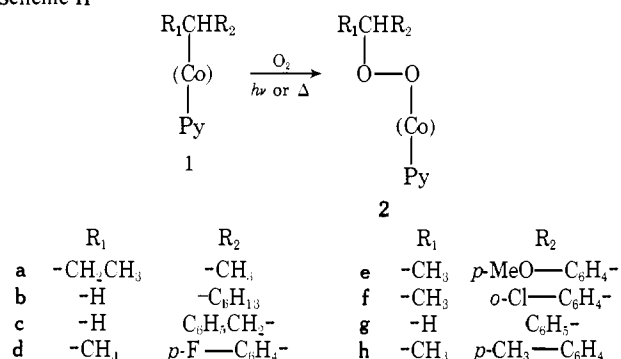


**Table III.** Reduction Products of Alkyldioxycobaloximes **2** by NaBD<sub>4</sub> or LiAlD<sub>4</sub><sup>a</sup>

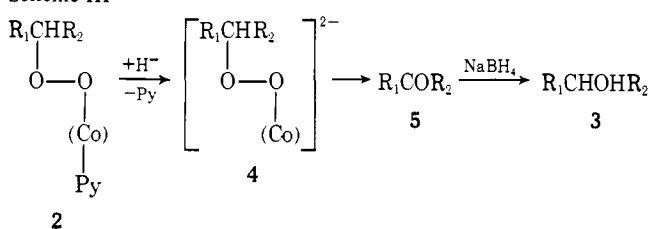
Com- pounds	Reducing agent	Yield, %	% products <sup>b</sup>	
			R <sub>1</sub> CDR <sub>2</sub>   OH	R <sub>1</sub> CHR <sub>2</sub>   OH
<b>2b</b>	NaBD <sub>4</sub>	70	80	20
<b>2c</b>	NaBD <sub>4</sub>	70	70	30
<b>2c</b>	LiAlD <sub>4</sub>	80	25	75
<b>2h</b>	NaBD <sub>4</sub>	90	65	35

<sup>a</sup> The reductions were carried out in MeOH (NaBD<sub>4</sub>) or THF (LiAlD<sub>4</sub>) using a fivefold excess of the deuterated hydride. <sup>b</sup> The percentages of deuterated and undeuterated alcohols were determined by NMR and mass spectroscopy.

Scheme II



Scheme III



The reduction of **2d** by excess NaBH<sub>4</sub> was studied as a function of time. The results (Table II) suggest that *p*-fluoracetophenone is the primary reduction product, which is subsequently reduced to *p*-fluorophenyl-1-ethanol.

The results shown in Table III are further proof that alcohols are not the main primary reduction products. Compounds **2b**, **2c**, and **2h** were reduced with excess NaBD<sub>4</sub> and the corresponding alcohols were shown by their NMR and mass spectra to be deuterated to an extent of 65 to 80%. Product **2c** was also reduced by excess LiAlD<sub>4</sub> in THF: NMR and mass spectroscopy reveal that the reaction product contains 30% deuterium in the α-position.

Scheme III gives a possible mechanism for the reduction of alkyldioxycobaloximes by NaBH<sub>4</sub>: the first step is a two-electron reduction of the alkyldioxycobaloxime to a Co<sup>I</sup> complex **4** which decomposes into the corresponding carbonyl compound **5**. This mechanism is consistent with previous studies on the reduction of cobalt(III) complexes.<sup>5</sup>

The formation of some nondeuterated alcohols by reduction of peroxycobaloximes with NaBD<sub>4</sub> or LiAlD<sub>4</sub> suggests that an alternative pathway leading directly to the alcohols is also operative, possibly via the alkylhydroperoxide.<sup>6</sup>

From these results it is clear that the sequence of reactions (Scheme I) used to establish the stereochemistry of oxygen insertion<sup>1,2</sup> is not appropriate and can lead to erroneous conclusions due to the lack of information concerning the reactions

involved. For the same reasons, the method described by Shinozaki et al.<sup>3</sup> seems to be invalid. We are presently investigating more direct methods to establish the stereochemical course of the insertion reaction.

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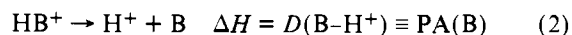
Centre d'Orsay, 91120-Orsay, France

Received March 9, 1976

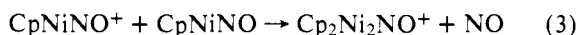
## Quantitative Metal-Ligand Bond Dissociation Energies in the Gas Phase by Ion Cyclotron Resonance Spectroscopy

Sir:

Any description of the energetic changes associated with reactions catalyzed by transition metal ions suffers from a paucity of quantitative metal-ligand bond dissociation energies. These data are directly accessible in experiments utilizing the techniques of ion cyclotron resonance spectroscopy (ICR).<sup>1</sup> We wish to describe the experimental methodology for these studies and its application to the determination of the binding energies (eq 1) of 30 *n*-donor ligands to the cyclopentadienyl nickel cation, (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ni<sup>+</sup>, and to compare the scale of base strengths thus determined with results previously obtained for proton binding energies (eq 2).<sup>2,3</sup>



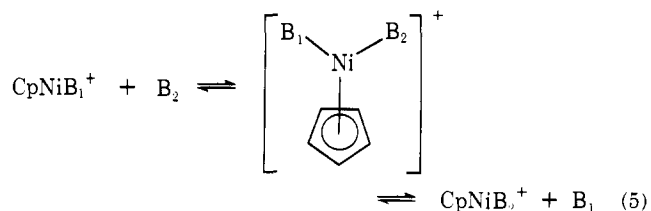
In cyclopentadienyl nickel nitrosyl alone, only the parent ion, CpNiNO<sup>+</sup>, is observed at low electron energies (8.5–10.5 eV), and reacts with the precursor in accordance with process 3 ( $k = (7.5 \pm 1.5) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ).



In the presence of excess base, B, fast ligand displacement reactions, such as generalized in eq 4,







are observed (e.g.,  $k = (1.4 \pm 0.3) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for B = NH<sub>3</sub>). With a mixture of bases, attainment of equilibrium in transfer of CpNi<sup>+</sup> between B<sub>1</sub> and B<sub>2</sub> (eq 5) is ob-

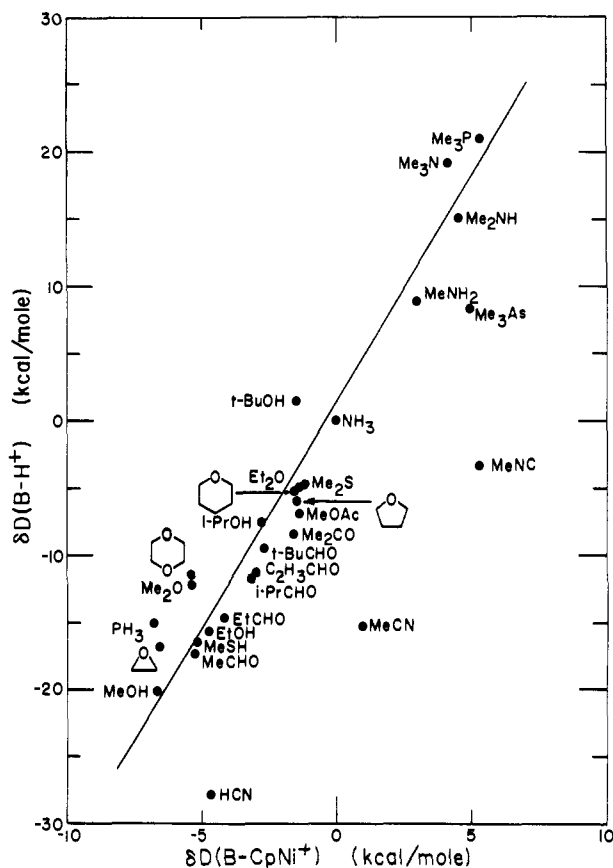


served to be rapid in comparison to any further reactions of the complexes with the neutrals present. The rapid exchange of monodentate *n*-donor ligands is promoted by the coordination vacancy of the 16-electron complex, CpNiB<sup>+</sup>, which facilitates binding of a second pair donor to form the 18-electron intermediate indicated in eq 5. The displacement of a monodentate ligand by a bidentate or polydentate ligand (e.g., butadiene, benzene, and pyridine) results in the formation of an 18-(or

**Table I.** Relative Gas Phase Ligand Binding Energies,  $\delta D(\text{B}-\text{CpNi}^+)$ , and Proton Affinities,  $\delta D(\text{B}-\text{H}^+)^a$ 

Base	$\delta D(\text{B}-\text{H}^+)^b$	$\delta D(\text{B}-\text{CpNi}^+)$	Base	$\delta D(\text{B}-\text{H}^+)^b$	$\delta D(\text{B}-\text{CpNi}^+)$
PH <sub>3</sub>	-15.0	-6.8		-5.2	-1.6
MeOH	-20.1	-6.7	Me <sub>2</sub> CO	-8.4	-1.6
	-16.8 <sup>c</sup>	-6.6		-5.9	-1.5
NO	-75 <sup>d</sup>	-6.4	<i>t</i> -BuOH	1.5 <sup>g</sup>	-1.5
Me <sub>2</sub> O	-12.2	-5.4	MeOAc	-6.9	-1.4
	-11.4	-5.4	Et <sub>2</sub> O	-4.9	-1.4
MeCHO	-17.3	-5.3	Me <sub>2</sub> S	-4.7	-1.2
MeSH	-16.4	-5.2	NH <sub>3</sub>	0.0 <sup>h</sup>	0.0 <sup>i</sup>
EtOH	-15.6	-4.8	MeCN	-15.3	0.9
HCN	-27.8	-4.7	MeNH <sub>2</sub>	8.9	2.9
EtCHO	-14.3	-4.2	Me <sub>3</sub> N	19.2	4.1
<i>i</i> -PrCHO	-11.7	-3.2	Me <sub>2</sub> NH	15.1	4.5
C <sub>2</sub> H <sub>3</sub> CHO	-11.3 <sup>e</sup>	-3.0	Me <sub>3</sub> As	8.3 <sup>j</sup>	4.9
<i>i</i> -PrOH	-7.5 <sup>f</sup>	-2.8	MeNC	-3.3 <sup>k</sup>	5.3
<i>t</i> -BuCHO	-9.5	-2.7	Me <sub>3</sub> P	21.0 <sup>l</sup>	5.3

<sup>a</sup> All values in kcal/mol. <sup>b</sup> Unless otherwise noted, all  $\delta D(\text{B}-\text{H}^+)$  are from ref 2. <sup>c</sup> R. H. Staley, R. R. Corderman, M. S. Foster, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 1260 (1974). <sup>d</sup> A. E. Roche, M. M. Sutton, D. K. Bohme, and H. I. Schiff, *J. Chem. Phys.*, **55**, 5480 (1971). <sup>e</sup> B. S. Freiser and J. L. Beauchamp, unpublished results. <sup>f</sup> R. T. McIver, Jr., unpublished results. <sup>g</sup> J. L. Beauchamp and M. C. Caserio, *J. Am. Chem. Soc.*, **94**, 2638 (1972). <sup>h</sup>  $D(\text{NH}_3-\text{H}^+) = 202 \pm 3$  kcal/mol, ref 2. <sup>i</sup>  $D(\text{NH}_3-\text{CpNi}^+) = 52.4 \pm 5$  kcal/mol is obtained from the literature value of  $D(\text{NO}-\text{CpNi}^+) = 46 \pm 5$  kcal/mol<sup>5</sup> and the measured value of  $\delta D(\text{NO}-\text{CpNi}^+) = -6.4$  kcal/mol. <sup>j</sup> R. V. Hodges and J. L. Beauchamp, *Inorg. Chem.*, **14**, 2887 (1975). <sup>k</sup> J. F. Vogt and J. L. Beauchamp, unpublished results. <sup>l</sup> R. H. Staley and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 6252 (1974).



**Figure 1.** Comparison of two scales of gas phase basicity; binding energies of molecules to H<sup>+</sup>,  $\delta D(\text{B}-\text{H}^+)$ , and to CpNi<sup>+</sup>,  $\delta D(\text{B}-\text{CpNi}^+)$ .

more) electron complex which reacts very slowly, if at all, in further ligand exchange reactions.

The relative free energies of binding B<sub>1</sub> and B<sub>2</sub> can be determined from equilibria observed for process 5 with an accuracy of  $\pm 0.2$  kcal/mol for  $\Delta G \leq 3$  kcal/mol. These data are converted to enthalpies by assuming  $\Delta S$  is zero except for small corrections due to changes in symmetry numbers.<sup>4</sup> Data for

30 *n*-donor bases relative to NH<sub>3</sub> are summarized in Table I.<sup>5</sup> Included for comparison are proton affinities for the same series of bases, also relative to NH<sub>3</sub>. Absolute values of  $D(\text{NH}_3-\text{CpNi}^+) = 52.4 \pm 5$  kcal/mol<sup>5</sup> and  $D(\text{NH}_3-\text{H}^+) = 202 \pm 3$  kcal/mol<sup>2</sup> can be assigned using available literature data. Weakly basic ligands which do not displace NO from CpNiNO<sup>+</sup> and thus have  $\delta D(\text{B}-\text{CpNi}^+) < -7.0$  kcal/mol include CO, O<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>S, H<sub>2</sub>CO, EtF, and C<sub>3</sub>H<sub>6</sub>.

Several trends in  $\delta D(\text{B}-\text{CpNi}^+)$  are apparent from the data of Table I. First,  $\delta D(\text{B}-\text{CpNi}^+)$  generally increases with increasing substitution of alkyl groups for H on the basic site (Me<sub>3</sub>P > PH<sub>3</sub>, Me<sub>2</sub>O > MeOH > H<sub>2</sub>O, Me<sub>2</sub>S > MeSH > H<sub>2</sub>S). Interestingly, the  $\delta D(\text{B}-\text{CpNi}^+)$  ordering of the alkyl amine series is irregular, with Me<sub>2</sub>NH > Me<sub>3</sub>N > MeNH<sub>2</sub> > NH<sub>3</sub>, similar to the behavior the amines exhibit towards Li<sup>+</sup>.<sup>6</sup>  $\delta D(\text{B}-\text{CpNi}^+)$  increases with increasing methyl substitution on the carbon  $\alpha$  to the basic site (Me<sub>3</sub>COH > Me<sub>2</sub>CHOH > EtOH > MeOH, Et<sub>2</sub>O > Me<sub>2</sub>O, MeCN > HCN).  $\delta D(\text{B}-\text{CpNi}^+)$  increases with increasing alkyl substitution on carbon remote to the basic site (Me<sub>2</sub>CCHO > Me<sub>2</sub>CHCHO > MeCH<sub>2</sub>CHO > CH<sub>3</sub>CHO). Finally,  $\delta D(\text{B}-\text{CpNi}^+)$  is greater for second-row *n*-donor ligands than for first-row species (Me<sub>3</sub>P > Me<sub>3</sub>N, Me<sub>2</sub>S > Me<sub>2</sub>O).<sup>7</sup>

The metal-ligand bond dissociation energies are most striking in their comparison to proton affinities. Excluding the compounds NO, HCN, MeCN, MeNC, and Me<sub>3</sub>As, a surprisingly good linear correlation (correlation coefficient 0.964) is observed (Figure 1, eq 6).

$$\delta D(\text{B}-\text{NiCp}^+) = 0.296\delta D(\text{B}-\text{H}^+) - 0.453 \quad (6)$$

The correlation may be of predictive value, e.g., from  $\delta D(\text{H}_2\text{O}-\text{H}^+) = -32.0$  kcal/mol,<sup>2</sup>  $\delta D(\text{H}_2\text{O}-\text{NiCp}^+) = -9.9 \pm 2$  kcal/mol is obtained.

The notable exceptions to the observed correlation of metal-ligand bond dissociation energies with proton affinities are compounds which are expected to have substantial  $\pi$ -bonding ability.<sup>8-10</sup> These include NO, HCN, MeCN, MeNC, and Me<sub>3</sub>As, which all exhibit a greater preference for bonding to CpNi<sup>+</sup> than predicted by eq 6. The low symmetries of the complexes and intricacies of bonding associated with the cyclopentadienyl group make it impossible to deduce simply the

relative orbital energies and hence their occupancy. Consequently, the relative importance of ligand-metal vs. metal-ligand electron donation remains obscure and will likely be resolved only with the help of ab initio calculations.<sup>11</sup> The fact that phosphorus compounds, with empty 3d orbitals ( $\pi$  acceptors), fit the correlation reasonably well, suggests that metal-ligand donation is unimportant. This may, however, be the fortuitous result of a stronger  $\pi$  bond canceling the effects of a weaker  $\sigma$  bond to CpNi<sup>+</sup>.<sup>8,9</sup> Additional studies of complexes which bind and readily exchange more than one ligand may help to further resolve such questions.

There are myriad possibilities for further studies of the ion chemistry, photochemistry,<sup>12-15</sup> and ligand binding energetics of transition metal complexes.<sup>16,17</sup> Of particular interest are ICR photodissociation spectra<sup>12-14</sup> of CpNiB<sup>+</sup>, which currently are being explored to provide information relating electronic excitation energies to  $D(B-CpNi^+)$  in these complexes.

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## Synthesis of Di- and Trinuclear Methyl Osmium Complexes via *cis*-Hydridomethyltetracarbonylosmium

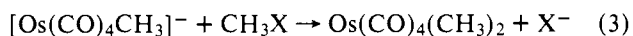
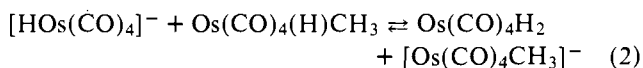
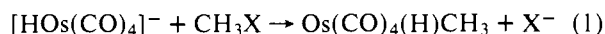
Sir:

Although they are frequently postulated as intermediates in homogeneous catalysis, transition metal complexes with both alkyl and hydrogen ligands are almost never stable.<sup>1-4</sup> Current interest in hydrocarbon activation<sup>5</sup> and our interest in elimination processes involving *cis* organic ligands<sup>6</sup> suggested the development of a synthesis of *cis*-Os(CO)<sub>4</sub>(H)CH<sub>3</sub> (**1**) and the investigation of its chemistry. Reported as a minor by-

product of several reactions,<sup>7,8</sup> **1** proved stable enough to be observed spectroscopically. In this regard it contrasts with the analogous iron complexes Fe(CO)<sub>4</sub>(H)R which are too unstable to be detected.<sup>9</sup>

We first attempted to synthesize **1** via the preparation and protonation of [Os(CO)<sub>4</sub>CH<sub>3</sub>]<sup>-</sup>. However, attempts to make [Os(CO)<sub>4</sub>CH<sub>3</sub>]<sup>-</sup> by methods similar to those used for the analogous iron alkyl anions<sup>9a</sup> are thwarted by its high nucleophilicity. Even a weak methylating agent such as methyl chloride converts Na<sub>2</sub>Os(CO)<sub>4</sub><sup>8,10-12</sup> speedily to Os(CO)<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub>. These results agree with the generalization<sup>13</sup> that anions of third-row transition elements are much more nucleophilic than their first-row counterparts.<sup>14,15</sup>

Methylation of the previously known<sup>7</sup> hydride anion HOs(CO)<sub>4</sub><sup>-</sup> proves somewhat more satisfactory. However, its reaction with such reagents as methyl tosylate gives a mixture of Os(CO)<sub>4</sub>H<sub>2</sub>, Os(CO)<sub>4</sub>(H)CH<sub>3</sub>, and Os(CO)<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub> in the approximate ratio 1:2:1. This mixture presumably arises from competition between the desired alkylation of [HOs(CO)<sub>4</sub>]<sup>-</sup> (reaction 1) and deprotonation by [HOs(CO)<sub>4</sub>]<sup>-</sup> of Os(CO)<sub>4</sub>(H)CH<sub>3</sub> (reaction 2).



Although Os(CO)<sub>4</sub>(H)CH<sub>3</sub> is probably less acidic than Os(CO)<sub>4</sub>H<sub>2</sub>, the high nucleophilicity of [Os(CO)<sub>4</sub>CH<sub>3</sub>]<sup>-</sup> and the consequent speed of reaction 3 make dimethylation an important side reaction.

The best way to overcome this side reaction is the use of methyl fluorosulfonate to increase the speed of reaction 1. In a typical preparation 94 mg of Na<sub>2</sub>Os(CO)<sub>4</sub> is suspended in tetraglyme under nitrogen and protonated with 1 equiv of trifluoroacetic acid, and 2 equiv of methyl fluorosulfonate are then added. Under high vacuum at room temperature a mixture of product and methyl trifluoroacetate distills into a -196° cold trap. Redistillation through a -63° bath traps 60 mg (70% yield) of Os(CO)<sub>4</sub>(H)CH<sub>3</sub>. NMR<sup>16</sup> shows the material to be 97% pure, with 3% Os(CO)<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub>.

In the absence of air and light, Os(CO)<sub>4</sub>(H)CH<sub>3</sub> decomposes slowly (several days) at room temperature. One-half equivalent of methane, but no carbon monoxide, is evolved. Preparative TLC allows the separation and identification of the initial organometallic product, a colorless liquid which yellows immediately upon exposure to light, as HOs(CO)<sub>4</sub>Os(CO)<sub>4</sub>CH<sub>3</sub> (**2**).<sup>17</sup> This characterization was confirmed by the conversion of **2** upon treatment with CCl<sub>4</sub> to the expected derivative ClOs(CO)<sub>4</sub>Os(CO)<sub>4</sub>CH<sub>3</sub> (**3**), a stable white solid.<sup>18</sup>

A product such as **2** was expected from the thermolysis of **1** by analogy to the H<sub>2</sub>Os<sub>2</sub>(CO)<sub>8</sub> previously observed<sup>6</sup> as the primary decomposition product of Os(CO)<sub>4</sub>H<sub>2</sub>. The absence of observable coupling between the methyl and hydride protons in the NMR of **2** and the resemblance of its infrared spectrum to those of H<sub>2</sub>Os<sub>2</sub>(CO)<sub>8</sub><sup>19</sup> and X<sub>2</sub>Os<sub>2</sub>(CO)<sub>8</sub><sup>19,20</sup> suggest the structure shown below and its conformers. Compound **2** thus resembles the recently reported clusters HOs<sub>3</sub>(CO)<sub>10</sub>R, where R contains a coordinating double bond or organic carbonyl.<sup>21,22</sup> However, **2** is stable without such additional binding of its organic ligand.

