Notes

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Entropy of Binding Molecular Hydrogen and Nitrogen in the Complexes $(P(C_6H_{11})_3)_2M(CO)_3$ (M = Cr, Mo, W)

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The initial goal of this work was to determine the thermodynamic functions for binding hydrogen and nitrogen to the complex $(P(C_6H_{11})_3)_2Cr(CO)_3$[1] as shown in eq 1 and 2. The chromium compound resembles the tungsten complex $(P(C_6H_{11})_3)_2W(CO)_3$ discovered by Kubas and co-workers.[2] It reversibly binds molecular hydrogen and dinitrogen. Due to the generally weaker Cr–L versus W–L bond strength, at room temperature the Cr complex requires pressures of 300 psi (H_2) or 1500 psi (N_2) for near-quantitative binding. The higher pressures needed for quantitative binding of nitrogen suggested a weaker Cr–N_2 versus Cr–H_2 bond enthalpy. This contrasts with the majority of complexes where dinitrogen will readily replace molecular hydrogen.[2] In addition, solution calorimetric studies[3] indicated that the enthalpy of reaction 3 was endothermic by 3.5 kcal/mol. We began this work expecting to find a reversal in relative M–L bond enthalpies in going from Cr to W in group VI.

$$(P(C_6H_{11})_3)_2Cr(CO)_3 + H_2 \rightleftharpoons (P(C_6H_{11})_3)_2Cr(CO)_3(H_2) \quad (1)$$

$$(P(C_6H_{11})_3)_2Cr(CO)_3 + N_2 \rightleftharpoons (P(C_6H_{11})_3)_2Cr(CO)_3(N_2) \quad (2)$$

$$(P(C_6H_{11})_3)_2W(CO)_3(N_2) + H_2 \rightarrow (P(C_6H_{11})_3)_2W(CO)_3(H_2) + N_2 \quad (3)$$

Thermodynamic data for the chromium system could not be obtained under normal calorimetric conditions since high pressures are required for quantitative binding. Variable-temperature infrared spectra for binding of H_2 and N_2 in tetrahydrofuran solution[4] are shown in Figure 1. These data can be used to calculate equilibrium constants by using the assumption that the extinction coefficients of the major carbonyl bands are equal.[5] Equilibrium data for binding of N_2 and H_2 to the Cr and Mo complexes are collected in Table I. Plots of ln K_{eq} versus $1/T$ for reactions 1 and 2 are shown in Figure 2. Thermodynamic data calculated from these data are collected in Table III.

Table I. Equilibrium Data for $(P(C_6H_{11})_3)_2M(CO)_3 + L \rightleftharpoons (P(C_6H_{11})_3)_2M(CO)_3(L)$ ($L = H_2, N_2$)

T, °C	$K_{eq}(N_2)$, atm^{-1}	T, °C	$K_{eq}(H_2)$, atm^{-1}
	M = Cr		
45	0.0545	45	0.278
35	0.0863	35	0.431
25	0.139	25	0.555
18	0.213	18	0.865
10	0.369		
	M = Mo		
35	0.331	42	0.235
28	0.508	34	0.315
21	0.783	25	0.4523
		17	0.531
		10	0.8463

[a] For details see the Experimental Section and ref 4 and 5.

Table II. Equilibrium Data[a] for $(P(C_6H_{11})_3)_2W(CO)_3(N_2) + H_2 \rightleftharpoons (C_6H_{11})_3)_2W(CO)_3(H_2) + N_2$

T, °C	35	30	25	20	15
K_{eq}	0.854	0.729	0.648	0.574	0.513

[a] For details see the Experimental Section and ref 4 and 5.

Table III. Calculated Enthalpies and Entropies of Binding for $(P(C_6H_{11})_3)_2M(CO)_3 + L \rightleftharpoons (P(C_6H_{11})_3)_2M(CO)_3(L)$ (M = Cr, Mo, W; $L = H_2, N_2$)

M	L	ΔH,[a] kcal/mol	$\Delta\Delta H$,[b] kcal/mol	ΔS, cal/(mol deg)	$\Delta\Delta S$,[c] cal/(mol deg)
Cr	N_2	−9.3 ± 0.2		−35.4 ± 2.3	
Cr	H_2	−7.3 ± 0.1	−2.0 ± 0.3	−25.6 ± 1.7	−9.8 ± 2.6
Mo	N_2	−9.0 ± 0.6		−32.1 ± 3.2	
Mo	H_2	−6.5 ± 0.2	−2.5 ± 0.8	−23.8 ± 2.1	−8.3 ± 3.9
W	N_2	−13.5 ± 1.0			
W	H_2	−10.0 ± 1.0	−4.4 ± 0.4[d] −3.5 ± 2.0[d]		−13.8 ± 3.5

[a] Enthalpies of reaction and refer to reaction of the complexes in THF solution with the ligands in the gas state. [b] The term $\Delta\Delta H$ refers to the difference in enthalpy of binding between nitrogen and hydrogen ligands. [c] The term $\Delta\Delta S$ refers to the difference in entropy of binding between nitrogen and hydrogen ligands. [d] This value was measured by solution calorimetry as described in the text.

It is clear from these data that the preferred binding of hydrogen to the chromium and molybdenum complexes is due to entropic rather than enthalpic factors. As was found to be the case for W, Cr and Mo show more favorable metal–ligand bond enthalpies for dinitrogen than for molecular hydrogen. It was of interest to see if the lower *entropy* of binding molecular hydrogen carried over to the tungsten system as well. At room temperature and pressure, binding of hydrogen and nitrogen to tungsten is nearly quantitative, and it was not practical to measure separate equilibrium constants for the tungsten complex. Under pressures of N_2/H_2 mixtures, it was straightforward to obtain the equilibrium data for eq 3 collected in Table II. A plot of ln K_{eq} versus $1/T$ is shown in Figure 3 for this reaction. The enthalpy of reaction, $\Delta H = +4.4 \pm 0.4$ kcal/mol, is in good agreement with the value determined earlier[3] by solution calorimetry, $\Delta H = +3.5 \pm 2.0$ kcal/mol.[4] The entropy of binding, $\Delta S = +13.8 \pm 3.5$ cal/mol, again favors binding of hydrogen over nitrogen and tends to counterbalance the enthalpy term.

Combined data for the enthalpies and entropies of binding are listed in Table III. The overall enthalpies of binding are in the order Mo ≅ Cr < W and account for the observed stronger binding at 1 atm of pressure of the tungsten complex. For each metal,

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(3) Gonzalez, A. A.; Kai, Z.; Nolan, S. P.; de la Vega, R. L.; Mukerjee, S. L.; Hoff, C. D.; Kubas, G. J. *Organometallics* **1988**, *7*, 2429.

(4) All thermodynamic data listed refer to reactions of the complexes in THF solution and hydrogen and nitrogen as gases. The enthalpies of reaction with the complexes in toluene solution are similar. Due to the increased solubility of the complexes in THF, this solvent was preferred for obtaining quantitative data.

(5) Due to the very air-sensitive nature of the coordinatively unsaturated complexes, it was not possible to measure accurate extinction coefficients for the infrared bands. Equilibrium constants are "spectroscopic" in that we have assumed the extinction coefficients are equal for the major carbonyl bands. This is certainly the case within a multiplication factor of 2. Any errors in this assumption may result in changes in the absolute values of the equilibrium constants but will have little influence on the calculated thermodynamic data. The enthalpy of reaction, which depends only on the slope of a line of ln K_{eq} versus $1/T$, will not be influenced at all by any errors introduced by this assumption. The entropy of reaction will be in error by $R \ln [\epsilon_{Cr-H_2}]/[\epsilon_{Cr-}]$. On the basis of the conservative estimate that the extinction coefficients could differ by as much as a factor of 2, the maximum error in this assumption is $R \ln 2 = 1.4$ cal/(mol deg). Error estimates for entropies of reaction have been increased to include this term.

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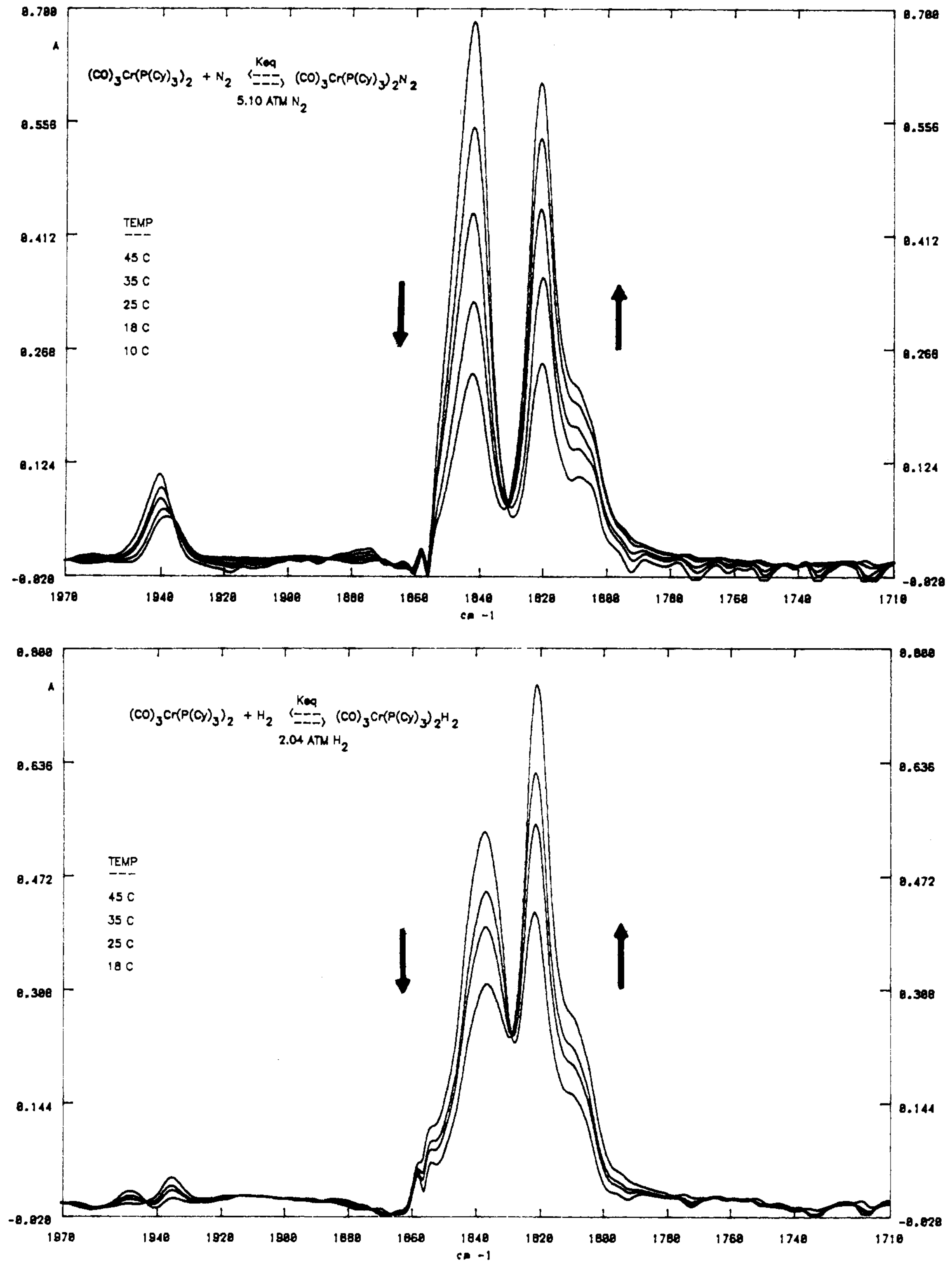

Figure 1. Variable-temperature spectra for the equilibrium binding of nitrogen and hydrogen to $(C_6H_{11})_3)_2Cr(CO)_3$: (a, top) nitrogen; (b, bottom) hydrogen.

dinitrogen is preferred with regard to the enthalpy of binding but disfavored with regard to the entropy of binding. The *differences* in enthalpies of binding between nitrogen and hydrogen, $\Delta\Delta H$ appear to increase in going from Cr (2.0 kcal/mol) to Mo (2.5 kcal/mol) to W (4.4 kcal/mol). The *differences* in entropies of binding are spanned by the value 11 ± 4 cal/(mol deg).

The lower entropy of binding of molecular hydrogen compared to nitrogen will influence the stability of the complexes as a function of temperature. For displacement reactions such as that shown in eq 3, $K_{eq} = 1$ when $T = \Delta H/\Delta S$. Above this temperature, the H_2 complex will be favored; below this temperature, the N_2 complex will be favored. It is clear from examination of the data in Tables I and II that the "crossover" temperature occurs at temperatures near −70, +28, and +46 °C for Cr, Mo, and W, respectively.

The origin of the reduced entropy of binding of hydrogen warrants further discussion. At first it seemed possible that since H_2 is a side-bound ligand and may show relatively free rotation,[2] the reduced entropy could be due to this additional degree of freedom. In this view, complexed H_2 would behave as a "one-dimensional" gas. It seems likely that the real explanation is simpler. Compared to nitrogen, hydrogen has less translational and rotational entropy to lose upon binding to a metal in the first place.

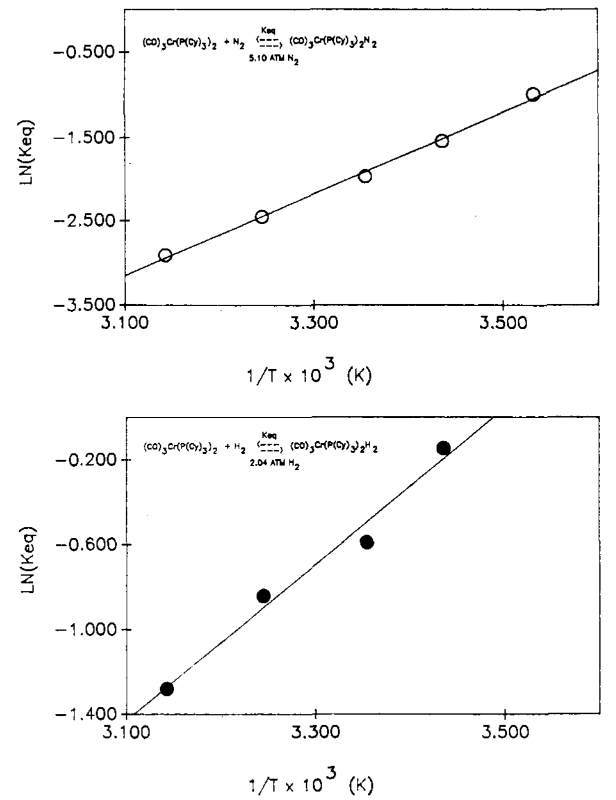

Figure 2. Plot of ln K_{eq} versus $1/T$ (K) for $(P(C_6H_{11})_3)_2Cr(CO)_3 + L \rightarrow (P(C_6H_{11})_3)_2Cr(CO)_3(L)$: (a, top) L = N_2; (b, bottom) L = H_2.

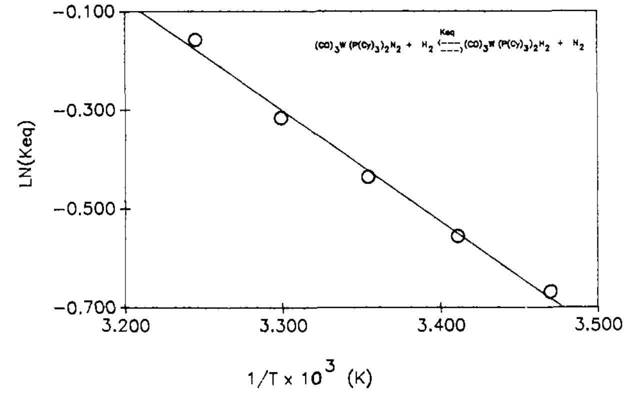

Figure 3. Plot of ln K_{eq} versus $1/T$ (K) for $(P(C_6H_{11})_3)_2W(CO)_3(N_2) + H_2 \rightarrow (C_6H_{11})_3)_2W(CO)_3(H_2) + N_2$.

The entropy of ligand binding for a gaseous ligand to a complex in solution reflects the difference in total entropies of the species involved:

$$ML_n(soln) + H_2(g) \rightarrow ML_n(H_2)(soln) \quad (4)$$

Binding a gaseous ligand to a metal increases the total entropy of the metal complex $ML_n(H_2)$ relative to ML_n but does so by a relatively minor amount compared to the entropy lost by the ligand.[6] On that basis the total entropy of exchange for general reaction 5 should depend primarily on the differences in absolute

$$ML_n(N_2)(soln) + H_2(g) \rightarrow ML_n(H_2)(soln) + N_2(g) \quad (5)$$

entropies for N_2(g) and H_2(g). The "third-law" entropies of the two gases can be calculated by using standard formulas of statistical thermodynamics.[7] At room temperature, the entropy is due exclusively to the translational and rotational components. Due to its lower mass and moment of inertia, the absolute entropy of H_2 (31.2 cal/(mol deg)) is 14.6 cal/(mol deg) lower than the absolute entropy of N_2 (45.8 cal/(mol deg)). If eq 5 is examined again, it is clear that if the total entropies of the complexes in solution exactly canceled, the predicted entropy change would be 14.6 cal/(mol deg). This is reasonably close to the value we obtain, 11 ± 4 cal/(mol deg) for the three complexes. The residue may be due to several factors,[6,7] including differences in vibrational partition functions for the complexes.

It is clear that the large entropy of ligand exchange is due to the fact that H_2 has the smallest absolute entropy of any diatomic gas. In the absence of unusual vibrational frequency changes upon complexation, this should be general for molecular hydrogen and nitrogen complexes. The net result is that, at higher temperatures, molecular hydrogen will be more competitive relative to dinitrogen. This could have important implications for catalysis. Additional work on the thermodynamics and kinetics of binding nitrogen, hydrogen, and nitrogen hydrides is in progress for these and related complexes.

Experimental Section

The complexes $(P(C_6H_{11})_3)_2M(CO)_3$ were prepared by published procedures for M = Cr,[1] Mo,[2] and W.[2] All manipulations were carried out in a glovebox or by using standard Schlenk techniques. The solvents THF and toluene were freshly distilled from sodium benzophenone ketyl under an argon atmosphere. Vibrational spectra were run on a Perkin-Elmer 1850 FTIR instrument. High-pressure spectra were run in a special CaF_2 cell obtained from Harrick Scientific, Ossining, NY. The cell was attached via Swagelok fittings to a 40-mL high-pressure bomb in such a way that, by rotation of the entire apparatus, fresh solution could be taken from the bomb into the infrared cell. A calibrated platinum resistance thermometer obtained from Omega Engineering, Stamford, CT, was inserted via a high-pressure fitting directly into the bulk of the solution and allowed direct reading of temperatures. The entire apparatus was placed inside a "water-bag" constructed from an old glovebox glove. A constant-temperature alcohol/water bath was circulated around the entire apparatus through holes cut in the glove and secured by hose clamps to metal tubing. The entire apparatus was placed in an optical bench/glovebox that will be described in detail elsewhere.[9] Measurements were made at a given temperature until no further change occurred in the spectra on three successive runs. Spectroscopic equilibrium constants[5] were measured at at least three different total pressures, and reported values represent an average of these determinations.

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New and General Route to the Synthesis of Oxopolymetalates via Peroxometalates in Aqueous Medium: Synthesis and Crystal and Molecular Structure of $(PPN)_2[W_6O_{19}]$ (PPN = Bis(triphenylphosphine)nitrogen(1+) Cation)

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Effective methods of synthesis of oxopolymetalates have been found to vary with the specific identity of the metal. The preparation[2] of $Mo_6O_{19}^{2-}$ and $M_6O_{19}^{8-}$ (M = Nb, Ta)[3] is achieved in a conventional manner by the treatment of alkaline MO_4^{2-} so-

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