to brown occurred, and after 1 h the mixture was concentrated and extracted with ether. The solvent was removed, and γ-butyrolactone (**15**) was characterized by comparison with an authentic sample.

$(CO)_5Cr[S{=}\overline{CO(CH_2)_2CH_2}]$ (16). Sulfur (0.4 g) was added to a solution of 5 mmol of **7** in 25 mL of ether. The mixture was warmed under reflux for 24 h and filtered. The solvent was evaporated, and the residue was purified by chromatography on silica gel at –25 °C by using dichloromethane/pentane (1/4) as eluent. After unreacted **7** (0.11 g) the thiono lactone complex **16** was obtained as yellow crystals: mp 71 °C; yield 1.23 g (84%); IR (hexane) ν_{CO} 2067 (m), 1949 (vs), 1930 (s) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 0.93 (qui, 2 H, 4-CH_2), 2.02 (t, 2 H, 5-CH_2, $^3J_{H,H}$ = 7 Hz), 3.65 (t, 2 H, OCH_2); ^{13}C NMR (acetone-d_6) 25.2 (4-C), 45.0 (5-C), 82.5 (3-C), 216.3 (CO_{cis}), 223.8 (CO_{trans}), 228.7 ppm (1-C); Anal. Calcd for $C_9H_6CrO_6S$: C, 36.74; H, 2.05; Cr, 17.67; O, 32.63; S, 10.90; mol wt, 294.20. Found: C, 36.54; H, 2.00; Cr, 17.46; O, 32.28; S, 10.60; mol wt, 294.

$S{=}\overline{CO(CH_2)_2CH_2}$ (17). A solution of 1.4 mmol of **16** in 20 mL of di-*n*-butyl ether was warmed to 130 °C for 4 h. The mixture was filtered, the solvent was removed, and the residue was worked up by thick-layer chromatography. Elution with dichloromethane afforded the thiono lactone **17** which was characterized by comparison with an authentic sample; yield 0.08 g (56%).

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Registry No. **5**, 927-74-2; **6**, 5390-04-5; **7**, 54040-15-2; **8**, 58410-46-1; **9**, 98703-36-7; **10**, 108452-73-9; **11**, 1084-74-8; **12**, 108452-74-0; **13a**, 108509-38-2; **13b**, 108452-72-8; **14**, 108452-75-1; **15**, 96-48-0; **16**, 108452-76-2; **17**, 39700-44-2; $Cr(CO)_6$, 13007-92-6; $W(CO)_6$, 14040-11-0; (η^5-$C_5H_4CH_3$)$Mn(CO)_3$, 12108-13-3; H_3C-$C{\equiv}CN(C_2H_5)_2$, 4231-35-0; $H_2C{=}P(CH_3)_3$, 14580-91-7; dimethylamine, 124-40-3.

Energetics of Molybdenum–Azobenzene, Titanium–Azobenzene, Titanium–Iodide, and Titanium–Carbonyl Bonds in Bis(cyclopentadienyl) Complexes

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The energetics of Mo–N_2Ph_2, Ti–N_2Ph_2, Ti–I, and Ti–CO bonds in bis(cyclopentadienyl) complexes have been investigated. Metal–azobenzene and metal–iodine bond enthalpy terms, *E*(M–L), and bond dissociation enthalpies, *D*(M–L), were obtained by using calorimetric results for the standard enthalpies of formation of $M(Cp)_2(PhN{=}NPh)$ (M = Mo, Ti; Cp = η^5-C_5H_5) and $Ti(Cp)_2I_2$. The "low" *E*(M–N) values derived for the azo complexes indicate an interaction between the metal and the azobenzene ligand that is not very strong, in agreement with the proposed bonding model for $Ti(Cp)_2(PhN{=}NPh)$. Analysis of the Ti–I bond energetics enabled a discussion on the validity of transferring metal–halogen bond enthalpy terms. Knudsen effusion measurements on $Ti(Cp)_2(CO)_2$ allowed the re-evaluation of Ti–CO bond enthalpies.

Introduction

The available industrial processes for direct reduction of dinitrogen to ammonia (Haber process) or amines (Cyanamide process) require drastic conditions of temperature and pressure, which cause a high consumption of expensive and nonrenewable fossil fuels.[1,2] This has fostered the search for alternative methods to reduce dinitrogen under milder conditions.[1,2] Since the conversion of N_2 to NH_3 via the enzyme nitrogenase takes place in nature at 1 atm and 298 K and this process seems to be promoted by a transition-metal ion at the enzyme site, it should be possible to reproduce the enzymatic reactions in simple model systems.[1–4] Research efforts on the mechanism of nitrogenase action were paralleled by theoretical[1c] and experimental[1b,5] studies on the preparation, structure, bonding, and reactivity of nitrogen-containing complexes, enabling the development of catalytic systems to reduce dinitrogen to nitrogen hydrides or organic nitrogen compounds.[1b,2–4] This interest contrasts with the present paucity of data on the energetics of transition-metal–nitrogen bonds which are relevant for the N_2 fixation processes.[6–9] Thermochemical studies of transition-metal complexes containing M–N bonds have been restricted to the η^1-coordination mode,[6–9] and only in one case[9] was the ligand dinitrogen; no information exists about the energetics of η^2 coordination of azo compounds to metals despite the fact that a side-on-coordinated diimide (HN=NH) intermediate has been postulated for the activation of coordinated dinitrogen.[4]

The well-known activity of some molybdenum and titanium compounds toward activation of dinitrogen[1–4] and the common use of azobenzene as a model for diimide[10]

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led us to investigate the thermochemistry of $M(Cp)_2(PhN{=}NPh)$ complexes (M = Ti, Mo; Cp = η^5-C_5H_5).

To derive thermochemical data for $Ti(Cp)_2(PhN{=}NPh)$, it was necessary to determine the enthalpy of formation of $Ti(Cp)_2I_2$ from the reaction of $Ti(Cp)_2(CO)_2$ with iodine. Subsequent analysis of the energetics of the Ti–I bond proved to be valuable in discussing the transferability of metal–halogen bond enthalpy terms which is a basic assumption for the calculation of bond enthalpies in bis(cyclopentadienyl) complexes.

This paper also describes vapor pressure measurements on $Ti(Cp)_2(CO)_2$, enabling the re-evaluation of Ti–CO bond enthalpy term and the estimation of bond dissociation enthalpies.

Experimental Section

Compounds. The complexes were synthesized and purified as described in the literature.[11] *trans*-Azobenzene was made by Vogel's procedure and purified by chromatography.[12,13] To prepare *cis*-azobenzene, a saturated solution (500 mL) of the trans isomer in acetic acid was irradiated at 0 °C with a 200-W light bulb for about 16 h. Hartley's method was used to extract the compound, which was then purified by chromatography.[13,14] The reaction solutions for the calorimetric experiments were prepared from Merck p.a. toluene and B.D.H. AnalaR iodine, which were used without further purification. For the titanium–azobenzene experiments, the solvent was also dried and distilled over sodium and kept under argon.

Vapor Pressure Measurements. The enthalpy of sublimation of $Ti(Cp)_2(CO)_2$ was derived from pressure-temperature data obtained with a Knudsen cell.[15] The $Ti(Cp)_2(CO)_2$ vapor effused through a circular hole with an area of 9.09×10^{-3} cm^2, drilled in a 2.09×10^{-3} cm thick copper foil soldered on a bronze lid. The temperature was controlled to ±0.01 K by a Haake ED "Unitherm" thermostat and measured to ±0.01 K with a calibrated mercury thermometer. The mass loss was determined by weighting the cell to $\pm 10^{-5}$ g with a Sartorius 2474 balance. When the same sample was used for ca. three or four runs, some decomposition could be detected at the upper surface of the solid in the form of greenish yellow spots. This problem was avoided by charging the cell with freshly sublimed $Ti(Cp)_2(CO)_2$ before each experiment. No signs of reaction between the complex and the bronze cell were observed.

Calorimetry. The reaction and solution enthalpies were measured in the reaction solution calorimeter previously described.[16] To ensure an inert atmosphere in the calorimetric vessel, pure argon or nitrogen was bubbled through the solvent for 45 min before each run. This procedure was followed in all the systems studied. The glass bulbs containing the samples for the calorimetric runs were sealed under argon or nitrogen.

Reactions. Thermochemical measurements on reactions 1–3

$$Mo(Cp)_2(PhN{=}NPh)(c) + I_2(soln) \rightarrow Mo(Cp)_2I_2(c) + trans\text{-}PhN{=}NPh(soln) \quad (1)$$

$$Ti(Cp)_2(PhN{=}NPh)(c) + I_2(soln) \rightarrow Ti(Cp)_2I_2(soln) + trans\text{-}PhN{=}NPh(soln) \quad (2)$$

$$Ti(Cp)_2(CO)_2(c) + I_2(soln) \rightarrow Ti(Cp)_2I_2(soln) + 2CO(g) \quad (3)$$

were used to derive the standard enthalpies of formation of the complexes. The reactions were assumed to be quantitative, as described in the literature,[11,17] and the products were confirmed by IR analysis. Molar ratios of iodine:complex varied from ~5.0 to 8.0, ~3.0 to 6.0, and ~1.7 to 3.0, respectively, for reactions 1–3. The absence of *cis*-azobenzene as a product of reactions 1 and 2 is discussed in the Results.

Table I. Vapor Pressure of $Ti(Cp)_2(CO)_2$

T/K	t/s	m/g	10^4p/torr
296.88	111 104	0.013 29	2.5710
297.50	81 011	0.010 67	2.8332
298.45	80 682	0.011 87	3.1687
298.85	105 889	0.016 20	3.2970
299.44	81 480	0.013 30	3.5204
300.01	77 318	0.012 85	3.5876
300.09	79 191	0.013 79	3.7589
300.67	80 220	0.014 81	3.9882
301.14	84 496	0.016 83	4.3049

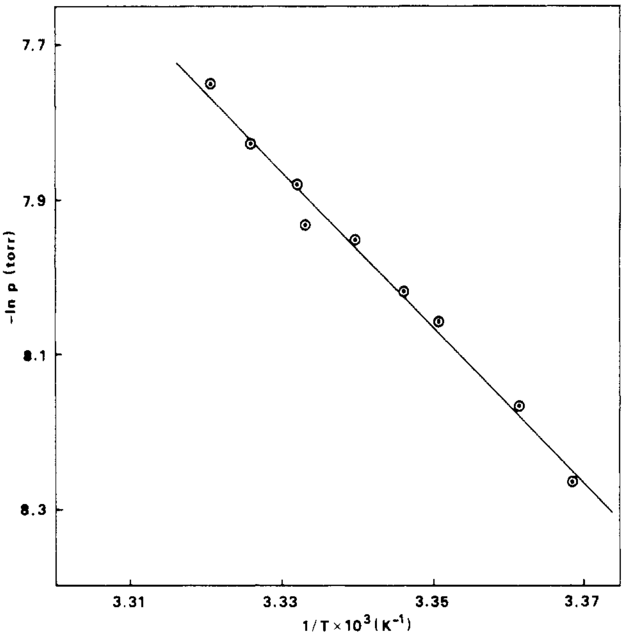

Figure 1. Vapor pressures of crystalline $Ti(Cp)_2(CO)_2$.

Results

Vapor Pressure Measurements. Results from the effusion measurements are shown in Table I and Figure 1.

The vapor pressures (p/torr) were calculated through eq 4 and 5[15,18] where m/g is the weight loss of compound

$$p = \frac{m}{At}\left(\frac{2\pi RT}{M}\right)^{1/2}\left(\frac{3l + 8r}{8r}\right)\left(\frac{1}{1 + 0.48r/2\lambda}\right) \quad (4)$$

$$\lambda = kT/(2)^{1/2}\pi\sigma^2 p \quad (5)$$

from the cell during the time t/s, A/cm^2 is the area of the effusion hole, M/g mol^{-1} is the molecular weight of the gaseous species, T/K is the temperature, r/cm is the hole radius, l/cm is the thickness of the foil where the hole was drilled, λ/cm is the mean free path, k and R are the Boltzmann and gas constants, and σ/cm is the collision diameter of the complex (a value of 710 pm was estimated from projections of the molecular structure of the complex[19a] on the x, y, z planes; van der Waals radii were considered[19b]). A change of ca. 10% in the collision di-

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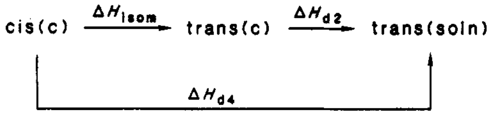
Table II. Auxiliary Thermochemical Data (kJ mol^{-1})

molecule	ΔH_f°	ΔH_s° [a]
$Mo(Cp)_2Cl_2$(c)	−95.8 ± 2.5[b]	(100.4 ± 4.2)[b]
$Mo(Cp)_2I_2$(c)	69.8 ± 7.8[c]	(100.4 ± 4.2)[c]
$Mo(Cp)_2H_2$(c)	210.3 ± 5.7[d]	92.5 ± 2.1[b]
$Ti(Cp)_2Cl_2$(c)	−383.2 ± 7.5[b]	118.8 ± 2.1[b]
TiI_4(g)	−277.3 ± 8.4[e]	
trans-PhN=NPh(c)	320.5 ± 1.7[f]	93.6 ± 2.8[h]
	311.3 ± 3.4[g]	
cis-PhN=NPh(c)	362.8 ± 2.5[f]	
	367.2 ± 1.6[g]	92.92 ± 0.12[g]
Ph–NH–NH–Ph(c)	220.6 ± 4.0[f]	
CO(g)	−110.53 ± 0.17[i]	
I_2(g)	62.421 ± 0.080[i]	
Ti(g)	470.7 ± 4.2[j]	
Cl(g)	121.302 ± 0.008[i]	
I(g)	106.762 ± 0.040[i]	

[a] Standard enthalpy of sublimation or vaporization. Values in parentheses are estimates. [b] Reference 21. [c] Reference 16. [d] Reference 22. [e] Reference 23. [f] Reference 24. [g] Reference 25. [h] Reference 20. [i] Reference 26. [j] Reference 7.

Scheme I



ameter affects the vapor pressure by about 0.1%.[15] Values from Table I were adjusted to Clausius–Clapeyron equation by the least-squares method, yielding the linear relation 6 from which $\Delta H_S^\circ[Ti(Cp)_2(CO)_2]$ = 84.2 ± 3.5 kJ

$$\ln(p/\text{torr}) = (25.850 \pm 1.388) - (10123.74 \pm 415.31)/T \quad (6)$$

mol^{-1} was derived. The uncertainty intervals presented include Student's factor for 95% confidence level. The precision of the vapor pressures given by eq 6 is poor, but this does not affect the value obtained for ΔH_S°. No self-cooling effects were observed.

Thermochemistry. Auxiliary values needed for calculating the thermochemical results were quoted from the literature[7,20-26] and are collected in Table II, which also includes two independent determinations of the enthalpy of formation of *cis*- and *trans*-azobenzene.[24,25] These two pairs of enthalpies of formation, both obtained from combustion experiments, yield enthalpies of cis(c) → trans(c) isomerization, ΔH_{isom} = −42.3 ± 3.0[24] or −55.9 ± 3.8[25] kJ mol^{-1}. While it is difficult to select one of these results from the original literature, we made a simple set of experiments which enabled the calculation of ΔH_{isom}. Scheme I summarizes these experiments. ΔH_{d4} was obtained by breaking ampules with ~0.04–0.07 g of *cis*-PhN=NPh in 125 mL of toluene containing iodine and $Ti(Cp)_2I_2$ (molar ratios of I_2/*cis*-azobenzene ≈ 2 and $Ti(Cp)_2I_2$/*cis*-azobenzene ≈ 1), and ΔH_{d2} was measured by breaking ampules of *trans*-PhN=NPh in a similar solution (the role of I_2 and $Ti(Cp)_2I_2$ in the cis(c) → trans(soln) isomerization is discussed below). These values (see below) give ΔH_{isom} = −49.8 ± 0.6 kJ mol^{-1}, suggesting that a redetermination of the enthalpies of formation of the two isomers is desirable. In this study we arbitrarily chose the values from ref 24. A different selection leads only to minor adjustments in the calculated bond enthalpies.

Table III. Thermochemical Results (kJ mol^{-1})

complex	$-\Delta H_r$	ΔH_{d1}	ΔH_{d2}
$Mo(Cp)_2$(PhN=NPh)	168.8 ± 3.1	0[a]	20.51 ± 0.35
$Ti(Cp)_2$(PhN=NPh)	157.9 ± 10.0	5.8 ± 2.0	18.95 ± 0.59
$Ti(Cp)_2(CO)_2$	84.25 ± 0.53	5.8 ± 2.0	0[b]

[a] Reference 16. [b] The molar fraction of CO in toluene (at 1 atm of partial pressure and 298 K) is 8.11 × 10^{-4} and ΔH_d = 1.87 kJ mol^{-1} (Wilhelm, E.; Battino, R. *Chem. Rev.* 1973, *73*, 1). Therefore ΔH_{d2} was taken as zero for our experimental conditions.

The thermochemical results are summarized in Table III. All reaction and solution enthalpies presented are mean values of five independent experiments at 298 K. The uncertainties are twice the standard deviation of the mean in each case. ΔH_r stands for the enthalpy of reaction 1, 2, or 3; ΔH_{d1} refers to the enthalpy of solution of the diiodide complex in toluene containing iodine (residues of the titanium diiodide complex were observed when measuring ΔH_{d1}, but the resulting errors must be within the uncertainty interval); ΔH_{d2} is the enthalpy of solution of the ligand in solutions containing iodine and a stoichiometric amount of the diiodide complex. The enthalpy of solution of iodine in toluene was taken as ΔH_{d3} = 15.92 ± 0.16 kJ mol^{-1}.[16]

Several low values of ΔH_r were measured for reaction 2. These were attributed to noticeable premature decomposition of the complex [$Ti(Cp)_2$(PhN=NPh) is very sensitive to oxygen and moisture; it was found that those runs for which the inicial black color of the complex was slightly brownish led to low ΔH_r]. The result in Table III is the average of the five highest results obtained in a total of 13 experiments by using four different batches of $Ti(Cp)_2$(PhN=NPh). The above difficulties led us to overestimate the uncertainty interval from ±3.6 to ±10 kJ mol^{-1}.

To check that *cis*-azobenzene was not present (or at least its concentration was negligible) in reaction 2 several tests were made. First its enthalpy of solution in argon-saturated toluene was determined as 12.4 ± 1.4 kJ mol^{-1} (average of three measurements); differences between the "cooling constants"[27] for the calibration and solution processes were about 14%, thus suggesting the occurrence of slow cis → trans isomerization. When this experiment was repeated in toluene containing amounts of iodine, similar to those used for measuring ΔH_r, a fast exothermic process was observed (ΔH = −29.6 ± 1.4 kJ mol^{-1}, average of three measurements) and an even faster exothermic reaction occurred (ΔH_{d4} = −30.8 ± 0.2 kJ mol^{-1}, average of two measurements; see Scheme I) when the solvent contained both iodine and $Ti(Cp)_2I_2$. In each case the agreement between "cooling constants" indicated that the exothermic process was completed within the time of reaction 2. The obtained endothermic value for the enthalpy of solution of *trans*-azobenzene in toluene containing iodine and $Ti(Cp)_2I_2$ (ΔH_{d2} in Table III) shows that the pattern observed is specific of the cis isomer. All these results seem to support the fact that no significant amount

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Table IV. Enthalpies of Formation, $\Delta H_f°(c)$ and $\Delta H_f°(g)$ (kJ mol^{-1})

complex	$\Delta H_f°(c)$	$\Delta H_S°$ [a]	$\Delta H_f°(g)$
$Mo(Cp)_2(PhN{=}NPh)$	563.7 ± 8.6	(70 ± 15)	633.7 ± 17.3
$Ti(Cp)_2(PhN{=}NPh)$	338.8 ± 16.7	(90 ± 15)	428.8 ± 22.4
$Ti(Cp)_2(N_3)_2$	436.4 ± 8.4	(70 ± 10)	506.4 ± 13.1
$Ti(Cp)_2(NC_8H_6)_2$	181.9 ± 12.1	(109 ± 10)	290.9 ± 15.7
$Ti(Cp)_2(CO)_2$	−295.3 ± 12.9[b]	84.2 ± 3.5	−211.1 ± 13.4
$Ti(Cp)_2I_2$	−148.4 ± 13.1	(120 ± 10)	−28.4 ± 16.5

[a] Values in parentheses are estimates. [b] Ribeiro da Silva, M. D. Tese de Doutoramento, Faculdade de Ciências do Porto, Porto, 1985.

Table V. Bond Enthalpy Terms, Bond Dissociation Enthalpies, and Reorganization Energies (kJ mol^{-1})[a]

complex	$E(M–L)$[b]	D/ $\bar{D}(M–L)$[c]	ER_1[d]	ER_3[d]	ER_L[e]
$Mo(Cp)_2(PhN{=}NPh)$	49 ± 12[f]	192 ± 23	−62[g]	−82	−198
$Ti(Cp)_2(PhN{=}NPh)$	144 ± 12[f]	381 ± 24	−5[h]	−11	−198
$Ti(Cp)_2(N_3)_2$[i]	329 ± 10	385 ± 22	−8	−11	56[j]
$Ti(Cp)_2(NC_8H_6)_2$[i]	348 ± 10		−22	−11	
$Ti(Cp)_2(CO)_2$	174 ± 8	172 ± 8	0[k]	−11	−2[l]
$Ti(Cp)_2I_2$	298 ± 9	298 ± 9	−11[m]	−11	0

[a] Uncertainty intervals do not include errors from the theoretical calculations. [b] Values not affected by $(ER_3 - ER_1)/2$ but including ER_L. See text. [c] Values not affected by $ER_3/2$ (see text). Data for the azobenzene complexes are bond dissociation enthalpies (cis isomer as product), and for the other molecules are *mean* bond dissociation enthalpies. [d] Values obtained from the curves in ref 30. [e] Values obtained from MNDO calculations unless indicated otherwise. [f] Bond enthalpy term for *one* M–N bond. [g] Estimated Cp–Mo–Cp angle of 133°. [h] Cp–Ti–Cp angle of 133°.[35] [i] Reference 29. [j] Estimated by the Laidler scheme and extended Hückel calculations (see ref 29). [k] Cp–Ti–Cp angle of 138.6°.[19a] [l] MINDO/3 result. Extended Hückel calculations give −13 kJ mol^{-1} (see ref 34a). [m] Estimated Cp–Ti–Cp angle of 131°.

of *cis*-azobenzene was present in reaction 2. A similar assumption was accepted for the molybdenum system without further evidence apart from the agreement of "cooling constants" in reaction 1 and the fact that catalysis of cis → trans isomerization by several molecules including I_2 and $Mo(Cp)_2H_2$ is a well-known process.[28]

The standard enthalpies of formation of the crystalline and gaseous complexes are collected in Table IV, together with the enthalpies of sublimation at 298 K. The table also includes values for two similar complexes containing titanium–nitrogen bonds which have been studied earlier.[29] Data for $Ti(Cp)_2(NC_8H_6)_2$ differ from those originally reported due to a correction to account for acid dilution.

Discussion

Bond enthalpy terms, $E(M–L)$, bond dissociation enthalpies, $D(M–L)$, and mean bond dissociation enthalpies, $\bar{D}(M–L)$, in the complexes studied are presented in Table V. These values were calculated from eq 7 and 8.[30,31]

$$E(M\text{–}L) = E(M\text{–}Cl) + \frac{n}{2}\Delta H_f°(L^*,g) - \Delta H_f°(Cl,g) - \{\Delta H_f°[M(Cp)_2L_n,g] - \Delta H_f°[M(Cp)_2Cl_2,g]\}/2 + (ER_3 - ER_1)/2 \quad (7)$$

$$\bar{D}(M\text{–}L) = E(M\text{–}Cl) + \frac{n}{2}\Delta H_f°(L,g) - \Delta H_f°(Cl,g) - \{\Delta H_f°[M(Cp)_2L_n,g] - \Delta H_f°[M(Cp)_2Cl_2,g]\}/2 + ER_3/2 \quad (8)$$

Here an asterisk indicates a nonreorganized fragment, and ER_1 and ER_3 represent the reorganization energies of the moieties $M(Cp)_2$ from the complex $M(Cp)_2L_n$ and from the "reference" molecule $M(Cp)_2Cl_2$, respectively. $E(M–Cl)$ are the bond enthalpy terms in the dichloride complexes and were taken as 303.8 ± 7.1 (M = Mo) and 430.5 ± 1.3 kJ mol^{-1} (M = Ti). These are actually the bond enthalpy terms from the metal chlorides $MoCl_6$ and $TiCl_4$ which are therefore transferred to the complexes. The implications and tests of this assumption have been discussed in early papers.[30-32] Some results of the present work provide additional evidence of its reliability for M = Ti (see below).

The E values shown in Table V for the azobenzene complexes were derived by making $n = 1$ in eq 7. Since metal–nitrogen *mean* bond dissociation enthalpies, $\bar{D}(M–N)$, are clearly meaningless parameters in those two cases, values of $D(M–N_2Ph_2) = 2\bar{D}(M–N)$ are presented in Table V. $\bar{D}(M–N)$ values were obtained through eq 8 with $n = 1$.

The reorganization energies ER_1 and ER_3 were estimated by using results of extended Hückel calculations. The energy of fragments $M(Cp)_2$ is mainly a function of Cp–M–Cp angles, and curves relating these two parameters are available.[30] The obtained values are collected in Table V, and it is noted that the corrections $(ER_3 - ER_1)/2$ in eq 7 are negligible. The same happens for $ER_3/2$ in eq 8 when the titanium complexes are considered. The Hückel results indicate, however, that the reorganization of $Mo(Cp)_2$ fragment from $Mo(Cp)_2Cl_2$ is very exothermic, implying a considerable decrease ($ER_3 \approx -82$ kJ mol^{-1}; see Table V) of $D(Mo–N_2Ph_2)$ reported in Table V. It must be stressed that this value and all the remaining bond enthalpy data in Table V do not include the reorganization energies ER_1 and ER_3 since we prefer to use these corrections in a semiquantitative way.

The enthalpies of formation of nonreorganized ligands, $\Delta H_f°(L^*,g)$, are also necessary to calculate $E(M–L)$. The usual procedure when L is a radical is to assume that the molecular structures of the fragment are identical in $M(Cp)_2L_n$ and LH. The enthalpy of formation of L^* is then obtained by taking the Laidler term $E(L–H)$ or by using plots of $E(L–H)$ vs. L–H bond lengths and making $\Delta H_f°(L^*,g) = E(L–H) + \Delta H_f°(LH,g) - \Delta H_f°(H,g)$.[30,31,33] The method has been used, for example, in the case of the complexes $Ti(Cp)_2(N_3)_2$ and $Ti(Cp)_2(NC_8H_6)_2$, the details being given elsewhere.[29]

The use of Laidler terms to estimate $\Delta H_f°(L^*)$ or the reorganization energies of L, $ER_L = D(L–H) - E(L–H)$, has at least the merit of providing a set of internally consistent $E(M–L)$ data, which can be used to predict enthalpies of formation of organometallic molecules and also to estimate partial bond dissociation enthalpies.[30,34] However $E(M–L)$ values derived in this way cannot be regarded as physically meaningful quantities. This point has been raised before (see, e.g., ref 30), but it is important to have it in mind when comparing the bond enthalpy terms in Table V.

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While E(Ti–N) for N_3 and NC_8H_6 were obtained through the method described, ER_L for N_2Ph_2 and CO were estimated through theoretical calculations (see below), thus yielding E(M–L) values that may not be comparable with those relying on the Laidler scheme. The problem could of course be avoided by applying the theoretical methods to every ligand. This work is in progress, but the prediction capabilities of the empirical scheme have been the main reason for using the bond enthalpy term concept.

The structure of azobenzene in the molybdenum complex was assumed to be similar to the one observed in the titanium analogue.[35] ER_L (Table V) was then obtained by computing the energies of the free and the complexed ligand through MINDO/3 and MNDO calculations.[36] E(M–N_2Ph_2) and D(M–N_2Ph_2) (M = Mo, Ti) in Table V refer to the cis isomer. When the cis → trans isomerization is considered, those bond enthalpy values decrease by ca. 42 kJ mol^{-1} which is the accepted result for ΔH_{isom} in the gas phase.

Curves relating CO energy with C–O bond length, obtained from MINDO/3 calculations,[37] enabled the estimate of the reorganization energy shown in Table V. This negligible correction contrasts with the large ER_L observed for azobenzene.

The M–N bond enthalpy terms in Table V were calculated on the basis of *two* metal–nitrogen bonds. It is noted that E(Ti–N) for the azobenzene complex is considerably lower than the corresponding values for the monodentate ligands. It is very unlikely that this trend is caused by the different methods used to estimate $\Delta H_f°(L^*,g)$ (see discussion above). Azobenzene is coordinated to the metal in a distorted cis form, reflecting a balance between the energetically more favorable trans conformation and the steric repulsion involving the phenyl and the cyclopentadienyl rings.[11b,35] Although the Ti–N bond lengths in the azobenzene complex (196.8 pm)[35] are smaller than in $Ti(Cp)_2(N_3)_2$ (203 pm)[38] and in $Ti(Cp)_2(NC_4H_4)_2$ (209 pm)[39] that geometry does not seem to favor both the σ- and π-bonding between Ti and N_2Ph_2. Therefore, even if some double-bond character can eventually be postulated for the Ti–N_2Ph_2 bonds,[11b] this interaction is weak, as suggested by the "low" E(Ti–N) value obtained. Interestingly, ab initio molecular orbital calculations on the model system $TiCl_2(CH_3N{=}NCH_3)$ yielded $2E(\text{Ti–N}) \approx 280$ kJ mol^{-1} compared with $2E(\text{Ti–N}) \approx 288$ kJ mol^{-1} from Table V.[11b]

The same conclusions may also hold for the molybdenum azobenzene complex. The difference $E(\text{Ti–N}_{az}) - E(\text{Mo–N}_{az}) \approx 95$ kJ mol^{-1} is in the range observed for a variety of ligands in $M(Cp)_2L_2$ complexes (M = Ti, Mo);[30,32,34b] i.e., E(Ti–L) – E(Mo–L) are constant within 10 or 20 kJ mol^{-1}.

Despite the numerous thermochemical studies involving transition-metal carbonyls, no data have yet been reported for the energetics of Ti–CO bond. The values shown in Table V are in the range observed for homoleptic carbonyl complexes.[7,40] $\bar{D}$(Ti–CO) is considerably lower than $\bar{D}$(Ti–CH_3) = 298 kJ mol in $Ti(Cp)_2(CH_3)_2$[34b] and $2\bar{D}$(Ti–CO) is also lower than D(Ti–N_2Ph_2) as shown in Table V. Interestingly, reaction 9, which is of synthetic interest,[41] is

$$Ti(Cp)_2(CO)_2(soln) + \textit{trans}\text{-}PhN{=}NPh(soln) \rightarrow Ti(Cp)_2(PhN{=}NPh)(soln) + 2CO(g) \quad (9)$$

spontaneous at room temperature. When solution enthalpies are neglected and the enthalpies of formation are taken from Tables II and IV, $\Delta H(9) = 92.5$ kJ mol^{-1} is obtained. This considerable endothermic effect must be offset by the large positive entropic contribution due to the formation of 2 mol of gaseous CO ($S° = 197.6$ J mol^{-1} K^{-1}).[42]

A method described elsewhere allows us to estimate the first and the second Ti–CO bond dissociation enthalpies in the complex as ca. 170 and 174 kJ mol^{-1}, respectively.[34a,43]

Interesting tests of the calculation method used to derive E(Ti–L), namely, the assumption that E(Ti–Cl) in the reference molecule $Ti(Cp)_2Cl_2$ is similar to E(Ti–Cl) in $TiCl_4$, are provided by E(Ti–N) in the azide and in the indolate complexes and by E(Ti–I) in the diiodide complex. As noted before,[30,31a] the titanium–nitrogen bond enthalpy terms in those molecules compare with the value of ca. 325 kJ mol^{-1} observed in $Ti(NR_2)_4$ (R = CH_3, C_2H_5).[44] In the case of $Ti(Cp)_2I_2$, E(Ti–I) = 298 kJ mol^{-1} (Table V) is in excellent agreement with E(Ti–I) = 294 kJ mol^{-1} in TiI_4, obtained from the auxiliary data in Table II.

The transferability of titanium–ligand bond enthalpy terms in $Ti(Cp)_2L_2$ complexes has been discussed recently,[45] the main conclusion being that E(Ti–L) are relatively constant in $Ti(Cp)_2L_2$ and $Ti(Cp)_2LL'$ ($L \neq L'$). Additional evidence for this point is provided by a recent study of equilibrium 10 in deuteriated benzene.[46] The measured

$$Ti(Cp)_2I_2(soln) + Ti(Cp)_2Cl_2(soln) \rightleftarrows 2Ti(Cp)_2(I)Cl(soln) \quad (10)$$

equilibrium constant ($K = 4$) gives $\Delta G \approx -3.4$ kJ mol^{-1}. With the assumption that $\Delta S \approx 0$ and that the solvation enthalpies cancel, $\Delta H(10)$ is close to zero, indicating constant E(Ti–I) and E(Ti–Cl).[47] From the obtained enthalpy of formation of the diiodide complex (Table IV), $\Delta H_f°[Ti(Cp)_2(I)Cl,c] \approx -267.5$ kJ mol^{-1} is derived.

The results of the present study enable us to analyze the thermodynamics of some interesting reactions (auxiliary data in Table II). An example is provided by the hydro-

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[43] $D_1 - D_2 = 2ER_1' - ER_1$, ER_1' being the reorganization energy of the fragment $Ti(Cp)_2(CO)$; ER_1 is defined in this paper. $D_1 \approx D_2$ results from the negligible values of ER_1' and ER_1. Details are given in ref 34a, where provisional values for E(Ti–CO) and $\bar{D}$(Ti–CO) were presented. The differences between these and the ones reported here are due, e.g., to an estimated enthalpy of sublimation of the complex and to the fact that the reorganization energy of CO was taken as -13 kJ mol^{-1} (see note *l* of Table V).

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[45] See ref 34b for a detailed discussion.

[46] Bruce, M. R. M.; Tyler, D. R. *Organometallics* **1985**, *4*, 528.

[47] The balance of the reorganization energies of fragments $Ti(Cp)_2$ from the three complexes is close to zero. See ref 34b.

genation of azobenzene by dihydrogen or by metal hydrides.[10] Comparison between the enthalpies of reactions 11 and 12, $\Delta H(11) = -99.9 \pm 4.3$ kJ mol^{-1} and $\Delta H(12) =$

$$trans\text{-PhN}{=}\text{NPh(c)} + \text{H}_2\text{(g)} \rightarrow \text{PhNH}{-}\text{NHPh(c)} \quad (11)$$

$$\text{Mo(Cp)}_2\text{H}_2\text{(c)} + 2\,trans\text{-PhN}{=}\text{NPh(c)} \rightarrow \text{Mo(Cp)}_2(\text{N}_2\text{Ph}_2)\text{(c)} + \text{PhNH}{-}\text{NHPh(c)} \quad (12)$$

-67.0 ± 11.6 kJ mol^{-1}, indicates that the process is enthalpically less favorable for the metallic system. A crude estimate of the respective entropy changes (i.e., $\Delta S(11) = -S^\circ(\text{H}_2\text{,g}) = -130.57$ J mol^{-1} K^{-1}[42] and $\Delta S(12) \approx 0$) yields similar ΔG for both reactions. Since reaction 11 requires drastic pressure and temperature conditions[10b] while reaction 12 occurs in solution at ambient pressure and ~65 °C,[11a] this shows the importance of the metallic system in lowering the H_2 activation barrier.

Conclusions

The transferability of titanium–nitrogen bond enthalpy terms seems to be a reasonable assumption, provided that the ligands involved are not too different in their bonding modes. E(Ti–N) is in the range of 320–350 kJ mol^{-1} for several σ-bonded nitrogen ligands but is considerably lower for azobenzene. Analysis of the bond enthalpy terms and bond lengths in the titanium–azobenzene and the titanium–azide complexes stresses the fact that stronger bonds do not necessarily imply shorter bonds, particularly if different types of bonding are involved.

E(Ti–I) in $\text{Ti(Cp)}_2\text{I}_2$ and in TiI_4 are in good agreement, thus supporting the assumption of identical E(Ti–Cl) in $\text{Ti(Cp)}_2\text{Cl}_2$ and TiCl_4. Titanium-carbonyl bond enthalpy is substantially lower than titanium-methyl bond enthalpy in $\text{Ti(Cp)}_2\text{L}_2$ complexes.

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Registry No. $\text{Ti(Cp)}_2\text{(PhN{=}NPh)}$, 51159-65-0; $\text{Mo (Cp)}_2\text{(PhN{=}NPh)}$, 53417-82-6; $\text{Ti(Cp)}_2\text{I}_2$, 12152-92-0; $\text{Ti(Cp)}_2\text{(CO)}_2$, 12129-51-0; $\text{Mo(Cp)}_2\text{I}_2$, 12184-29-1; $\text{TiCl}_2\ (\text{CH}_3\text{N{=}NCH}_3)$, 88667-79-2; $\text{Ti(Cp)}_2(\text{N}_3)_2$, 1298-37-9; $\text{Ti(Cp)}_2(\text{NC}_8\text{H}_6)_2$, 84934-81-6.

Cobaltacycles in Three Oxidation States: Redox Properties and Reaction Routes

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The electrochemical reduction and oxidation of the Co(III) metallacycle $\text{Cp(PPh}_3\text{)CoC}_4\text{Ph}_4$ (1) and its analogues have been studied. Oxidation is reversible ($E^\circ = +0.35$ V vs. SCE) in dichloromethane to give a persistent cation radical which was characterized by ESR spectroscopy. A second oxidation ($E^\circ = +1.17$ V) gives a more reactive dication which ultimately decomposes by disruption of the metallacycle. Reduction goes by fast one-electron transfer to a 19-electron complex which rapidly loses phosphine to give a transient 17-electron coordinatively unsaturated anion. In the presence of phosphines PR_3 which are more basic than PPh_3, efficient substitution of PPh_3 by PR_3 accompanies the reduction, in a partially electrocatalytic process. In the absence of added ligands, the 17-electron anion undergoes protonation and subsequent reduction via a ECEC mechanism to give a π-butadiene complex. The electrochemical results are interpreted in terms of previously published molecular orbital calculations on this class of molecules.

Introduction

Since metallacycles exhibit an extensive chemistry and are postulated or demonstrated intermediates in a number of stoichiometric and catalytic reactions, they have been under intense investigation.[1] This class of compounds has been shown to have interesting redox properties, but the literature in this area is still sparse.[2-11] Because the chemistry of 18-electron and 16-electron metallacycles is so rich, we thought it would be of interest to prepare a series of metallacyclic 17- or 19-electron radical ions for the purpose of comparing their physical and chemical properties with those of their even-electron counterparts.

This paper reports our first set of results, on the oxidation and reduction of cobaltacyclopentadienes of the type 1–3.

This class of compounds has received considerable attention,[12-14] due in part to the fact that thermal dissocia-

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