)_3)]_2$ is largely dissociated at room temperature [16].

Using the value of 32.5 kcal/mol for the Mo–Mo bond strength determined from kinetic measurements [17] leads to an estimate of 65 kcal/mol for the Mo–H bond strength. We recently reported [20] a bond strength estimate of 66 ± 7 kcal/mol based on thermochemical analysis of reaction 13. The agreement between the two different methods is good, and gives added confidence to our earlier assignment.



(13)

The bond strength estimate of 55.9 kcal/mol for the tungsten–tungsten bond in the dimer [18] leads to an estimate of 80.7 kcal/mol for the tungsten–hydrogen bond strength. To our knowledge this is the largest transition metal–hydride bond strength so far reported. Bond strength estimates for organoactinide hydrides in excess of 90 kcal/mol have recently been reported [21].

Finally, these data can also be used to calculate the enthalpy of the metal exchange between dimers and mononuclear hydrides given by eq. 14.

$$2HM(CO)_3C_5H_5 + [M'(CO)_3C_5H_5]_2 \rightarrow 2HM'(CO)_3C_5H_5 + [M(CO)_3C_5H_5]_2 \qquad (14)$$

The relative stabilities are Cr > W > Mo. This is in keeping with the observations of Hoffman and Brown [22] where reaction 14 was observed to occur for M = Mo and M′ = W but not in the reverse situation.

Conclusion

Solution thermochemical studies have been described for the addition of hydrogen to dimeric complexes. Unlike coordinately unsaturated mononuclear complexes where no metal–metal bonds are broken, such reactions are only marginally favored (Cr, W), or slightly disfavored (Co, Mo) with regard to the enthalpy of reaction. For this reason, solvent and substituent effects should play a more critical role in determining the position of thermodynamic equilibrium. Since two mol of metal hydride are generated per mol of metal–metal bond broken, a uniform increase in both metal–metal and metal–hydride bond strengths will favor formation of the metal hydrides (thermodynamically) on descending the chromium triad. This trend has been seen for the Group VI dimers, $[M(CO)_3C_5H_5]_2$, with chromium occupying an anomalous position which we attribute to its unusually weak metal–metal bond without a correspondingly weak metal–hydrogen bond. Further thermochemical studies on these and related complexes are in progress.

Experimental

General. All operations involving air sensitive organometallic complexes were done using standard Schlenk tube and high vacuum techniques, or performed in a Vacuum/Atmospheres glove box filled with argon containing less than 1 ppm O_2 and H_2O. Solvents were distilled under argon from appropriate drying agents into flame-dried glassware immediately prior to use. All reactions used for calorimetric measurements were reinvestigated under conditions as close as possible to the actual measurements to verify their quantitative nature and the nature of the products formed using IR and NMR spectroscopy. The complexes $HM(CO)_3C_5H_5$ and $[M(CO)_3C_5H_5]_2$ were prepared by standard procedures [23]. Special care was taken to insure the purity of these materials. All compounds were subjected to a minimum of two purification steps involving either recrystallization or high vacuum sublimation. Only material of high crystalline quality and spectroscopic purity were used for calorimetric measurements. Typical calorimetric procedures are described below.

Enthalpies of iodination. These reactions were studied using a Guild solution calorimeter as previously described [20]. The calorimeter is housed in a Vacuum/Atmospheres glove box with an argon atmosphere which contained less than 1 ppm oxygen and water. The purity of the atmosphere in the glove box was checked using chromous acetylacetonate, or more critically $HCr(CO)_3C_5H_5$ which turns from yellow to green in the presence of even traces of oxygen. Electrical leads (Conax) pass through the wall of the glove box so that only the calorimetric vessel is in the glove box. Water from a constant temperature bath maintained at 25.0°C is pumped through a closed loop system which maintains a constant thermal head across the calorimeter surfaces.

In a typical reaction the calorimeter is loaded with 500 ml of freshly distilled dichloromethane and 5.0 g of iodine, assembled and left stirring overnight to reach thermal equilibrium. Samples of the organometallic compound to be studied (0.15–0.3 g) are weighed into thin walled ampoules in the glove box, capped with rubber septa, taken out of the glove box and flame sealed under vacuum. The sealed ampoules are attached to a glass rod with a teflon holder and broken by crushing against the bottom of the calorimeter. Empty ampoules, or ampoules filled with solvent were broken periodically to verify that no heat of ampoule breaking could be detected. The enthalpy of reaction is determined by electrical calibrations done before and after each reaction. The entire system has been standardized using the TRIS reaction [24] and the enthalpy of solution of KCl in water [11] on several different occasions and is accurate within 1%. It is our experience that great care must be taken to insure the purity of solvents and reactants in order to obtain reproducible results, particularly regarding the reactions of hydrides. All results reported are the average of typically eight, and in some cases as many as twenty separate determinations.

Enthalpy of solution of HI and I_2. In order to complete the thermochemical cycle involving iodination of the complexes, the enthalpy of solution of HI gas in an I_2 solution of dichloromethane had to be determined. Anhydrous HI was prepared as described in the literature [25] and purified by repeated trap to trap distillation on a high vacuum line. We found it necessary to pass the HI gas over a bed of P_2O_5 to remove the last traces of moisture. Bulbs of known volume (about 20 ml) were filled with HI gas (typically 0.6–0.7 atm) and subsequently broken within the calorimeter. Due to the large volume of these bulbs the heat of empty bulb breaking had to be subtracted. Completely evacuated bulbs of the same volume were broken within the calorimeter allowing us to measure the heat associated with this process. Errors in determination of bulb volumes proved to be one of the greatest difficulties in these determinations. We consider the value of $\Delta H^{\text{soln HI}}_{\text{CH}_2\text{Cl}_2} = -3.0$ kcal/mol to be accurate with the (rather high) error limits of ± 0.6 kcal/mol. This result agrees reasonably well with the enthalpy of solution of HCl in CCl_4 (-3.03) and $HCCl_3$ (-2.63) and HBr in CCl_4 (-3.20) and $HCCl_3$ (-3.29) [11].

The enthalpy of solution of I_2 in CH_2Cl_2 was measured by breaking thin-walled ampoules containing about 1 g of solid I_2 into the calorimeter as previously described. The value of 5.6 ± 0.3 kcal/mol is close to that of 5.3 kcal/mol for the heat of solution of I_2 in $CHCl_3$ [11].

Enthalpy of reaction with 1,3-cyclohexadiene. These reactions were investigated using a Calvet twin cell calorimeter, Setaram C-80, obtained from Astra Scientific, Santa Clara, California. The calorimeter is calibrated by the factory, however it was checked by determination of the enthalpy of solution of KCl [11] in water, the enthalpy of melting of naphthalene [26], and the heat capacity of ammonium nitrate [27]. All of these measurements were accurate within 1% error.

In a typical reaction the mixing cells were dried in an oven, and then taken into the glove box. The reference cell was loaded with 0.180 g $[Cr(CO)_3C_5H_5]_2$ in the lower chamber, capped and sealed with 1.5 ml of Hg then 4.0 ml of 50% solution of 1,3-cyclohexadiene in heptane were added and the reference vessel closed. The sample vessel was loaded with 0.180 g $HCr(CO)_3C_5H_5$ which had been freshly sublimed, and the lower chamber capped and sealed with 1.5 ml of Hg. After adding 4.0 ml of 50% cyclohexadiene in heptane, the sample vessel was sealed. Both vessels were taken from the glove box and loaded into the calorimeter. After thermal equilibration (1–2 h), the calorimeter was rotated, mixing the chromium hydride with the diene solution in the sample cell at the same time as the chromium dimer is mixed with the diene solution in the reference cell. The measured enthalpy for the reaction is the difference between the heat generated in the reference and sample cells, thus the enthalpy of solution of the chromium dimer is automatically subtracted. The dimer is virtually insoluble in alkane solvents and can be isolated as dark green crystals at the end of the experiment. Similar procedures were used for the molybdenum and tungsten complexes, except that the calorimeter was operated at 50 and 80°C for Mo and W, respectively.

Differential scanning calorimetry of $HM(CO)_3C_5H_5$. The high pressure cells of the calorimeter were cleaned, dried in an oven and taken into the glove box. The reference cell was loaded with 0.293 g of $[Cr(CO)_3C_5H_5]_2$ and the sample cell with 0.295 g of $HCr(CO)_3C_5H_5$. The two vessels were closed and connected by 3 mm pressure/vacuum tubing to a Hamilton three way valve which was connected to a bubbler filled with high-vacuum pump oil. The entire apparatus was assembled in the glove box, then taken out and loaded into the calorimeter. After thermal equilbration, the temperature was scanned from 30–135°C at a rate of 0.2°C/min. Starting at around 58°C an endothermic peak appeared. Concomitant with this a steady stream of bubbles was observed through the exit bubbler. By the end of the scan, the signal had returned to baseline, and could be integrated to determine the total enthalpy. At the end of the reaction both cells were taken into the glove box and examined. The blue-green appearance in both the reference and sample cell (typical of the chromium dimer) were identical as were the infrared spectra of the materials in both dichloromethane and heptane solutions. A total of 0.258 g of sample could be recovered by scraping the walls of the vessel which had contained the hydride. The infrared spectra of the reference and sample materials were superimposable. Both spectra showed that the major portion of the sample was the dimer $[Cr(CO)_3C_5H_5]_2$, however a band at 1880 cm^{-1} [28] showed some presence of triply bonded dimer, $[Cr(CO)_2C_5H_5]_2$, in equal amounts for both samples.

In similar experiments, the molybdenum and tungsten hydrides were investigated over the same temperature range. No evolution of H_2 was observed and the thermograms showed only an endothermic enthalpy of melting of 5.9 kcal/mol at 58°C for the molybdenum hydride and +3.93 kcal/mol at 67°C for the tungsten hydride.

Acknowledgements

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