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Evidence for the Formation of Free 16-Electron Species Rather than Solvate Complexes in the Ultraviolet Irradiation of $CpCo(CO)_2$ in Liquefied Noble Gas Solvents

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It is now generally well established that photodissociation of a ligand from many transition metal complexes results in the formation of a solvent-stabilized metal center within picoseconds of ligand loss, even in saturated hydrocarbon solvents.[1−6] For example, Rayner and co-workers have determined that, in the gas phase, interaction between the tungsten center and hydrocarbons (RH) in $(CO)_5W(RH)$ can be as high as 12 kcal/mol,[7] and Yang and co-workers have established an approximately 8 kcal/mol binding energy for the first-row metal complex $Cp(CO)_3Mn$(*n*-heptane) in the liquid alkane.[8]

Even in unconventional solvents such as liquid Xe and Kr, there is compelling evidence for such metal−solvent interactions following the loss of a CO ligand from the metal complex.[9,10] The interaction energy between a metal center and a noble gas atom (Kr and Xe) has been estimated to be on the order of 5−10 kcal/mol, with the M−Xe bond a few kilocalories stronger than the M−Kr bond. Therefore, while noble gas atoms appear to bind to unsaturated metal centers somewhat less strongly than do hydrocarbons, the metal−noble gas bond energies are significant.

Consistent with the above observations, recently we obtained strong evidence for the formation of Cp*Rh(CO)(Xe) and Cp*Rh(CO)(Kr) complexes after photolysis of $Cp^*Rh(CO)_2$ in liquid Xe and Kr, respectively.[11,12] These molecules reacted with cyclohexane (or neopentane) to give an uninserted metal−alkane complex, $Cp^*Rh(CO)(C_6H_{12})$, which in a unimolecular step proceeded to yield the C−H activation product, $Cp^*Rh(CO)(H)(C_5H_{11})$. In analogy to the rhodium (and analogous iridium) system, irradiation of the isoelectronic cobalt complex $CpCo(CO)_2$ results in CO loss. However, the intermediate generated in the cobalt reaction does not result in overall activation of the C−H bonds of hydrocarbons. Assuming that (in analogy to the $Cr(CO)_5$, $W(CO)_5$, and $CpMn(CO)_3$ fragments studied earlier) cobalt−noble gas and cobalt−alkane complexes were probably formed in these reactions but were stable to further reaction, we decided to study the photochemistry of $CpCo(CO)_2$ in liquid Kr and Xe in the presence of hydrocarbons in order to estimate directly the relative strengths of the CpCo(CO)−noble gas and CpCo(CO)−alkane interactions.[8] However, we have found that in dramatic contrast to Cp*Rh(CO) and the coordinatively unsaturated organometallic complexes summarized above, CpCo(CO) and Cp*Co(CO) *do not bind detectably to either a noble gas atom or cyclohexane.*

The experimental apparatus has been described in detail previously.[11] Photolysis of a solution of $CpCo(CO)_2$ with 308 nm UV light in liquid Kr at 173 K generates a single transient absorption at 1999 cm^{-1} and corresponding bleaching of the parent CO stretching absorptions at 1977 and 2037 cm^{-1}. Because the 1999 cm^{-1} transient forms within the laser flash and only one CO stretching frequency is observed, we assign this absorption to a transient species containing a single carbonyl ligand. This assignment is consistent with an earlier study.[13] As shown in Figure 1a, at 186 K this transient exhibits a first-order decay with an observed rate constant of $(2.0 \pm 0.3) \times 10^6\ s^{-1}$. Significantly, there is no change in the observed rate as the cell temperature is increased from 173 to 193 K. However, the observed rate does depend linearly on the initial concentration of the parent dicarbonyl, suggesting that the fast decay of the monocarbonyl transient is due to reaction with the starting complex $CpCo(CO)_2$. A difference FTIR spectrum shows the presence of two new peaks that grow in after photolysis at 1823 and 1972 cm^{-1}. These absorptions are assigned to $Cp_2Co_2(CO)_3$, which is formed by the reaction of the monocarbonyl transient with the parent dicarbonyl.[14] If a bimolecular reaction is assumed between the monocarbonyl complex and the starting material ($[CpCo(CO)_2] = 9.3 \times 10^{-5}$ M), then the bimolecular rate constant for this reaction is $(2.1 \pm 0.4) \times 10^{10}\ M^{-1}\ s^{-1}$. Thus the intermediate reacts with $CpCo(CO)_2$ at an essentially diffusion-controlled rate.[15] The observed pseudo-first-order reaction of CpCo(CO) with $CpCo(CO)_2$ suggests that the concentration of the monocarbonyl formed upon photolysis is at most one-tenth that of the parent dicarbonyl.

Analogous results are obtained with $Cp^*Co(CO)_2$; the parent absorptions at 1955 and 2014 cm^{-1} are bleached, and a single transient at 1972 cm^{-1} appears. At 186 K this transient species decays with a first-order rate constant of $(1.4 \pm 0.2) \times 10^6\ s^{-1}$, and, as above, no temperature dependence is observed. Once again, a rate constant of $(2.3 \pm 0.4) \times 10^{10}\ M^{-1}\ s^{-1}$ is obtained by assuming a bimolecular reaction between the monocarbonyl transient and $Cp^*Co(CO)_2$.

The diffusion-controlled rate constants and lack of temperature dependence of reaction indicate that the monocarbonyl cobalt transient is exceptionally reactive compared to its rhodium congener. As noted in the introductory paragraphs, M−RH and M−Xe interactions are typically stronger than M−Kr interactions. If the above reactions involved solvates, albeit weakly bound ones, we should therefore expect that the more strongly coordinating "ligands" cyclohexane and xenon should inhibit the rates of reaction of the transient monocarbonyl with $CpCo(CO)_2$.

In contrast to this expectation, neither Xe nor cyclohexane affects the behavior of the monocarbonyl. Thus, the observed decay rates of CpCo(CO) and Cp*Co(CO) are unaffected by the addition of cyclohexane to the Kr solution, and no new product is observed in the IR spectrum. Therefore, neither CpCo(CO) nor Cp*Co(CO) appears to bind cyclohexane. Similarly, photolysis of a 2.6×10^{-4} M solution of $CpCo(CO)_2$ in liquid Xe at 217 K generates a single transient absorption at 1993 cm^{-1} and bleaching of the parent CO stretching absorptions at 1971 and 2031 cm^{-1}. The CO stretching frequency of CpCo(CO) shifts from 2010 cm^{-1} in the gas phase to 1999 cm^{-1} in liquid Kr and finally to 1993 cm^{-1} in liquid Xe. Because the CO stretching frequencies of the parent molecule $CpCo(CO)_2$ undergo very similar shifts (2045. 1985 cm^{-1} in the gas phase; 2031, 1971 cm^{-1} in liquid Xe; and 2037, 1977 cm^{-1} in liquid Kr), we believe that the shifts observed for CpCoCO are not suggestive of noble gas binding to the metal center but

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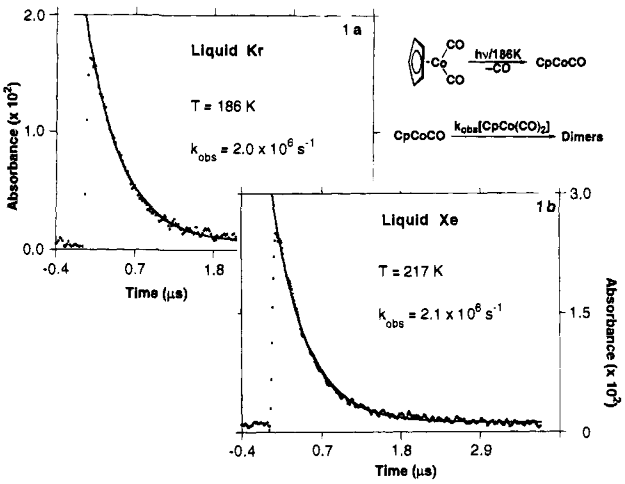

Figure 1. (a) Transient due to the cobalt monocarbonyl complex observed at 1999 cm^{-1} following UV photolysis of CpCo(CO)$_2$ in liquid Kr at 186 K. (b) Analogous monocarbonyl species observed at 1993 cm^{-1} in liquid Xe at 217 K. The solid lines represent single exponential fits to the data.

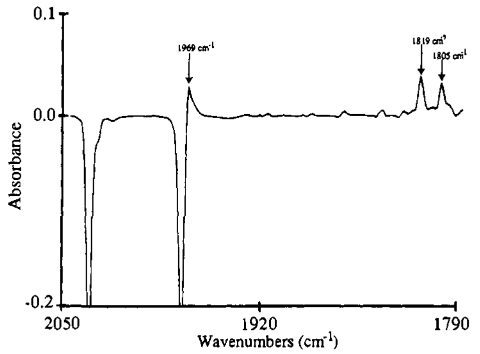

Figure 2. Difference FTIR spectrum obtained after prolonged photolysis of CpCo(CO)$_2$ in liquid Xe at 213 K. The peaks at 1969 and 1819 cm^{-1} are assigned to Cp$_2$Co$_2$(CO)$_3$. The third peak at 1805 cm^{-1} is assigned to Cp$_2$Co$_2$(CO)$_2$.

instead probably reflect interaction of solvent molecules with the oxygen end of the metal-bound CO dipole, which could be quite similar in the mono- and dicarbonyl complexes.

As shown in Figure 1b, the monocarbonyl complex absorbing at 1993 cm^{-1} decays with an observed rate of 2.3 × 10^6 s^{-1}. Once again, assuming that the decay of the monocarbonyl complex is due to a bimolecular reaction with the parent ([CpCo(CO)$_2$] = 2.6 × 10^{-4} M), the rate constant for this reaction is (8.8 ± 0.2) × 10^9 M^{-1} s^{-1}. As in liquid Kr, the reaction rate is independent of the temperature at which the experiment is conducted. As shown in Figure 2, an FTIR spectrum taken after prolonged photolysis of a solution of CpCo(CO)$_2$ in liquid Xe shows the presence of new peaks at 1819 and 1969 cm^{-1}, which are assigned to dimers (see figure caption).[16] As in liquid Kr, the rate at which CpCo(CO) decays is unaffected by addition of cyclohexane.

In summary, the transient monocarbonyl complexes generated upon irradiation of CpCo(CO)$_2$ and Cp*Co(CO)$_2$ have the following properties that distinguish them from Cp*Rh(CO)(S) solvates. First, there is no spectroscopic evidence for the formation of solvates or alkane complexes. Second, the transients react with the starting dicarbonyl at near diffusion-controlled rates that are not temperature dependent. Finally, the most surprising observation in the present study is the fact that the rate of reaction between the monocarbonyl and dicarbonyl cobalt complexes is essentially unaffected by changing the solvent from liquid Kr to liquid Xe, adding cyclohexane, or making the cyclopentadienyl ligand substantially more hindered (i.e., changing Cp to Cp*). These findings are dramatically different from those observed in the photochemistry of Cp*Rh(CO)$_2$ in liquid noble gases.[11,12,17] The rate of reaction between the rhodium monocarbonyl transient and Cp*Rh(CO)$_2$ is much less than that between Cp*Co(CO) and Cp*Co(CO)$_2$, and there is a dramatic reduction in the rhodium rate when the reaction is conducted in liquid Xe versus liquid Kr.

The diffusion-limited rate at which CpCo(CO) reacts with the parent dicarbonyl to form Cp$_2$Co$_2$(CO)$_3$ is consistent with an earlier study in which this rate was measured to be 3.6 × 10^9 M^{-1} s^{-1} in cyclohexane at room temperature.[18] The observed rate is also similar to the rate of reaction between CpCo(CO) and 1-hexene (k = 1.4 × 10^{10} M^{-1} s^{-1}) determined by Heilweil and co-workers at room temperature in n-hexane solvent.[13]

While it seems unreasonable to suggest that the amount of interaction between the Co center and the solvent is essentially zero, our results clearly show that this interaction is significantly weaker than that which has been observed for the analogous Rh complex and for other coordinatively unsaturated transition metal complexes studied thus far.[19] Based on our earlier experiments, and the more quantitative studies of Weitz and Yang summarized in the introduction to this paper, we can estimate that the Rh−Xe bond energy in Cp*Rh(CO)(Xe) is probably 8−10 kcal/mol and the Rh−Kr bond energy in the corresponding Kr complex is approximately 5 kcal/mol. If the (at least) 3 orders of magnitude difference in substitution rates between the rhodium and cobalt transients can be associated with a change in bond energies, we can conservatively estimate that the cobalt−xenon interaction energy that exists in solutions of CpCoCO in liquid Xe is at most 2 kcal/mol. However, it may be difficult to estimate bond strength by a kinetic method when spin forbiddenness is also present (see next paragraph). Therefore, it appears that the CpCo(CO) complex formed in solution is closely analogous to the "naked" 16e$^-$ CpCo(CO) complex that is generated in the gas phase upon photolysis of CpCo(CO)$_2$.

We do not understand the physical source of this unique behavior, especially since at least one other closely analogous first-row metal fragment (CpMn(CO)$_2$) appears to bind relatively strongly to hydrocarbons. Recently, however, Siegbahn has carried out preliminary *ab initio* calculations[20,21] on CpCoCO; these predict that the ground state of this molecule is a triplet, in contrast to earlier calculations that predict singlet ground states for CpRhCO and CpIrCO.[22] An attractive explanation for our results is that, like other triplet metal complexes,[20] the CpCoCO triplet exhibits essentially zero affinity for weakly-binding molecules such as alkanes (and presumably noble gases), but that it reacts rapidly with more strongly-binding ligands (e.g., CO, CpCo(CO)$_2$) by an essentially concerted coordination/spin crossover process. Further experimental and theoretical work will be necessary to explore this interesting possibility.

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[16] For reasons that remain unclear, the analogous peak is not observed when CpCo(CO)$_2$ is photolyzed in liquid Kr.

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[19] Another explanation for the rapid reaction between CpCo(CO)$_2$ and CpCo(CO) is that, for some unknown reason, CpCo(CO)$_2$ is a particularly good nucleophile, specifically toward the monocarbonyl complex. It is therefore possible that the reaction rate would be unaffected by the strength of any Cp(CO)Co−solvent interaction that may exist. However, we think this is an unlikely possibility based on the spectroscopic evidence discussed in the text and the fact that there is such a small difference in the rates at which the monocarbonyl transient undergoes reaction with any given ligand in Kr and Xe solution.

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