

H<sub>2</sub>O; found, Cl<sup>-</sup> < NH<sub>3</sub> < H<sub>2</sub>O).<sup>26</sup>

(2) If the average axial and equatorial parameters (that is, the average bonding strengths) are not very different, as for X = H<sub>2</sub>O and NCS<sup>-</sup>, even small state splittings appear sufficient to favor either <sup>4</sup>B<sub>2</sub> or <sup>4</sup>E reaction. It should be noticed, however, that especially when small separations are involved, the spectral differences may not properly reflect the differences between the states from which chemistry proceeds, because of presumably different distortions from octahedral geometry during vibrational equilibration.

(3) The combined ratios of axial quantum yields establish the following propensity to photolabilization: F<sup>-</sup> < NCS<sup>-</sup> < CN<sup>-</sup> < H<sub>2</sub>O, suggesting a stronger Cr-NCS<sup>-</sup> bonding than inferred spectroscopically. As was originally pointed out,<sup>8</sup> some of the  $\sigma$  and  $\pi$  values may bear uncertainties, which could become crucial at the present level of detail. Especially for thiocyanato complexes, the obtaining of correct parameters may be hampered by the lack of splitting (or asymmetry) in the LF bands,<sup>21,23,33,34,62</sup> due to the close spectrochemical positions of NCS<sup>-</sup> and amines. In addition, a charge-transfer band partially obscures one of the LF maxima<sup>33</sup> (see Figure 1). Separation of  $\sigma$  from  $\pi$  contributions in eq 1 and in analogous relations by help of Gaussian analysis of the spectra may be sometimes too approximate. Values of  $\sigma_{\text{NCS}^-}$  and  $\pi_{\text{NCS}^-}$  somewhat higher than in ref 10, but such that  $10Dq_{\text{NCS}^-}$  remains unaffected, would justify  $\Phi_{\text{CN}^-} > \Phi_{\text{NCS}^-}$ . Also, the latter parameter has been recently reported<sup>63</sup> to be 370 cm<sup>-1</sup> larger than

that in the literature.<sup>10</sup> Our general preparative experience with thiocyanate<sup>17</sup> and literature aquation and anation data<sup>23,33,64,65</sup> indicate that NCS<sup>-</sup> is a very good nucleophile (comparable to F<sup>-</sup>) toward chromium(III). Photochemistry may thus be helpful in assessing more correct parameter values.

(4) The constancy of product ratios for the prompt and slow photochemistry suggests a unique reactive precursor. In a conventional description, this can be accounted for by back intersystem crossing as the main pathway of doublet deactivation. An equivalent, but perhaps more adequate, interpretation is that in terms of a single potential surface, with intercommunicating minima of quartet and doublet character, resulting from spin-orbit coupling under reduced symmetry.<sup>43,66</sup> The transition state for reaction should then either correspond to the quartet minimum or at least retain some memory of its antibonding distribution.

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**Registry No.** *trans*-[Cr(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)(CN)]<sup>2+</sup>, 74523-68-5; *trans*-[Cr(NH<sub>3</sub>)<sub>4</sub>(CN)(NCS)]<sup>+</sup>, 108561-55-3; *trans*-[Cr(NH<sub>3</sub>)<sub>4</sub>(CN)F]<sup>+</sup>, 108561-56-4; [Cr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>3-</sup>, 15054-01-0.

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Contribution from the Department of Chemistry and the Scarborough Campus, University of Toronto, Toronto, Ontario, Canada M5S 1A1

## Dihydrogen vs. Dihydride. Correlations between Electrochemical or UV PES Data and Force Constants for Carbonyl or Dinitrogen Ligands in Octahedral, d<sup>6</sup> Complexes and Their Use in Explaining the Behavior of the Dihydrogen Ligand

Robert H. Morris,\* Kelly A. Earl, Rudy L. Luck, Natalie J. Lazarowych, and Andrea Sella

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For d<sup>6</sup>, octahedral carbonyl complexes there is a linear correlation between  $E_{1/2}(\text{ox})$  values for reversible d<sup>5</sup> ↔ d<sup>6</sup> couples at room temperature and carbonyl force constants  $k(\text{CO})$  for values reported in the literature and measured here:  $E_{1/2}(\text{ox}) = 0.567(k(\text{CO}) + \Delta k_L) - 8.02$ . The correlation coefficient,  $r$ , is 0.97, and  $\sigma = 0.17$  V when the force constant is corrected for the effect of the ligand trans to the CO by the ligand parameter  $\Delta k_L$ . The first ionization energies, IP, of such complexes as determined by UV PES show a poorer correlation:  $\text{IP} = 0.873(k(\text{CO}) + \Delta k_L) - 6.34$ ,  $r = 0.92$ ,  $\sigma = 0.28$  eV. The correlation  $E_{1/2}(\text{ox}) = 0.688 \text{ IP} - 4.22$ ,  $r = 0.94$ , is obtained from data for 12 complexes where both  $E_{1/2}(\text{ox})$  and IP values have been measured; this equation is close enough to the one derived from combining the first two equations to verify the internal consistency of the correlations. Octahedral, d<sup>6</sup> dinitrogen complexes also show a fair correlation:  $E_{1/2}(\text{cor}) = 0.434(k(\text{N}_2) + 2\Delta k_L) - 7.74$ , where  $E_{1/2}(\text{cor}) = E_{1/2}(\text{ox})$  for 4d metals and  $E_{1/2}(\text{cor}) = E_{1/2}(\text{ox}) - 0.26$  for 5d metals,  $\sigma = 0.18$  V, and  $r = 0.91$ . Here the trans ligand appears to have twice the effect on  $k(\text{N}_2)$  as on  $k(\text{CO})$  and equivalent complexes of 5d metals have lower  $k(\text{N}_2)$  values than those of 4d metals with the same  $E_{1/2}(\text{ox})$  value. The  $\Delta k_L$  parameters can be related to both Timney's and Bursten's parameters. The correlations can be used to estimate the  $E_{1/2}(\text{ox})$  (or IP) values of matrix-isolated species like Cr(N<sub>2</sub>)(CO)<sub>5</sub>. They can also be used to postulate that stable molecular hydrogen complexes, M( $\eta^2$ -H<sub>2</sub>)L<sub>5</sub>, where all L groups are not usually the same in the complex, are obtained for complexes that have  $\eta^2$ -H<sub>2</sub> trans to CO and that form derivatives M(N<sub>2</sub>)L<sub>5</sub> or M(CO)L<sub>5</sub> with  $E_{1/2}(\text{ox}) \approx 0.0$  V or for those that have  $\eta^2$ -H<sub>2</sub> trans to a good  $\sigma$ -donor like H<sup>-</sup> and that have  $E_{1/2}(\text{ox}) \approx 1.0$  V for dinitrogen or carbonyl derivatives. This translates into a range,  $\nu(\text{N}_2) = 2060\text{--}2150$  cm<sup>-1</sup>, for the dinitrogen derivatives where the corresponding H<sub>2</sub> complex will be stable to homolytic cleavage or irreversible H<sub>2</sub> loss at 25 °C.

A well-known phenomenon of transition-metal carbonyl coordination chemistry is that as complexes become more reducing because of a change of ligand<sup>†</sup> or a reduction in the oxidation state of the metal, then the C–O stretching frequencies of carbonyl ligands in the complexes decrease. The same trend is observed for other ligands like thiocarbonyl, dinitrogen, isocyanides, and nitrosyl, whose bonding involves  $d\pi(\text{metal}) \rightarrow p\pi^*(\text{ligand})$  back-donation. Thus, infrared and Raman spectroscopy are useful tools for indirectly probing the energetics of metal complexes. We present here useful equations that are determined for octahedral carbonyl or dinitrogen complexes with the metal in the d<sup>6</sup> oxidation

state that roughly express these trends. The equations are best linear fits to an extensive set of force constant, electrochemical, and photoelectron data. They are applied here to understand the bonding and reactivity of related molecular hydrogen complexes, which are of current interest.<sup>1–14</sup>

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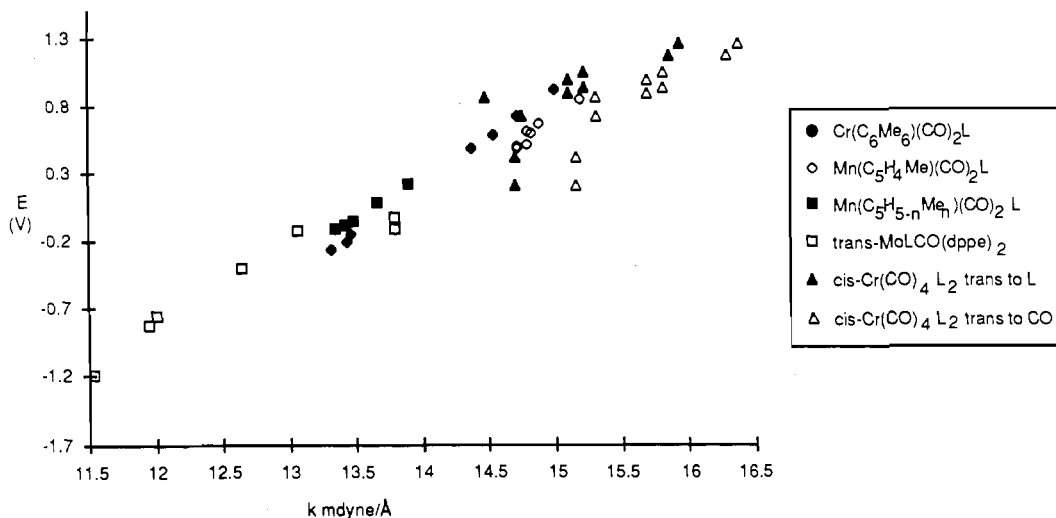


Figure 1. Plot of  $E_{1/2}(\text{ox})$  vs.  $k(\text{CO})$  for series of carbonyl complexes. Data are from ref 16–18 and 23.

Both valence photoelectron spectroscopy and electrochemistry give information about the energy of the highest occupied molecular orbital of a transition-metal complex. For the low-valent complexes under consideration here, the HOMO is usually a metal-localized d orbital. The degeneracy of the  $t_{2g}$  ( $d_{xy}$ ) set of orbitals is often lifted because of the different abilities of carbonyl and other ligands in the same molecule to accept  $d\pi$  electrons.<sup>15</sup> Correlations have been noted between infrared data and half-wave potentials,  $E_{1/2}(\text{ox})$ , for the metal  $d^5 \leftrightarrow d^6$  reversible couple in several studies of series of related complexes. Connelly and Kitchen demonstrated that a plot of  $k(\text{CO})$  vs.  $E_{1/2}(\text{ox})$  was linear for the series of complexes  $\text{Mn}(\eta^5\text{-C}_5\text{H}_5\text{-}n\text{Me}_n)(\text{CO})_2\text{L}$  ( $E = 0.71(k(\text{CO})) - 9.79$ ) and  $\text{Cr}(\eta^6\text{-C}_6\text{Me}_6)(\text{CO})_2\text{L}$  ( $E = 0.64(k(\text{CO})) - 8.74$ ), where L was a variety of phosphorus-donor ligands.<sup>16</sup> Hershberger and Kochi studied the related series  $\text{Mn}(\eta^6\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2\text{L}$  and found that although phosphine ligands gave a rough correlation similar to the one above ( $E = 0.88(k(\text{CO})) - 12.46$  with correlation coefficient  $r = 0.86$ ), the data for N- and C-donor ligands did not fall near this line.<sup>17</sup> Researchers at the Unit of Nitrogen Fixation have reported linear correlations between stretching frequencies and  $E_{1/2}(\text{ox})$  for series of complexes where the trans ligand, L, is varied:  $\text{trans-Mo}(\text{CO})\text{L}(\text{dppe})_2$  ( $E = 0.0080(\nu(\text{CO})) - 14.84$ ,  $r = 0.99$ );<sup>18</sup>  $\text{trans-Mo}(\text{N}_2)\text{L}(\text{dppe})_2$  ( $E = 0.0080(\nu(\text{N}_2)) - 16.14$ ,  $r = 0.997$ );<sup>18</sup>  $\text{trans-Mo}(\text{NO})\text{L}(\text{dppe})_2$

( $E \approx 0.0059(\nu(\text{NO})) - 8.68$ ).<sup>19</sup> These equations were calculated by us from slopes and data provided in these articles. Further work revealed that changing the cis P- or N-donor ligands, L, cis to N<sub>2</sub> in the series  $\text{trans-Re}(\text{N}_2)\text{Cl}(\text{L})_4$  gave a linear relationship ( $E = 0.0047(\nu(\text{N}_2)) - 9.0$ ,  $r = 0.99$ )<sup>20</sup> whereas changing the bidentate ligands cis to N<sub>2</sub> in the complexes  $\text{trans-M}(\text{N}_2)_2(\text{PR}_2\text{CH}_2\text{CH}_2\text{PR}_2)_2$ , M = Mo, W gave a curved plot of  $E$  vs.  $\nu(\text{N}_2)(\text{A}_{2u})$ .<sup>21</sup> Recently the data for all molybdenum dinitrogen complexes including the series  $\text{trans-Mo}(\text{N}_2)_2(\text{PMePh}_2)_3\text{L}$  have been shown to follow a poor correlation ( $E = 0.44(k(\text{N}_2)) - 7.44$ ,  $r = 0.85$ ).<sup>22</sup> Complexes of the type  $\text{M}(\text{CO})_4(\text{PR}_2\text{CH}_2\text{CH}_2\text{PR}_2)_2$ , R = F, Cl, C<sub>6</sub>F<sub>5</sub>, OCH<sub>3</sub>, and C<sub>6</sub>H<sub>5</sub>, give a linear correlation between  $E$  and  $k(\text{CO})$  although the complexes with R = CH<sub>3</sub> and C<sub>6</sub>H<sub>11</sub> fall below the line.<sup>23</sup>

If the data for the series of carbonyl complexes above are plotted as in Figure 1, then the expected trend is apparent: as the metal complexes become more reducing, the CO force constant decreases because of enhanced  $d \rightarrow \pi^*$  back-donation. The approximate linearity of Figure 1 encouraged us to examine more literature values and develop some equations that, although not exact, could prove to be of use in estimating the  $E_{1/2}(\text{ox})$  value of a metal site from its infrared spectrum. The equations can be extended to photoelectron data. One linear correlation of this type has been reported between  $(\nu(\text{CO}))^2$ , which is proportional to  $k(\text{CO})$ , and metal d-orbital ionization potentials for the series  $\text{Mn}(\text{CO})_5\text{L}$ .<sup>24</sup> Ionization potentials (IP) can also be related to  $E_{1/2}(\text{ox})$  values. The IP values of a broad range of organic compounds vary linearly with  $E_{1/2}(\text{ox})$  values,<sup>25–28</sup> and so metal-containing complexes are also likely to show a correlation as will be demonstrated here.

The equations reported here go hand in hand with models for predicting carbonyl stretching frequencies,<sup>29</sup>  $E_{1/2}(\text{ox})$  values,<sup>15</sup> and  $d\pi$ -electron energies (from PES)<sup>30</sup> of organometallic compounds by use of additive ligand parameters. These parameters and trends

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derived from electrochemical,<sup>19-21,23,31-35</sup> PES,<sup>36-41</sup> or infrared data<sup>23,42,43</sup> often reflect a partial separation of  $\sigma$  and  $\pi$  components of the metal-ligand interaction. Infrared data<sup>44-46</sup> and  $E_{1/2}(\text{ox})$  data<sup>18,32,35</sup> have also been used as indicators of reactivity of transition-metal complexes. In this paper the bonding and reactivity of coordinated dihydrogen are examined in the light of our correlations.

### Experimental Section

The cyclic voltammograms of complexes **51**, **52**, **109**, and **110** were recorded here. Work on the series of dinitrogen complexes **111-118** in our labs has been reported elsewhere.<sup>22</sup> The  $d^5 \leftrightarrow d^6$  redox couples were reversible in all cases at sweep rates of 50 mV s<sup>-1</sup> as judged by  $i_p(\text{ox})/i_p(\text{red}) \approx 1$  and by peak separations comparable to those observed for known reversible couples. Solutions were approximately 0.002 M in complex and 0.2 M in electrolyte (NBu<sub>4</sub>BF<sub>4</sub>) and were handled under N<sub>2</sub> at all times. The solvent was THF that had been distilled first from sodium-benzophenone ketyl and then LiAlH<sub>4</sub>. The voltammograms were measured by use of a BAS CV 1B instrument and a glassy-carbon working electrode and a Ag/AgCl reference electrode. Values are reported relative to the saturated calomel electrode (SCE).

### Calculations

An extensive although probably not exhaustive data base of infrared, electrochemical, and photoelectron-derived ionization potential data for carbonyl and dinitrogen complexes was compiled by using the Microsoft program Excel, which runs on the Macintosh microcomputer. The metal is in the  $d^6$ , low-spin configuration and in an approximately octahedral coordination geometry in all cases.  $\eta^6$ -Arene and  $\eta^5$ -cyclopentadienyl ligands are assumed to occupy three coordination sites on the octahedron.

This program was also used to compute Cotton-Kraihanzel (C-K) force constants<sup>47</sup> from stretching frequencies and to carry out regression and graphical analyses of the data. In a few cases it was necessary to estimate the values of interaction force constants between trans-carbonyl or -dinitrogen ligands when only the A<sub>2u</sub> mode ( $D_{4h}$  local symmetry) was reported. These were taken from data for closely related complexes or calculated by using the formulas of Timney.<sup>29</sup> Force constants for mixed carbonyl-isocyanide complexes were calculated by using the Wilson GF matrix method and the programs of McIntosh and Peterson.<sup>48</sup> The inclusion of interaction force constants between isocyanide and carbonyl groups in the cations Mn(CO)<sub>n</sub>(CNR)<sub>6-n</sub><sup>+</sup> caused deviations from the force constants as estimated by the C-K method that were insignificant compared to the scatter of the data in the correlations. This was also the finding of Sarapu and Fenske.<sup>49</sup> The use of these interaction force constants in the

calculations on the neutral complexes Cr(CO)<sub>n</sub>(CNR)<sub>6-n</sub> did result in significant changes, and so force constants (mdyn Å<sup>-1</sup>) from the Wilson method are utilized for the correlations. For Cr(CO)<sub>5</sub>(CNMe),<sup>50</sup>  $k(\text{CN}) = 17.95$ ,  $k_1(\text{CO}) = 15.80$ ,  $k_2(\text{CO}) = 16.43$ ,  $k_{\text{cis}}(\text{CO-CO}) \approx 0.22$ ,  $k_{\text{trans}}(\text{CO-CO}) = 0.47$ ,  $k_{\text{cis}}(\text{CO-CN}) \approx 0.16$ , and  $k_{\text{trans}}(\text{CO-CN}) = 0.49$ . For *cis*-Cr(CO)<sub>4</sub>(CNMe)<sub>2</sub>,<sup>50</sup>  $k(\text{CN}) = 17.50$ ,  $k_1(\text{CO}) = 15.62$ ,  $k_2(\text{CO}) = 15.61$ ,  $k_{\text{cis}}(\text{CO-CO}) \approx 0.4$ ,  $k_{\text{trans}}(\text{CO-CO}) = 0.6$ ,  $k_{\text{cis}}(\text{CO-CN}) \approx 0.22$ , and  $k_{\text{trans}}(\text{CO-CN}) = 0.64$ . The following distances (Å) were used in the calculation of the B matrices:<sup>48</sup>  $r(\text{M-CO}) = 1.83$ ,  $r(\text{M-CNR}) = 2.11$  (M = Cr, Mn),  $r(\text{C-O}) = 1.16$ ,  $r(\text{C-NR}) = 1.10$ ,  $r(\text{CN-R}) = 1.47$ .

Data for carbonyl complexes studied by both electrochemistry (cyclic voltammetry or polarography) and vibrational spectroscopy are listed in Table I. IR data for solutions were used in all cases except for complexes **48-50**. No account has been made for differences in polarity of the solvents used in different studies so that the force constant data have an error of about 0.2 mdyn/Å. Only  $E_{1/2}(\text{ox})$  values for reversible or quasi-reversible  $d^5 \leftrightarrow d^6$  couples are included. Porphyrin complexes of  $d^6$  metals are excluded because it is known that the oxidation takes place at the ligand for these. The reduction potentials were measured in CH<sub>3</sub>CN, CH<sub>2</sub>Cl<sub>2</sub>, or THF. Most of the values were referenced to the saturated calomel electrode and were used with no correction for solvent or electrolyte effect. The following corrections were added to values referenced to other standards: -0.06 for data referenced to Ag/AgCl,<sup>33,51-53</sup> -0.3 for data referenced to Ag/AgCl at -78 °C,<sup>34</sup> -0.24 for data referenced to NHE,<sup>28,54</sup> and +0.37 for data referenced to Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>/Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub><sup>+</sup> in CH<sub>3</sub>CN.<sup>55</sup> The lack of a common reference or solvent means that the  $E_{1/2}(\text{ox})$  data in Table I are only accurate to about ±0.1 V as the data for complex **2**, Cr(CO)<sub>6</sub>, would indicate, but this is sufficient for the development of a rough correlation with a standard deviation,  $\sigma$ , of 0.17 V (see below). A complete listing of solvents, reference electrodes, information on reversibility, calculated and observed force constants and interaction constants, and IR frequencies can be found as supplementary material.

Table II lists ionization potential data and force constants for  $d^6$  metal carbonyl complexes. The first ionization of the PES spectrum (IP) was always chosen, regardless of its fraction of metal  $d$  character, although in almost every case this fraction is thought to be close to 1.

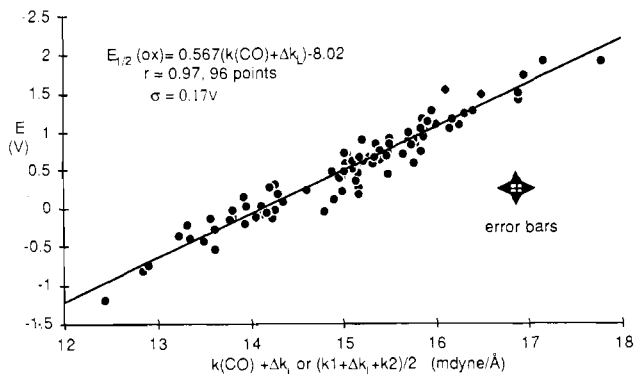
The electrochemical and force constant data for dinitrogen complexes are listed in Table III. Again only reversible couples are included and all values have been referenced to the SCE. Almost all redox data were measured on 10<sup>-3</sup> M solutions in THF apart from those for the pentaamines, M(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub><sup>2+</sup>, which were measured on 0.1 M HCl solutions and referenced relative to the NHE.<sup>54</sup>

**Carbonyl Complexes.** A linear fit of all  $\nu(\text{CO})$  vs.  $E_{1/2}(\text{ox})$  data gave a very poor correlation with the standard deviation  $\sigma = 50$  cm<sup>-1</sup> and the correlation coefficient  $r = 0.78$ . Better correlations with  $r = 0.90-0.96$  were obtained when force constants for a series of complexes with the same ligand trans to the CO were plotted against their  $E_{1/2}(\text{ox})$  data.<sup>16,17</sup> For example the force constant ( $k_2$  values) and  $E_{1/2}(\text{ox})$  values for CO ligands that are only trans to CO gave  $k_2 = 1.65(E_{1/2}(\text{ox})) + 14.23$ ,  $\sigma = 0.36$  mdyn Å<sup>-1</sup>, and  $r = 0.92$ . Similarly a plot of  $k_2$  vs. IP gave  $k_2 = 0.97(\text{IP}) + 8.62$ ,  $\sigma = 0.30$  mdyn Å<sup>-1</sup>, and  $r = 0.92$ .

It was found that lines for different trans ligands were approximately parallel so that a correction for each trans ligand,  $\Delta k_L$ , could be added to these equations to bring them onto one line. The correlations for  $k_2$  were chosen as the reference equations

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**Figure 2.** Plot of  $E_{1/2}(\text{ox})$  vs.  $k(\text{CO}) + \Delta k_L$  or  $(k_1 + \Delta k_L + k_2)/2$ , depending on which data are available for the carbonyl complexes. The line is the least-squares fit (eq 2).

( $\Delta k_L = 0$  for CO trans to CO). The optimized ligand parameters that put  $k_1$  values (CO trans to L) on the lines for  $k_2$  are listed in Table IV for cases where three or more data points for a particular ligand are available. It was impossible to obtain a consistent value for  $\Delta k_L$  for  $\text{P}(\text{OMe})_3$ ; they ranged from 0.1 to 0.7 with a slight minimum in the sum of deviations at 0.5. Thus for this ligand the uncertainty in  $\Delta k_L$  is large. Other  $\Delta k_L$  values (mdyn  $\text{\AA}^{-1}$ ) for ligands trans to CO in only one or two complexes are as follows:  $\text{N}_3^-$  (0.9),  $\text{CN}^-$  (0.9),  $\text{SCN}^-$  (0.9),  $\text{CH}_3^-$  (0.8),  $\text{S}_2\text{CNEt}_2^-$  (0.7),  $\text{NCR}$  (0.7),  $0.5 (\text{C}_6\text{F}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2$  (0.7),  $\eta^5\text{-C}_5\text{Me}_5^-$  (0.6),  $\eta^6\text{-C}_6\text{H}_3\text{Me}_3$  (0.6),  $0.5 (\text{MeO})_2\text{PCH}_2\text{CH}_2\text{P}(\text{OMe})_2$  (0.6),  $\text{PF}_3$  (0.5),  $\text{PBU}_3$  (0.4),  $0.5 \text{F}_2\text{PCH}_2\text{CH}_2\text{PF}_2$  (0.3),  $0.5 \text{Cl}_2\text{PCH}_2\text{CH}_2\text{PCl}_2$  (0.2),  $0.5 (\text{Cy})_2\text{PCH}_2\text{CH}_2\text{P}(\text{Cy})_2$  (0.1).

The correlation improved when the corrected force constant data (131 values of  $k_2$  or  $k_1 + \Delta k_L$ ) were plotted against  $E_{1/2}(\text{ox})$ . The equation of the least-squares line is

$$k(\text{CO}) = 1.613(E_{1/2}(\text{ox})) + 14.24 - \Delta k_L \quad (1)$$

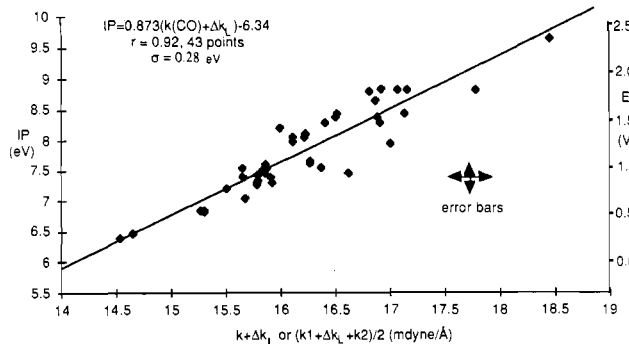
$$\sigma = 0.29 \text{ mdyn } \text{\AA}^{-1}, r = 0.96$$

Complexes with  $k_1$  values that differed from the calculated values by  $2\sigma$  were **15**, **69**, and **71**. The error for *cis*- $\text{Cr}(\text{CO})_4(\text{CNMe})_2$  (**15**) might lie in the estimation of the interaction between ligands in the force constant calculation. Complexes **69** and **71** as well as **72**, which are all of the type  $\text{Mn}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_2\text{L}$ , L = N-donor or olefin, have large deviations because eq 1 only accounts for the effect of the "trans"  $\eta^5\text{-C}_5\text{H}_4\text{CH}_3$  ligand on  $k(\text{CO})$  but not for *cis* effects of the other ligands. Equation 1 and the other equations we will present below will work best for complexes of the type  $\text{M}(\text{CO})_n\text{L}_{6-n}$  or for complexes with a variety of "soft" C-, N-, P-, and X-donor ligands. Complexes that differ in calculated and observed  $k_2$  values by more than  $2\sigma$  are  $\text{Cr}(\text{CO})_5\text{P}(\text{OMe})_3$  (**4**), *mer*- $\text{Cr}(\text{CO})_3(\text{P}(\text{O}Ph)_3)_3$  (**30**), and  $\text{Cr}(\text{CO})_4(\text{dmpe})$  (**14**). The  $E_{1/2}(\text{ox})$  value reported for **4**<sup>56</sup> seems too high considering that the value for  $\text{Cr}(\text{CO})_6$  is taken as  $\sim 1.45$  V. However, the  $\Delta k_L$  value for phosphite ligands is unreliable as mentioned above. Other complexes with large errors in calculated  $k(\text{CO})$  values are **9**, **10**, **15**, **16**, **19**, **29**, **31**, **41**, **45**, **46**, **52**, **53**, and **70**. No trends are apparent, but the errors can be associated with solvent effects, *cis* ligand effects, steric effects, or poor estimates of force constants due to interactions that have not been accounted for (e.g. for isocyanide ligands).

A more useful equation relates the  $E_{1/2}(\text{ox})$  data, which are often not known, with readily available IR data. This is obtained by plotting  $E_{1/2}(\text{ox})$  vs. corrected  $k(\text{CO})$  values,  $k(\text{CO}) + \Delta k_L$  or  $(k_2 + k_1 + \Delta k_L)/2$ , depending on which of the  $k_1$  and  $k_2$  data are available (Figure 2):

$$E_{1/2}(\text{ox}) = 0.567(k(\text{CO}) + \Delta k_L) - 8.02 \quad (2)$$

$$\sigma = 0.17 \text{ V}, r = 0.97$$



**Figure 3.** Plot of the ionization potential (IP) of carbonyl complexes as determined by PES vs.  $k(\text{CO}) + \Delta k_L$  or  $(k_1 + \Delta k_L + k_2)/2$ , depending on which data are available for the carbonyl complexes. The line is the least-squares fit (eq 4). The scale on the right-hand side was determined by use of eq 5 and can be used to estimate  $E_{1/2}(\text{ox})$  values of the complexes for which PES data are available.

The slope of eq 2 is not the inverse of that of eq 1 because of the different number of data points used in the correlations (131 vs. 96). Of the calculated  $E_{1/2}(\text{ox})$  values for 81 compounds listed in Table I, 57 lie within  $1\sigma$  and 78 lie within  $2\sigma$  of observed values. The complexes with the largest deviations are again  $\text{Cr}(\text{CO})_5\text{-P}(\text{OMe})_3$  (**4**) and  $\text{Mn}(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)(\text{CO})_2\text{L}$ , L = pyridine (**70**), piperidine (**71**), norbornene (**72**), and acetonitrile (**69**). Other complexes that deviate by more than 0.25 V are **14**, **15**, **19**, **41**, and **52**, although values of  $E_{1/2}(\text{ox})$  for **14** and **19** recorded in different solvents do fall within  $1\sigma$  (see Table I). The dependence of the data on the row of the periodic table of the metal was examined (see eq 7), but the fit did not improve enough over that of eq 2 to justify another parameter.

Similar equations have been derived for the PES data that make use of the same  $\Delta k_L$  parameters:

$$k(\text{CO}) = 0.967 \text{ IP} + 8.65 - \Delta k_L \quad (3)$$

$$\sigma = 0.30 \text{ mdyn } \text{\AA}^{-1}, r = 0.92$$

$$\text{IP} = 0.873(k(\text{CO}) + \Delta k_L) - 6.34 \quad (4)$$

$$\sigma = 0.28 \text{ eV}, r = 0.92$$

Again the slopes of eq 3 and 4 are not the inverse of one another because of the different number of data points (69 vs. 43 data points). Figure 3 is a plot of IP vs.  $k(\text{CO}) + \Delta k_L$  or  $(k_2 + k_1 + \Delta k_L)/2$  depending on which of the  $k_1$  and  $k_2$  data are available. Calculated IP values from eq 4 can be found in Table II. Of the values for 38 compounds, 26 are within  $1\sigma$ , 36 are within  $2\sigma$ , and two compounds,  $\text{W}(\text{CO})_5\text{P}(\text{OMe})_3$  (**96**) and  $\text{Cr}(\text{CO})_2(\text{NS})(\text{C}_5\text{H}_5)$  (**85**) fall beyond  $0.56$  eV of the calculated values. Equation 4 does not account for the powerfully electron withdrawing NS ligand *cis* to CO in **85**. As explained previously, the  $\Delta k_L$  parameter for the  $\text{P}(\text{OMe})_3$  ligand may be in error; a value of 0.2 for this ligand would give a good IP value for **96**, but this increases the deviation of other complexes.

Equations 2 and 4 can be combined to give

$$E_{1/2}(\text{ox}) = 0.649 \text{ IP} - 3.91 \quad (5)$$

Both  $E_{1/2}(\text{ox})$  and PES data have been measured for 11 compounds, almost all of Cr, that appear in both Tables I and II; these are complexes **2**, **4**, **5**, **6**, **7**, **9**, **10**, **12**, **24**, **25**, and **55**. In addition, the IP (6.63 eV)<sup>57</sup> and  $E_{1/2}(\text{ox})$  (0.13 V vs. SCE)<sup>58</sup> values have been reported for  $\text{Mn}(\text{CO})_2(\text{NH}_3)(\text{C}_5\text{H}_5)$ . The best fit for these data is

$$E_{1/2}(\text{ox}) = 0.688 \text{ IP} - 4.22 \quad (6)$$

$$\sigma = 0.15 \text{ V}, r = 0.94$$

Equations 5 and 6 deviate by only  $\pm 0.08$  V in the range IP = 6–10

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Table I. Electrochemical and Infrared Data for Octahedral Carbonyl Complexes of d<sup>6</sup> Metals<sup>a</sup>

no.	M(L) <sub>n</sub>	E(obsd), V	E(calcd), V	ref	k <sub>1</sub> (CO), mdyn Å <sup>-1</sup>	k <sub>2,trans</sub> (CO), mdyn Å <sup>-1</sup>	ref	Δk <sub>L</sub> , mdyn Å <sup>-1</sup>
1	V(CO) <sub>6</sub> <sup>-</sup>	0.02	-0.10	55		13.96	73	0.0
2	Cr(CO) <sub>6</sub>	1.49	1.34	55		16.50	47	0.0
		1.43	1.56	31		16.89	74	0.0
		1.41	1.56	23		16.89	74	0.0
		1.50	1.56	34		16.89	74	0.0
3	Cr(CO) <sub>5</sub> PPh <sub>3</sub>	1.15	0.99	56	15.50	15.88	47	0.4
4	Cr(CO) <sub>5</sub> P(OMe) <sub>3</sub>	1.54	1.11	56	15.79	15.92	75	0.5
5	Cr(CO) <sub>5</sub> PMe <sub>3</sub>	1.18	0.98	56	15.60	15.83	76	0.3
6	Cr(CO) <sub>5</sub> PEt <sub>3</sub>	1.10	1.00	56	15.60	15.80	77	0.4
7	Cr(CO) <sub>5</sub> (C(OMe)- <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> )	0.92	0.94	56	15.76	15.93	41	-0.1
8	Cr(CO) <sub>5</sub> (C(OMe)- <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> )	0.86	0.93	56	15.72	15.94	41	-0.1
9	Cr(CO) <sub>5</sub> NH <sub>3</sub>	0.71	0.86	56	15.09	15.42	76	0.8
10	Cr(CO) <sub>5</sub> (CNMe)	1.10	1.20	56	15.80	16.43	50	0.3
11	Cr(CO) <sub>5</sub> NCMe	1.05	1.14	34	15.40	16.20	76	0.7
12	Cr(CO) <sub>5</sub> py	0.90	0.92	34	14.61	15.84	78	1.1
		0.91	0.92	56	14.61	15.84	78	1.1
13	<i>trans</i> -Cr(CO) <sub>4</sub> (PPh <sub>3</sub> ) <sub>2</sub>	0.64	0.64	51		15.28	47	0.0
14	Cr(CO) <sub>4</sub> (dmpe)	0.27	0.58	23	14.83	15.30	23	0.2
		0.46	0.58	56	14.83	15.30	23	0.2
15	<i>cis</i> -Cr(CO) <sub>4</sub> (CNMe) <sub>2</sub>	0.59	0.92	50	15.62	15.61	50	0.3
16	<i>cis</i> -Cr(CO) <sub>4</sub> (CNPh) <sub>2</sub>	0.74	0.96	31	15.91	15.88	50	-0.1
17	Cr(CO) <sub>4</sub> (bpy)	0.61	0.61	56	14.03	15.20	78	1.2
18	Cr(CO) <sub>4</sub> (dppe)	0.86	0.69	23	14.49	15.32	47	0.9
		0.74	0.76	23	14.75	15.32	23	0.9
19	Cr(CO) <sub>4</sub> ((Cy) <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> P(Cy) <sub>2</sub> )	0.21	0.48	23	14.71	15.17	23	0.1
		0.41	0.48	23	14.71	15.17	23	0.1
20	Cr(CO) <sub>4</sub> (F <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> PF <sub>2</sub> )	1.25	1.23	23	15.94	16.39	23	0.3
21	Cr(CO) <sub>4</sub> (Cl <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> PCl <sub>2</sub> )	1.17	1.16	23	15.87	16.30	23	0.2
22	Cr(CO) <sub>4</sub> ((C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> P(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> )	0.94	0.98	23	15.23	15.83	23	0.7
		1.05	0.98	23	15.23	15.83	23	0.7
23	Cr(CO) <sub>4</sub> ((MeO) <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> P(OMe) <sub>2</sub> )	0.89	0.89	23	15.11	15.71	23	0.6
		1.00	0.89	23	15.11	15.71	23	0.6
24	Cr(CO) <sub>3</sub> (C <sub>6</sub> H <sub>3</sub> Me <sub>3</sub> )	0.64	0.71	53	14.90		79	0.5
		0.77	0.71	28	14.90		79	0.5
25	Cr(CO) <sub>3</sub> (C <sub>6</sub> H <sub>6</sub> )	0.82	0.91	53	15.15		80	0.6
		0.84	0.91	28	15.15		80	0.6
26	Cr(CO) <sub>3</sub> (C <sub>6</sub> Me <sub>6</sub> )	0.69	0.75	28	14.77		79	0.7
27	<i>fac</i> -Cr(CO) <sub>3</sub> (P(OMe) <sub>3</sub> ) <sub>3</sub>	0.50	0.53	52	14.58		52	0.5
28	<i>fac</i> -Cr(CO) <sub>3</sub> (PMe <sub>2</sub> Ph) <sub>3</sub>	0.18	0.08	52	13.89		52	0.4
29	<i>mer</i> -Cr(CO) <sub>3</sub> (P(OMe) <sub>3</sub> ) <sub>3</sub>	0.36	0.56	51	14.82	14.94	51	0.5
30	<i>mer</i> -Cr(CO) <sub>3</sub> (P(OPh) <sub>3</sub> ) <sub>3</sub>	0.72	0.51	52	14.88	14.71	52	0.5
31	<i>trans</i> -Cr(CO) <sub>2</sub> (dppe) <sub>2</sub>	-0.37	-0.52	33		13.23	81	0.0
32	<i>cis</i> -Cr(CO) <sub>2</sub> (dppe) <sub>2</sub>	0.02	0.05	33	13.33		82	0.9
33	Cr(CO) <sub>2</sub> P(OPh) <sub>3</sub> (C <sub>6</sub> Me <sub>6</sub> )	0.23	0.26	83	13.90		83	0.7
34	Cr(CO) <sub>2</sub> P(OMe) <sub>3</sub> (C <sub>6</sub> Me <sub>6</sub> )	0.08	0.12	83	13.66		83	0.7
35	Cr(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (C <sub>6</sub> Me <sub>6</sub> )	-0.05	0.02	83	13.48		83	0.7
36	Cr(CO) <sub>2</sub> (PMePh <sub>2</sub> ) <sub>2</sub> (C <sub>6</sub> Me <sub>6</sub> )	-0.08	-0.01	83	13.43		83	0.7
37	Cr(CO) <sub>2</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> (C <sub>6</sub> Me <sub>6</sub> )	-0.11	-0.05	83	13.36		83	0.7
38	Mo(CO) <sub>4</sub> (dmpe)	0.60	0.67	56	14.98	15.46	23	0.2
39	Mo(CO) <sub>4</sub> (bpy)	0.62	0.61	56	14.09	15.15	78	1.2
40	Mo(CO) <sub>4</sub> ((C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> P(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> )	1.28	1.03	23	15.25	15.99	23	0.7
41	<i>cis</i> -Mo(CO) <sub>4</sub> (PBu <sub>3</sub> ) <sub>2</sub>	0.90	0.61	84	14.78	15.25	85	0.4
42	<i>trans</i> -Mo(CO)(N <sub>2</sub> )(dppe) <sub>2</sub>	-0.13	-0.33	19	13.07		86	0.5
43	<i>cis</i> -Mo(CO) <sub>2</sub> (bpy) <sub>2</sub>	-0.54	-0.30	87	12.41		87	1.2
44	<i>cis</i> -Mo(CO) <sub>2</sub> (dppe) <sub>2</sub>	0.30	0.07	33	13.37		82	0.9
		-0.02	0.07	56	13.36		82	0.9
45	<i>cis</i> -Mo(CO) <sub>2</sub> (dmpe) <sub>2</sub>	-0.23	-0.47	56	13.12		88	0.2
46	<i>trans</i> -Mo(CO) <sub>2</sub> (dppe) <sub>2</sub>	-0.11	-0.20	19		13.80	89	0.0
		-0.03	-0.20	33		13.80	89	0.0
47	<i>trans</i> -Mo(CO)(NCPh)(dppe) <sub>2</sub>	-0.40	-0.45	19	12.65		18	0.7
48	<i>trans</i> -Mo(CO)(CN)(dppe) <sub>2</sub> <sup>-</sup>	-0.83	-0.73	19	11.95		18	0.9
49	<i>trans</i> -Mo(CO)(SCN)(dppe) <sub>2</sub> <sup>-</sup>	-0.74	-0.70	19	12.01		18	0.9
50	<i>trans</i> -Mo(CO)(N <sub>3</sub> )(dppe) <sub>2</sub> <sup>-</sup>	-1.00	-0.97	19	11.53		18	0.9
51	Mo(CO)(η <sup>6</sup> -PhPMePh)(PMePh <sub>2</sub> ) <sub>2</sub>	0.03	-0.01	90	13.52		91	0.6
52	Mo(CO)(η <sup>6</sup> -PhPPH <sub>2</sub> )(dppe)	0.15	-0.12	90	13.33		92	0.6
53	<i>cis</i> -W(CO) <sub>2</sub> (dppe) <sub>2</sub>	0.28	0.03	33	13.30		82	0.9
54	<i>cis</i> -W(CO) <sub>2</sub> (bpy) <sub>2</sub>	-0.44	-0.37	87	12.30		87	1.2
55	Mn(CO) <sub>5</sub> Br	1.92	1.71	55	16.20	17.21	49	0.9
		1.92	2.06	55	16.79	17.88	93	0.9
56	<i>mer</i> -Mn(CO) <sub>3</sub> (CNMe) <sub>3</sub> <sup>+</sup>	1.73	1.60	15	16.63	16.99	49	0.3
57	Mn(CO) <sub>3</sub> (CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> )	1.10	1.06	17	15.71		17	0.3
58	Mn(CO) <sub>2</sub> (P(OPh) <sub>3</sub> )(C <sub>5</sub> H <sub>5</sub> )	0.92	0.77	16	15.00		16	0.5
59	Mn(CO) <sub>2</sub> (P(OMe) <sub>3</sub> )(CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> )	0.73	0.50	16	14.72		16	0.3
		0.68	0.59	17	14.88		17	0.3
60	Mn(CO) <sub>2</sub> (PPh <sub>3</sub> )(C <sub>5</sub> H <sub>5</sub> )	0.59	0.51	16	14.54		16	0.5

Table I (Continued)

no.	M(L) <sub>n</sub>	E(obsd), V	E(calcd), V	ref	k <sub>1</sub> (CO), mdyn Å <sup>-1</sup>	k <sub>2,trans</sub> (CO), mdyn Å <sup>-1</sup>	ref	Δk <sub>L</sub> , mdyn Å <sup>-1</sup>
61	Mn(CO) <sub>2</sub> (PEt <sub>3</sub> )(C <sub>5</sub> H <sub>5</sub> )	0.49	0.42	16	14.38		16	0.5
62	Mn(CO) <sub>2</sub> (PEt <sub>3</sub> )(CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> )	0.40	0.46	17	14.66		17	0.3
63	Mn(CO) <sub>2</sub> (PPh <sub>3</sub> )(CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> )	0.52	0.54	17	14.80		17	0.3
64	Mn(CO) <sub>2</sub> (P( <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> )(CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> )	0.50	0.50	17	14.72		17	0.3
65	Mn(CO) <sub>2</sub> (P( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> )(CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> )	0.60	0.56	17	14.83		17	0.3
66	Mn(CO) <sub>2</sub> (PMePh <sub>2</sub> )(CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> )	0.49	0.50	17	14.72		17	0.3
67	Mn(CO) <sub>2</sub> (P(OMe)Ph <sub>2</sub> )(CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> )	0.62	0.54	17	14.80		17	0.3
68	Mn(CO) <sub>2</sub> (P(OPh) <sub>3</sub> )(CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> )	0.85	0.77	17	15.20		17	0.3
69	Mn(CO) <sub>2</sub> (CH <sub>3</sub> CN)(CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> )	0.19	0.58	94	14.86		17	0.3
70	Mn(CO) <sub>2</sub> (py)(CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> )	0.11	0.43	17	14.60		17	0.3
71	Mn(CO) <sub>2</sub> (HN(CH <sub>2</sub> ) <sub>5</sub> )(CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> )	-0.04	0.37	17	14.50		17	0.3
72	Mn(CO) <sub>2</sub> (nbn)(CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> )	0.44	0.76	17	15.19		17	0.3
73	<i>trans</i> -Mn(CO) <sub>2</sub> (CNMe) <sub>4</sub> <sup>+</sup>	1.28	1.28	95		16.41	49	0.0
74	Mn(CO) <sub>2</sub> (PPh <sub>3</sub> )(η <sup>5</sup> -C <sub>6</sub> H <sub>6</sub> Ph)	0.59	0.67	96	14.83		96	0.5
75	Mn(CO)(dppe)(η <sup>5</sup> -C <sub>6</sub> H <sub>6</sub> Ph)	-0.06	0.01	96	13.67		96	0.5
76	Mn(CO)(PPh <sub>3</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> )	-0.21	-0.12	16	13.44		16	0.5
77	Mn(CO)(dppe)(CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> )	-0.16	-0.21	16	13.47		16	0.3
78	Mn(CO)(PPh <sub>3</sub> ) <sub>2</sub> (CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> )	-0.27	-0.30	16	13.32		16	0.3
79	Fe(CO)H(dppe) <sub>2</sub> <sup>+</sup>	1.04	0.97	19	15.35		97	0.5
80	Ru(CO)(NH <sub>3</sub> ) <sub>5</sub> <sup>2+</sup>	1.14	1.01	98	15.12		99	0.8
81	Os(CO)(NH <sub>3</sub> ) <sub>5</sub> <sup>2+</sup>	0.68	0.68	54	14.55		54	0.8

<sup>a</sup>The E<sub>1/2</sub>(ox) values (E(calcd)) were calculated by using eq 2 and the parameter Δk<sub>L</sub>. Abbreviations: py, pyridine; dmpe, 1,2-bis(dimethylphosphino)ethane; bpy, 2,2'-bipyridine; dppe, 1,2-bis(diphenylphosphino)ethane; Cy, cyclohexyl; nbn, norbornene.

Table II. Photoelectron Data and Infrared Data for d<sup>6</sup>, Octahedral Carbonyl Complexes<sup>a</sup>

no.	M(L) <sub>n</sub>	IP, eV	IP(calcd), eV	ref	k <sub>1</sub> (CO), mdyn Å <sup>-1</sup>	k <sub>2,trans</sub> (CO), mdyn Å <sup>-1</sup>	ref	Δk <sub>L</sub> , mdyn Å <sup>-1</sup>
2	Cr(CO) <sub>6</sub>	8.4	8.4	100		16.89	74	0
		8.4	8.06	100		16.50	47	0
4	Cr(CO) <sub>5</sub> P(OMe) <sub>3</sub>	8.0	7.72	40	15.79	15.92	75	0.5
5	Cr(CO) <sub>5</sub> PMe <sub>3</sub>	7.6	7.51	40	15.60	15.83	76	0.3
6	Cr(CO) <sub>5</sub> PEt <sub>3</sub>	7.6	7.44	40	15.46	15.72	77	0.4
7	Cr(CO) <sub>5</sub> (C(OMe)- <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> )	7.34	7.45	41	15.76	15.93	41	-0.1
82	Cr(CO) <sub>5</sub> (C(OMe)- <i>o</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> )	7.05	7.34	41	15.50	15.94	41	-0.1
83	Cr(CO) <sub>5</sub> (C(OMe)Ph)	7.26	7.43	41	15.72	15.93	41	-0.1
9	Cr(CO) <sub>5</sub> NH <sub>3</sub>	7.56	7.33	101	15.09	15.42	76	0.8
10	Cr(CO) <sub>5</sub> (CNMe)	7.61	7.86	101	15.80	16.43	50	0.3
12	Cr(CO) <sub>5</sub> py	7.3	7.43	101	14.61	15.84	78	1.1
24	Cr(CO) <sub>3</sub> (C <sub>6</sub> H <sub>3</sub> Me <sub>3</sub> )	7.2	7.19	102	14.90		79	0.6
25	Cr(CO) <sub>3</sub> (C <sub>6</sub> H <sub>6</sub> )	7.42	7.32	102	15.15		80	0.5
84	Cr(CO) <sub>2</sub> (NO)(C <sub>5</sub> H <sub>5</sub> )	7.56	7.96	103	15.88		104	0.5
85	Cr(CO) <sub>2</sub> (NS)(C <sub>5</sub> H <sub>5</sub> )	7.47	8.17	103	16.12		105	0.5
86	Mo(CO) <sub>6</sub>	8.42	8.61	64		17.13	74	0
		8.42	8.08	64		16.52	47	0
87	Mo(CO) <sub>5</sub> PEt <sub>3</sub>	7.54	7.52	30	15.48	15.87	106	0.4
88	Mo(CO) <sub>5</sub> P( <i>n</i> -Bu) <sub>3</sub>	7.4	7.55	30	15.58	15.84	42	0.4
89	Mo(CO) <sub>5</sub> P(OMe) <sub>3</sub>	8.1	7.83	40	15.90	16.06	42	0.5
90	Mo(CO) <sub>5</sub> PF <sub>3</sub>	8.8	8.34	40	16.59	16.54	42	0.5
91	<i>cis</i> -Mo(CO) <sub>4</sub> (PMe <sub>3</sub> ) <sub>2</sub>	6.84	7.02	64	15.03	15.28	107	0.3
		6.84	6.99	64	14.92	15.32	36	0.3
92	<i>trans</i> -Mo(CO) <sub>4</sub> (PMe <sub>3</sub> ) <sub>2</sub>	6.82	7.02	64		15.30	107	0
93	<i>fac</i> -Mo(CO) <sub>3</sub> (PMe <sub>3</sub> ) <sub>3</sub>	6.48	6.45	64	14.35		106	0.3
94	W(CO) <sub>6</sub>	8.3	8.42	39		16.91	74	0
		8.3	7.99	39		16.41	47	0
95	W(CO) <sub>5</sub> PMe <sub>3</sub>	7.46	7.48	38	15.56	15.81	43	0.3
96	W(CO) <sub>5</sub> P(OMe) <sub>3</sub>	8.2	7.62	40	15.64	15.84	43	0.5
97	W(CO) <sub>5</sub> PPh <sub>3</sub>	7.2	7.55	38	15.58	15.85	47	0.4
98	<i>fac</i> -W(CO) <sub>3</sub> (PMe <sub>3</sub> ) <sub>3</sub>	6.4	6.34	39	14.23		75	0.3
99	Mn(CO) <sub>5</sub> CH <sub>3</sub>	8.65	8.38	108	16.11	16.82	42	0.8
100	Mn(CO) <sub>5</sub> H	8.85	8.44	108	16.42	16.93	42	0.5
55	Mn(CO) <sub>5</sub> Br	8.83	8.64	100	16.20	17.21	49	0.9
		8.83	9.19	100	16.79	17.88	93	0.9
101	Mn(CO) <sub>3</sub> (C <sub>5</sub> H <sub>5</sub> )	8.05	7.82	109	15.72		110	0.5
102	Mn(CO) <sub>3</sub> (C <sub>5</sub> Me <sub>5</sub> )	7.46	7.51	109	15.26		109	0.6
103	Mn(CO) <sub>2</sub> (N <sub>2</sub> )(C <sub>5</sub> H <sub>5</sub> )	7.54	7.52	57	15.38		60	0.5
104	Re(CO) <sub>5</sub> Br	8.83	8.56	100	16.05	17.18	100	0.9
105	Re(CO) <sub>3</sub> (C <sub>5</sub> H <sub>5</sub> )	8.05	7.72	109	15.61		111	0.5
106	Fe(CO) <sub>4</sub> H <sub>2</sub>	9.65	9.77	108	18.00	18.40	112	0.5
107	Fe(CO) <sub>2</sub> (CH <sub>3</sub> )(C <sub>5</sub> H <sub>5</sub> )	7.79	7.86	111	15.77		111	0.5
108	Fe(CO) <sub>2</sub> (Br)(C <sub>5</sub> H <sub>5</sub> )	7.93	8.51	111	16.51		111	0.5

<sup>a</sup>Ionization energies (IP(calcd)) were calculated by using eq 4 and the parameter Δk<sub>L</sub>.

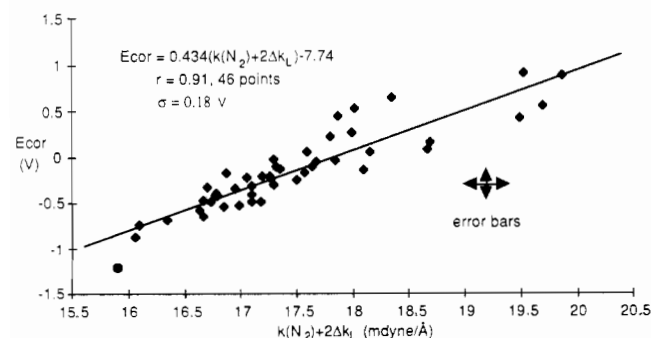
eV, and this is within the standard deviations involved. The equations are also consistent with results from a series of pyridine

N-oxide compounds (E<sub>1/2</sub>(ox) = 0.73 IP - 4.33)<sup>26</sup> and aromatic hydrocarbons (E<sub>1/2</sub>(ox) = 0.68 IP - 3.95 or E<sub>1/2</sub>(ox) = 0.71 IP

**Table III.** Electrochemical and Infrared Data for d<sup>6</sup>, Octahedral Dinitrogen Complexes<sup>a</sup>

no.	M(L) <sub>n</sub>	E(obsd), V	E(calcd), V	ref	k(NN), mdyn Å <sup>-1</sup>	ref	Δk <sub>L</sub> , mdyn Å <sup>-1</sup>
42	<i>trans</i> -Mo(N <sub>2</sub> )(CO)(dppe) <sub>2</sub>	-0.13	0.12	19	18.10	19	0.0
109	Mo(N <sub>2</sub> )(η <sup>6</sup> -C <sub>6</sub> H <sub>5</sub> PPhMe)(PMePh <sub>2</sub> ) <sub>2</sub>	-0.13	-0.21	90	16.16	113	0.6
110	Mo(N <sub>2</sub> )(η <sup>6</sup> -C <sub>6</sub> H <sub>5</sub> PPh <sub>2</sub> )(dppe) <sub>2</sub>	-0.03	0.01	91	16.65	91	0.6
111	Mo(N <sub>2</sub> ) <sub>2</sub> (P(OMe) <sub>3</sub> )(PMePh <sub>2</sub> ) <sub>3</sub>	-0.11	-0.22	22	16.32	22	0.5
112	<i>trans</i> -Mo(N <sub>2</sub> ) <sub>2</sub> (PMePh <sub>2</sub> ) <sub>4</sub>	-0.17	-0.41	22	15.88	22	0.5
113	<i>trans</i> -Mo(N <sub>2</sub> ) <sub>2</sub> (PPh <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SMe)(PMePh <sub>2</sub> ) <sub>2</sub>	-0.31	-0.32	22	16.10	22	0.5
114	Mo(N <sub>2</sub> ) <sub>2</sub> (3-Fpy)(PMePh <sub>2</sub> ) <sub>3</sub>	-0.40	-0.46	22	15.78	22	0.5
115	Mo(N <sub>2</sub> ) <sub>2</sub> (3-PPh <sub>2</sub> py)(PMePh <sub>2</sub> ) <sub>3</sub>	-0.42	-0.46	22	15.77	22	0.5
116	Mo(N <sub>2</sub> ) <sub>2</sub> (3-pic)(PMePh <sub>2</sub> ) <sub>3</sub>	-0.46	-0.51	22	15.67	22	0.5
117	Mo(N <sub>2</sub> ) <sub>2</sub> (4-pic)(PMePh <sub>2</sub> ) <sub>3</sub>	-0.48	-0.47	22	15.74	22	0.5
118	Mo(N <sub>2</sub> ) <sub>2</sub> ( <i>N</i> -MeIm)(PMePh <sub>2</sub> ) <sub>3</sub>	-0.65	-0.51	22	15.67	22	0.5
119	<i>trans</i> -Mo(N <sub>2</sub> ) <sub>2</sub> (( <i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> PCH <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub>	0.30	-0.01	21	16.80	21	0.5
120	<i>trans</i> -Mo(N <sub>2</sub> ) <sub>2</sub> (( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> PCH <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub>	0.05	-0.10	21	16.60	21	0.5
121	<i>trans</i> -Mo(N <sub>2</sub> ) <sub>2</sub> (( <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> PCH <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub>	-0.25	-0.15	21	16.50	21	0.5
122	<i>trans</i> -Mo(N <sub>2</sub> ) <sub>2</sub> (dppe) <sub>2</sub>	-0.16	-0.11	114	16.58	115	0.5
123	<i>trans</i> -Mo(N <sub>2</sub> ) <sub>2</sub> (( <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> PCH <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub>	-0.30	-0.23	21	16.30	21	0.5
124	<i>trans</i> -Mo(N <sub>2</sub> ) <sub>2</sub> (depe) <sub>2</sub>	-0.43	-0.45	114	15.80	21	0.5
125	<i>trans</i> -Mo(N <sub>2</sub> )(PhCN)(dppe) <sub>2</sub>	-0.48	-0.28	116	15.59	117	0.8
126	<i>trans</i> -Mo(N <sub>2</sub> )(CH <sub>3</sub> CN)(dppe) <sub>2</sub>	-0.58	-0.52	116	15.04	117	0.8
127	<i>trans</i> -Mo(N <sub>2</sub> )(SCN)(dppe) <sub>2</sub> <sup>-</sup>	-0.87	-0.77	19	14.27	19	0.9
128	<i>trans</i> -Mo(N <sub>2</sub> )(N <sub>3</sub> )(dppe) <sub>2</sub> <sup>-</sup>	-1.19	-0.84	19	14.11	19	0.9
129	<i>trans</i> -W(N <sub>2</sub> ) <sub>2</sub> (( <i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> PCH <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub>	0.23	0.03	21	16.30	21	0.5
130	<i>trans</i> -W(N <sub>2</sub> ) <sub>2</sub> (( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> PCH <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub>	0.06	-0.02	21	16.20	21	0.5
131	<i>trans</i> -W(N <sub>2</sub> ) <sub>2</sub> (dppe) <sub>2</sub>	-0.15	-0.05	114	16.11	115	0.5
132	<i>trans</i> -W(N <sub>2</sub> ) <sub>2</sub> (( <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> PCH <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub>	-0.22	-0.06	21	16.10	21	0.5
133	<i>trans</i> -W(N <sub>2</sub> ) <sub>2</sub> (( <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> PCH <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub>	-0.28	-0.16	21	15.86	21	0.5
134	<i>trans</i> -W(N <sub>2</sub> ) <sub>2</sub> (depe) <sub>2</sub>	-0.45	-0.38	114	15.35	21	0.5
135	<i>trans</i> -W(N <sub>2</sub> ) <sub>2</sub> (( <i>Cy</i> ) <sub>2</sub> PCH <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub>	-0.48	-0.49	21	15.10	21	0.5
136	Re(N <sub>2</sub> )(Cl)(CO)(P(OMe) <sub>3</sub> ) <sub>3</sub>	0.81	1.07	32	17.70	32	1.0
137	Re(N <sub>2</sub> )(Cl)(CO)(P(OMe) <sub>3</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	0.69	0.98	32	17.49	32	1.0
138	<i>trans</i> -Re(N <sub>2</sub> )(Cl)(P(OMe) <sub>3</sub> ) <sub>4</sub>	0.42	0.64	32	16.70	32	1.0
139	Re(N <sub>2</sub> )(NCPh)(dppe) <sub>2</sub> <sup>+</sup>	0.91	0.48	32	16.95	32	0.7
140	Re(N <sub>2</sub> )(NCMe)(dppe) <sub>2</sub> <sup>+</sup>	0.79	0.34	32	16.62	32	0.7
141	<i>trans</i> -Re(N <sub>2</sub> )(Cl)(dppe) <sub>2</sub>	0.29	0.40	20	16.16	20	1.0
142	<i>trans</i> -Re(N <sub>2</sub> )(Cl)(( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> PCH <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub>	0.52	0.33	20	16.00	20	1.0
143	<i>trans</i> -Re(N <sub>2</sub> )(Cl)(( <i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> PCH <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub>	0.71	0.27	20	15.87	20	1.0
144	<i>trans</i> -Re(N <sub>2</sub> )(Cl)(( <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> PCH <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub>	0.21	0.19	20	15.68	20	1.0
145	<i>trans</i> -Re(N <sub>2</sub> )(Cl)(( <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> PCH <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub>	0.15	0.18	20	15.64	20	1.0
146	<i>trans</i> -Re(N <sub>2</sub> )(Cl)(depe) <sub>2</sub>	0.03	0.02	20	15.28	20	1.0
147	<i>trans</i> -Re(N <sub>2</sub> )(Cl)(( <i>Cy</i> ) <sub>2</sub> PCH <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub>	0.04	-0.08	20	15.05	20	1.0
148	<i>trans</i> -Re(N <sub>2</sub> )(Cl)(PMe <sub>2</sub> Ph) <sub>4</sub>	0.05	0.02	118	15.27	119	1.0
149	Re(N <sub>2</sub> )(dtc)(PMe <sub>2</sub> Ph) <sub>3</sub>	-0.26	-0.11	118	15.59	120	0.7
150	Re(N <sub>2</sub> )(Cl)(py)(PMe <sub>2</sub> Ph) <sub>3</sub>	-0.09	-0.12	118	14.96	120	1.0
151	Fe(N <sub>2</sub> )H(dppe) <sub>2</sub> <sup>+</sup>	0.91	0.74	19	18.53	121	0.5
152	Ru(N <sub>2</sub> )(NH <sub>3</sub> ) <sub>5</sub> <sup>2+</sup>	0.88	0.88	54	18.27	54	0.8
153	Os(N <sub>2</sub> )(NH <sub>3</sub> ) <sub>5</sub> <sup>2+</sup>	0.34	0.62	54	17.07	54	0.8

<sup>a</sup> The  $E_{1/2}(\text{ox})$  values ( $E(\text{calcd})$ ) were calculated by using eq 7 and the parameter  $\Delta k_L$ . Abbreviations: pic, picoline; *N*-MeIm, *N*-methylimidazole; depe, 1,2-bis(diethylphosphino)ethane; dtc, dithiocarbamate.



**Figure 4.** Plot of  $E_{1/2}(\text{ox})$  values for dinitrogen complexes corrected for the row of the transition metal ( $E(\text{corr}) = E_{1/2}(\text{ox})$  for 3d or 4d metals,  $E(\text{corr}) = E_{1/2}(\text{ox}) - 0.26$  for 5d metals) vs.  $k(\text{N}_2)$  corrected for the influence of the trans ligand ( $k(\text{N}_2) + 2\Delta k_L$ ). The line is the least-squares fit (eq 7).

- 3.68),<sup>27,28</sup> where the  $E_{1/2}(\text{ox})$  data are referenced to the SCE. Different correlations are obtained if different reference electrodes are used.<sup>25,59</sup> The slope is always less than unity because the

difference in solvation energy of the d<sup>5</sup> and d<sup>6</sup> species is a function of the electron richness of the species as reflected by the  $E_{1/2}(\text{ox})$  values.<sup>26</sup> When the ionization potential data are converted into volts by using eq 5, then the best fit to the data is eq 2, as is expected; the line in Figure 3 is consistent with both eq 2 and eq 4.

**Dinitrogen Complexes.** For the dinitrogen data, a plot of  $E_{1/2}(\text{ox})$  vs.  $k(\text{N}_2)$  gives  $\sigma = 0.68$  mdyn Å<sup>-1</sup> and  $r = 0.74$ . It is expected that  $\nu(\text{N}_2)$  will be more sensitive than CO to the nature of trans and cis ligands and to the metal. The trans ligand effect can be accounted for by plotting  $E_{1/2}(\text{ox})$  vs.  $k(\text{N}_2) + x(\Delta k_L)$  and optimizing  $x$ . The value  $x = 2$  gave the highest correlation coefficient,  $r = 0.86$ ; thus, the  $\nu(\text{N}_2)$  mode appears to be about 2 times more sensitive to the nature of the trans ligand than  $\nu(\text{CO})$ . However, the data for the 5d metals were off the least-squares line defined by the 4d metals by 0.26 V so that a corrected  $E_{1/2}(\text{ox})$  value,  $E(\text{corr})$  was used:

$$E(\text{corr}) = 0.434(k(\text{N}_2) + 2\Delta k_L) - 7.74 \quad (7)$$

$$\sigma = 0.18, r = 0.91$$

where  $E(\text{corr}) = E_{1/2}(\text{ox})$  for 4d metals and  $E(\text{corr}) = E_{1/2}(\text{ox}) - 0.26$  for 5d metals. Therefore, the 5d metal complexes are a little less reducing than their  $\nu(\text{N}_2)$  values would suggest on the basis



**Table IV.** Ligand Parameters  $\Delta k_L$  Optimized for Use in Eq 1–4 and Eq 7 and  $\Delta k$  Derived from Timney's Parameters by Use of Eq 8

ligand	$\Delta k_L$ , mdyn Å <sup>-1</sup>	$\Delta k$ from eq 8, mdyn Å <sup>-1</sup>
C(OMe)Ar	-0.1 ± 0.2	
CO	0.0 ± 0.1	
0.5 dmpe	0.2 ± 0.2	
PMe <sub>3</sub>	0.3 ± 0.1	0.35
CNMe	0.3 ± 0.2	0.49
CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> <sup>-</sup>	0.3 ± 0.1	
PPh <sub>3</sub>	0.4 ± 0.2	0.43
PEt <sub>3</sub>	0.4 ± 0.1	0.35
P(OMe) <sub>3</sub>	0.5 ± 0.3	0.11
N <sub>2</sub>	0.5 ± 0.1	0.55
H <sup>-</sup>	0.5 ± 0.2	0.39
$\eta^5$ -C <sub>5</sub> H <sub>5</sub> <sup>-</sup>	0.5 ± 0.1	
C <sub>6</sub> H <sub>6</sub>	0.5 ± 0.2	
C <sub>6</sub> Me <sub>6</sub>	0.7 ± 0.1	
NH <sub>3</sub>	0.8 ± 0.2	1.04
Br <sup>-</sup>	0.9 ± 0.2	1.26
0.5 dppe	0.9 ± 0.2	
Cl <sup>-</sup>	1.0 ± 0.2	1.30
py	1.1 ± 0.2	1.07
bpy	1.2 ± 0.2	1.31

of equivalent complexes of 4d metals. It is not yet known whether the 3d metals will show a unique correlation as well since only one complex has been studied, **151**. The plot of  $E(\text{cor})$  vs.  $k(\text{N}_2) + 2\Delta k_L$  is shown in Figure 4. Of the 45 complexes listed in Table III, 33 are within 1 $\sigma$  and 42 are within 2 $\sigma$  of observed values. Complexes **139**, **140**, and **143** deviate by about 0.43 V from the observed values. The last of the three definitely involves a cis effect that has been previously discussed,<sup>21</sup> but this is not accounted for by eq 7.

Only one dinitrogen complex, Mn(C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>(N<sub>2</sub>), has been studied by PES.<sup>57</sup> The first IP is 7.54 eV. The calculated IP from the CO force constant of 15.38 mdyn Å<sup>-1</sup>,<sup>60</sup>  $\Delta k_L = 0.5$  for  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>, and eq 4 is 7.53 eV. The calculated IP from the N<sub>2</sub> force constant of 19.39 mdyn Å<sup>-1</sup> ( $\nu(\text{N}_2) = 2169 \text{ cm}^{-1}$ )<sup>60</sup> and eq 6 and 7 is 7.75 eV, which is within the standard deviation of the correlation. The  $E_{1/2}(\text{ox})$  value for this compound is predicted by eq 2 or 6 to be about 1.05 ± 0.17 V. The oxidation of this compound is actually irreversible.<sup>58</sup>

Equations 2 and 7 can be used to predict with some confidence the  $E_{1/2}(\text{ox})$  value of species that contain both dinitrogen and carbonyl ligands. An example is Cr(N<sub>2</sub>)(CO)<sub>5</sub>, which is stable only at very low temperatures.<sup>61</sup> Both eq 2 and 7 predict a value of 1.21 ± 0.17 V from the force constants  $k_1(\text{CO}) = 15.81$ ,  $k_2(\text{CO}) = 16.27$ ,  $k(\text{N}_2) = 20.63$ , and  $\Delta k_L = 0.5 \text{ mdyn Å}^{-1}$ . The  $P_L$  method of Chatt et al. predicts a value of about 1.4 V.<sup>19</sup>

**Comparison of Ligand Parameters.** The  $\Delta k_L$  parameters listed in Table IV are used in an effort to convert a force constant of a CO ligand trans to L ( $k_1$ ) to the force constant that would result if that CO ligand were trans to a CO ligand in the same molecule. Timney's successful method for predicting carbonyl force constants from additive cis and trans ligand parameters,  $\epsilon_L^{\text{cis}}$  and  $\epsilon_L^{\text{trans}}$ ,<sup>29</sup> can also be applied to make this correction. For example, in complexes of the type M(CO)<sub>3</sub>L, *cis*-M(CO)<sub>4</sub>L<sub>2</sub> and *mer*-M(CO)<sub>3</sub>L<sub>3</sub>, the difference in force constants for CO trans to L and CO trans to CO,  $\Delta k(\text{CO}) = k_2(\text{CO}) - k_1(\text{CO})$ , can be expressed as

$$\Delta k(\text{CO}) = \epsilon_L^{\text{cis}} - \epsilon_{\text{CO}}^{\text{cis}} + \epsilon_{\text{CO}}^{\text{trans}} - \epsilon_L^{\text{trans}} \quad (8)$$

These values, where available, are given in Table IV for comparison with our  $\Delta k_L$  values. The agreement on the whole is good. Once again the phosphite ligands in our treatment deviate; Timney's value of 0.1 is probably the better one. In fact, if the  $\Delta k(\text{CO})$  values are used in place of our values when possible, the correlation coefficients of eq 2 and eq 4 change very little, to 0.96 ( $\sigma = 0.18 \text{ V}$ ) and 0.94 ( $\sigma = 0.30 \text{ eV}$ ), respectively.

An even simpler approach is to assign more approximate  $\Delta k_L$  parameters: halides or pseudohalides (0.9), N-donors apart from N<sub>2</sub> (0.9), P-donors (0.5), N<sub>2</sub> (0.5), alkyl or hydride (0.5), cyclopentadienyl or  $\eta^6$ -arene (0.5), neutral  $\eta^1$ -C-donors (0). This approach gives a correlation coefficient of 0.95 ( $\sigma = 0.19$ ) for eq 2 and could be used to estimate  $E_{1/2}(\text{ox})$  values when the ligand parameters are not known. The  $\Delta k$  values may also be related to Bursten's ligand parameter "c", which expresses the splitting of the  $t_{2g}$  orbitals in d<sup>6</sup> complexes  $\text{ML}_n\text{L}'_{6-n}$ , because L' is a poorer  $\pi$  acceptor than L. The splitting in volts<sup>15</sup> or electronvolts<sup>30</sup> between the highest two occupied d orbitals is "c" for complexes with  $n = 5$ ,  $n = 4$  (*cis*),  $n = 3$  (*mer*),  $n = 2$  (*cis*), and  $n = 1$ . It is 2c for  $n = 4$  (*trans*) and  $n = 2$  (*trans*). If force constants respond in a linear fashion to orbital energy, as is suggested by eq 2 and eq 5, then  $k_1$  usually corresponds to the carbonyl  $\pi$ -bonded with the HOMO whereas  $k_2$  corresponds to a carbonyl conjugated with an orbital about an energy  $c$  below this HOMO. The value of "c" for the CNMe ligand in the complexes  $\text{Mn}(\text{CNMe})_n(\text{CO})_{6-n}$  and  $\text{Cr}(\text{CNMe})_n(\text{CO})_{6-n}$  is about 0.125 ± 0.010 V.<sup>15</sup> Our  $\Delta k_L$  value for CNMe is 0.3 ± 0.1 mdyn Å<sup>-1</sup>, which when converted to volts by use of eq 2 gives (0.567 V Å mdyn<sup>-1</sup>)(0.3 mdyn Å<sup>-1</sup>) = 0.17 ± 0.06 V. The value of "c" for the PMe<sub>3</sub> ligand in complexes  $\text{Mo}(\text{PMe}_3)_n(\text{CO})_{6-n}$  is 0.25 eV.<sup>30</sup> The  $\Delta k_L$  value for this ligand of 0.3 ± 0.1 mdyn Å<sup>-1</sup> gives a value of 0.26 ± 0.10 eV by use of eq 5. Similarly the value from  $\Delta k_L$  for PEt<sub>3</sub> gives 0.35 ± 0.10 eV whereas  $c = 0.26 \text{ eV}$ .<sup>30</sup> Thus the agreement is reasonable.

## Discussion

The reasonably good linear correlation between the  $E_{1/2}(\text{ox})$  potential for d<sup>6</sup>, octahedral complexes and force constants for the CO ligand displayed in Figure 2 and expressed by eq 2 indicates that the carbonyl stretching frequencies of a molecule can indeed be used to obtain a good measure of the electron richness or reducing character of the molecule. It is surprising that the correlation is so good ( $r = 0.97$ ) considering that the data represent a very wide range of transition-metal complexes and were measured under a variety of experimental conditions (solvent, electrode, temperature). The extremes in Figure 2 are the very electron rich anions **48–51** containing electron-donating ligands (phosphine and halide or pseudohalide ligands) and the very electron poor cations containing isocyanide ligands **56** and **73** and neutral species containing five or six carbonyl ligands, **2**, **4**, and **55**. Even anionic and cationic complexes are included despite the fact that the differences in solvation energies between the reduced (d<sup>6</sup>) and oxidized (d<sup>5</sup>) species will be quite different for each type. Equation 2 provides an estimate of the  $E_{1/2}(\text{ox})$  value of a compound to ±0.2 V when its carbonyl stretching frequencies are known.

The ligand parameter  $\Delta k_L$  for the ligand trans to the CO with the force constant of interest was introduced to give the good correlation. Although introducing separate cis and trans parameters might improve the fit, the introduction of another parameter is not justified considering the small number of experimental data for each cis ligand that exist to date. Braterman has stressed that CO force constants can be used as a qualitative probe of electron density but not as a probe of specific bonding.<sup>62</sup> Certainly cis effects are important (for example see ref 21) and the  $\Delta k_L$  parameter includes a component of these as well. This can be seen in its proposed relationship to Timney's additive ligand parameters (eq 8). Both  $\epsilon_L^{\text{cis}}$  and  $\epsilon_L^{\text{trans}}$  parameters are involved. It was shown above that the parameters derived by using eq 8 also give a good correlation coefficient when used in eq 3 or 5. It was also shown that  $\Delta k_L$  appears to approximate the "c" parameter of the ligand additivity scheme of Bursten,<sup>15</sup> which is a measure of the difference in the abilities of ligands L and CO (in this case) to stabilize  $d\pi$  orbitals by  $\pi$  back-bonding. It may also be possible to link  $\Delta k_L$  parameters to the  $P_L$  parameter for electrochemical data<sup>19</sup> and to group binding-energy shifts for XPS.<sup>63</sup>

The value of being able to predict  $E_{1/2}(\text{ox})$  or IP values by use of ligand additivity schemes has already been demonstrated by

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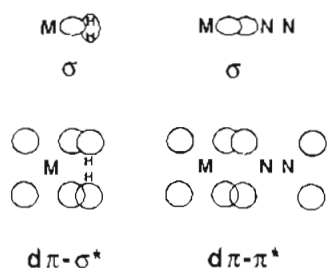


Figure 5. Similarities in orbital overlap between molecular hydrogen and molecular nitrogen coordinated to a transition metal, M.

the work of the groups of Chatt, Leigh, and Pickett<sup>18,19,32</sup> of Bursten,<sup>15,30</sup> and of Lichtenberger.<sup>30,64</sup> The identities of unstable complexes have been confirmed,<sup>18</sup> the differences in redox potentials or ionization of isomeric complexes have been explained,<sup>15,18,30</sup> and the reactivity of coordinated dinitrogen toward electron transfer or electrophilic attack<sup>18</sup> or even nucleophilic attack<sup>32</sup> has been rationalized on the basis of predicted values. The usefulness of Turney's parameters for carbonyl force constants has also been demonstrated in the identification of unstable carbonyl complexes by Poliakoff, Turner, and others (see ref 61 for example). Angelici's group has proven the utility of force constants in explaining and predicting the reactivity of carbonyl or ancillary ligands to nucleophilic attack.<sup>44,45</sup> Our correlations should also prove of use in rationalizing the structure and reactivity of carbonyl, dinitrogen, and dihydrogen complexes (see below).

**Molecular Hydrogen Complexes.** We were interested in obtaining such equations in order to better understand the energetics of bonding of the novel  $\eta^2$ -dihydrogen ligand. The questions to answer are which combination of oxidation state of the metal and donor abilities of the ancillary ligands favors the stable coordination of this unique ligand and at what stage is the metal complex so reducing that homolytic cleavage of the H-H bond results in the formation of a dihydride complex. We and others have noted that the binding site of  $\eta^2$ -H<sub>2</sub> in octahedral, d<sup>6</sup> complexes—M(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>, (M = Mo, W; R = Cy, *i*-Pr)<sup>1-3</sup> Mo(CO)(PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>,<sup>2</sup> M(CO)<sub>5</sub> (M = Cr,<sup>4-7</sup> Mo,<sup>5</sup> W<sup>5</sup>), M(H)(PR<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PR<sub>2</sub>)<sub>2</sub><sup>+</sup> (M = Fe, Ru; R = Ph, Et),<sup>11,12</sup> and MH<sub>2</sub>(PR<sub>3</sub>)<sub>3</sub> (M = Fe, Ru)<sup>9</sup>—also usually allows CO and N<sub>2</sub> coordination. The frequencies  $\nu$ (N<sub>2</sub>) for the dinitrogen complexes are all greater than 2050 cm<sup>-1</sup>. These are high compared to those in the electron-rich complexes M(N<sub>2</sub>)<sub>2</sub>(PR<sub>3</sub>)<sub>4</sub>, (M = Mo, W), which have  $\nu$ (N<sub>2</sub>) < 1950 cm<sup>-1</sup> and which reduce N<sub>2</sub> to ammonia when treated with strong acids. Thus, the  $\eta^2$ -H<sub>2</sub> binding sites do not back-bond strongly to N<sub>2</sub>. This accords with the binding sites' inability to back-donate  $d\pi$  electrons strongly enough into the  $\sigma^*$  orbital of the H<sub>2</sub> ligand to split it apart. We wondered what infrared data from related CO and N<sub>2</sub> ligands could tell us about the energy of these important  $d\pi$  electrons. Electrochemical measurements have not yet been reported for the molecular hydrogen complexes, but we find that a combination of force constant and electrochemical data for the N<sub>2</sub> derivatives and, to a lesser extent, CO derivatives explains much of the behavior of the  $\eta^2$ -H<sub>2</sub> ligand at different binding sites. The relationship between the  $\eta^2$ -H<sub>2</sub> and  $\eta^1$ -N<sub>2</sub> ligands is apparent from their orbital diagrams (Figure 5). Both ligands rely on some back-bonding for stability: the former involves  $d\pi \rightarrow \sigma^*$  back-bonding<sup>65</sup> whereas the latter uses  $d\pi \rightarrow \pi^*$  back-bonding into degenerate  $\pi^*$  orbitals on the dinitrogen.

The infrared data and redox potentials of carbonyl and dinitrogen adducts of three  $\eta^2$ -H<sub>2</sub> binding sites, Mo(CO)(dppe)<sub>2</sub>, Fe(H)(dppe)<sub>2</sub><sup>+</sup>, and Cr(CO)<sub>5</sub>, are plotted in Figure 6. The redox potential for Cr(CO)<sub>5</sub>(N<sub>2</sub>) was calculated above. Also plotted are lines derived from eq 1 for force constants for CO trans to CO ( $\Delta k_L = 0$ ) and CO trans to H<sup>-</sup> or N<sub>2</sub> ( $\Delta k_L = 0.5$ ) and from eq 7 for N<sub>2</sub> trans to CO ( $\Delta k_L = 0$ ) and N<sub>2</sub> trans to H<sup>-</sup> ( $2\Delta k_L$

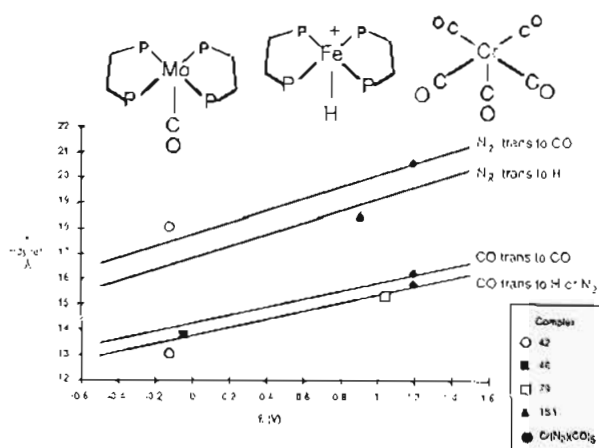


Figure 6. Plot of  $k(\text{CO})$  or  $k(\text{N}_2)$  vs.  $E_{1/2}(\text{ox})$  for binding sites for CO and N<sub>2</sub> that also coordinate  $\eta^2$ -H<sub>2</sub>. The points fall close to lines defined by eq 1 or eq 7 with the appropriate correction for the trans ligand ( $\Delta k_L = 0.5$  for CO trans to H<sup>-</sup> or N<sub>2</sub>,  $\Delta k_L = 0.0$  for CO trans to CO,  $2\Delta k_L = 1.0$  for N<sub>2</sub> trans to H<sup>-</sup>,  $2\Delta k_L = 0.0$  for N<sub>2</sub> trans to CO).

= 1.0) for a 3d or 4d metal. The Mo binding site is much more electron rich than the Fe or Cr sites, yet the Mo complex exists in solution as the  $\eta^2$ -H<sub>2</sub> complex and not as a classical dihydride.<sup>2</sup> The high  $k(\text{N}_2)$  value for this complex is the indicator that the trans CO ligand is also important in preventing too much back-donation into the  $\sigma^*$  orbital of the H<sub>2</sub> ligand, which would result in homolytic cleavage. Whereas the electron-rich complexes *trans*-Mo( $\eta^2$ -H<sub>2</sub>)(CO)(dppe)<sub>2</sub> and Mo(CO)<sub>5</sub>( $\eta^2$ -H<sub>2</sub>)(P(Cy)<sub>3</sub>)<sub>2</sub> (the dinitrogen adduct has  $k(\text{N}_2) \approx 18.5$  mdyn Å<sup>-1</sup>) are stable at room temperature with  $\eta^2$ -H<sub>2</sub> trans to CO, the complex Cr(CO)<sub>5</sub>(H<sub>2</sub>) is very unstable at these temperatures because it is electron poor as judged by its N<sub>2</sub> and CO derivatives (see Figure 6) and has  $\eta^2$ -H<sub>2</sub> trans to CO. Very little  $d\pi \rightarrow \sigma^*$  back-bonding is possible under these circumstances. The cationic Fe complex is also electron poor. It must be the trans H<sup>-</sup> ligand, a good  $\sigma$  donor, that is responsible for promoting, in an inductive fashion,  $d\pi \rightarrow \sigma^*$  back-bonding to the H<sub>2</sub> ligand or, in the case of the dinitrogen complex,  $d\pi \rightarrow \pi^*$  back-bonding to the N<sub>2</sub> ligand. The complex Ru(H<sub>2</sub>)(H)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub><sup>9</sup> probably also has  $\eta^2$ -H<sub>2</sub> trans to H<sup>-</sup>, and it also is electron poor with predicted  $E_{1/2}(\text{ox})$  values of 0.94 V for Ru(N<sub>2</sub>)(H)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> ( $\nu(\text{N}_2) = 2147$  cm<sup>-1</sup>,  $k(\text{N}_2) = 19.0$  mdyn Å<sup>-1</sup>) and 0.90 V for Ru(CO)(H)<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> ( $\nu(\text{CO}) = 1942$  cm<sup>-1</sup>,  $k(\text{CO}) = 15.23$  mdyn Å<sup>-1</sup>).<sup>66</sup>

Therefore, stable d<sup>6</sup> molecular hydrogen complexes should be obtained when the force constant,  $k(\text{N}_2)$ , of the related dinitrogen complex falls in the range of about 17.5–19.0 mdyn Å<sup>-1</sup> (2060–2150 cm<sup>-1</sup>). The extremes in this range occur when the N<sub>2</sub> (or  $\eta^2$ -H<sub>2</sub>) ligand is trans to CO in a fairly electron-rich complex ( $E_{1/2}(\text{ox}) \approx 0$  V) or trans to a good  $\sigma$ -donor in an electron-poor ( $E_{1/2}(\text{ox}) \approx 1$  V) complex. The corresponding carbonyl force constant range is about 14.0 when CO is trans to CO to 15.5 mdyn Å<sup>-1</sup> when CO is trans to a good  $\sigma$  donor (1860–1960 cm<sup>-1</sup>) although this is not as sensitive an indicator as the  $k(\text{N}_2)$  values because the  $E_{1/2}(\text{ox})/k(\text{CO})$  gradient is less than the  $E_{1/2}(\text{ox})/k(\text{N}_2)$  gradient and the trans ligand effect is less.

If  $k(\text{N}_2)$  of the related dinitrogen complex is lower than 17.5 mdyn Å<sup>-1</sup>, then homolytic cleavage of the H<sub>2</sub> ligand to hydrides is likely to occur. Thus, for example the ReH(dppe)<sub>2</sub> binding site cleaves H<sub>2</sub> to give ReH<sub>3</sub>(dppe)<sub>2</sub><sup>67</sup> because it is too electron rich for Re(H<sub>2</sub>)H(dppe)<sub>2</sub> to be stable as judged by its N<sub>2</sub> complex ( $k(\text{N}_2) = 16.2$  mdyn Å<sup>-1</sup>,  $E_{1/2} = 0.0$  V from eq 7) and by its CO complex ( $k(\text{CO}) = 13.75$  mdyn Å<sup>-1</sup>,  $E_{1/2} = 0.06$  V from eq 2).<sup>68</sup>

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The isoelectronic cation Os(H<sub>2</sub>)HL<sub>2</sub><sup>+</sup> (L = PEt<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PEt<sub>2</sub>), which is more electron poor, keeps the H-H bond,<sup>12</sup> and this is consistent with  $k(\text{N}_2) = 18.6 \text{ m dyn } \text{\AA}^{-1}$  for Os(N<sub>2</sub>)HL<sub>2</sub><sup>+</sup>. Similarly, seven-coordinate MoH<sub>2</sub>(PMe<sub>3</sub>)<sub>5</sub>,<sup>69</sup> with electron-donating ligands is a dihydride whereas Mo(H<sub>2</sub>)(CO)<sub>5</sub><sup>5</sup> with electron-withdrawing CO ligands is a thermally unstable  $\eta^2\text{-H}_2$  complex. The corresponding dinitrogen complexes have  $k(\text{N}_2) = 15.7^{70}$  and  $20.6^{71} \text{ m dyn } \text{\AA}^{-1}$ , respectively, with the latter value falling above the limit of about  $19 \text{ m dyn } \text{\AA}^{-1}$  for a stable  $\eta^2\text{-H}_2$  binding site at 25 °C. The recent ab initio calculations of Hay<sup>65</sup> show how, by replacement of PH<sub>3</sub> groups with CO ligands in WH<sub>2</sub>(PH<sub>3</sub>)<sub>3</sub>, the oxidative addition of H<sub>2</sub> is arrested in the complex W(H<sub>2</sub>)(P-H<sub>3</sub>)<sub>2</sub>(CO)<sub>3</sub>. Andrews, Kirtley, and Kesz made early use of the term "arrested oxidative addition" to describe the bonding in the complex Mn( $\eta^2\text{-HSiPh}_3$ )(C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>.<sup>72</sup> They suggested that

since oxidative addition of the HSi bond would require an increase by 1 in the valence bond structure around the metal, then the process might be arrested somewhere along the reaction coordinate by interligand repulsions. Our approach does not lead to a ready treatment of such repulsions for the dihydrogen complexes.

Another factor not taken into consideration by our approach is the strength of the hydride bonds formed if homolytic cleavage occurs; 5d metals near Ir in the periodic table will form strong bonds to H<sup>-</sup> so that stable Ir- $\eta^2\text{-H}_2$  binding will likely only occur for electron-poor complexes ( $E_{1/2} \approx 1 \text{ V}$ ).<sup>8,10</sup> If a binding site is too electron poor as judged by  $k(\text{N}_2) > 19 \text{ m dyn } \text{\AA}^{-1}$ , then the H<sub>2</sub> complex will be very unstable at room temperature.

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**Supplementary Material Available:** Expanded versions of Tables I-III, which contain information on solvents, reference electrodes, reversibility, calculated and observed force constants and interaction constants, and IR frequencies (4 pages). Ordering information is given on any current masthead page.

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