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Prediction of the Reactive Intermediates in Alkane Activation by Tris(pyrazolyl borate)rhodium Carbonyl

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Two intermediates are observed in the time-resolved IR spectra of the photoinitiated alkane (RH) activation reaction of Tp*Rh(CO)$_2$ (Tp* = HB−(3,5-dimethylpyrazolyl). Density functional calculations suggest that the first observed intermediate is (η^3-Tp*)Rh(CO)···(RH) (RH weakly bound), which subsequently rearranges to (η^2-Tp*)Rh(CO)(RH) (RH strongly bound) before undergoing oxidative addition to the product (η^3-Tp*)-Rh(CO)(R)(H).

Recently, Lian et al. reported time-resolved IR spectra of the photoinitiated alkane (RH) activation reaction of Tp*Rh(CO)$_2$ (Tp* = HB−(3,5-dimethylpyrazolyl). After initial photolysis and vibrational deactivation (66 ps), the spectrum shows a single intermediate with ν_{CO} of 1972 cm^{-1}. This intermediate decays with a time constant of 200 ps to a second more stable species with ν_{CO} of 1990 cm^{-1}. The latter species decays at a much slower rate to the oxidative-addition product Tp*Rh(CO)(R)H. Here, we report geometry optimizations on the singlet state of (Tp)Rh(CO) (Tp = HB−pyrazolyl) both with and without an agostically bound methane. These calculations suggest that the first observed intermediate is (η^3-Tp*)Rh(CO)···(RH) (RH weakly bound), which subsequently rearranges to (η^2-Tp*)Rh(CO)(RH) (RH strongly bound) before undergoing oxidative addition to the product (η^3-Tp*)Rh(CO)(R)(H).

Full geometry optimizations were performed using Gaussian 94's[2] implementation of density functional theory[3] on the model system TpRh(CO) + CH$_4$ (Tp = HB(C$_3$H$_3$N$_2$)$_3$). Since only one methane molecule is used to model the alkane solvent, true solvent or solvent cage effects are neglected in this study. The optimized structures are shown in Figure 1 (structures **1**−**3**). Photolysis of the singlet (η^3-Tp)Rh(CO)$_2$ should produce a singlet excited state that rapidly loses a CO to produce (η^3-Tp)Rh(CO), **1**. Since the singlet surface appears to be lower in energy than the triplet surface, **1** vibrationally relaxes to (η^3-Tp)Rh(CO)···CH$_4$, **2**, which is shown with a weakly coordinated methane. These two structures, **1** and **2**, have identical Rh−C and C−O bond lengths, a result that implies an identical ν_{CO}, which was calculated for **1** to be 1934 cm^{-1} by full second-derivative methods. The (η^3-Tp)Rh(CO) species, **2**, then could decay to a species in which the pyrazolyl borate has rearranged from an η^3 to an η^2 coordination mode. In this second intermediate, methane has strengthened its agostic interaction to form the "square-planar" d^8 species shown in **3**, which has a calculated ν_{CO} of 1956 cm^{-1}. The calculated difference, 22 cm^{-1}, is reasonably close to that observed, 18 cm^{-1}.

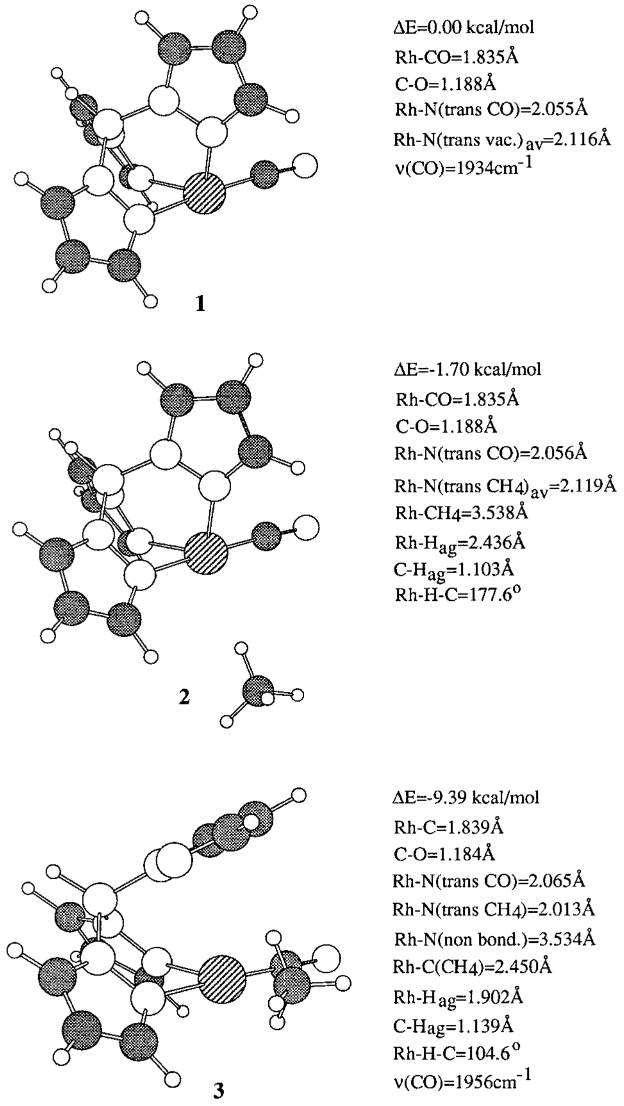

Figure 1. Optimized structures are (**1**) (η^3-Tp)Rh(CO) with a vacant coordination site (the energy includes that of free CH$_4$), (**2**) (η^3-Tp)-Rh(CO)(CH$_4$) with a weakly bound η^1-CH$_4$, and (**3**) (η^2-Tp)Rh(CO)-(CH$_4$) with a more strongly bound η^2-CH$_4$.

The energy differences, key structural parameters, and calculated ν_{CO} are also given in Figure 1. The frequency calculations show that both **1** and **3** are minima on the potential-energy surface. The agostic bonding is much stronger in (η^2-Tp)Rh(CO)(CH$_4$) (**3**) than it is in the η^3-Tp isomer (**2**). This difference is reflected in the structure, where the weaker agostic interaction in **2** is linear (η^1-CH$_4$) with a Rh−H−C angle of

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178° and the stronger interaction in **3** is bent (η^2-CH_4) with a Rh−H−C angle of 105°. Furthermore, the Rh···H agostic distance in **3** is 0.5 Å shorter than that in **2**. In (η^3-Tp)Rh($CO)_2$ the second carbonyl stabilizes the five-coordinate d^8 system. When a carbonyl (π acceptor) is removed, the (η^3-Tp) species is destabilized relative to the (η^2-Tp) species. A strong agostic interaction such as that in **3** further stabilizes the (η^2-Tp) species. Because the coordinated CH_4 is such a weak donor, the loss of the N donor in going from η^3-Tp to η^2-Tp results in a weaker Rh−C and stronger C−O bond in **3** compared with that in **2**.

As Lian et al. point out, one can postulate several alternative explanations and also raise objections to them.[1] First, one could postulate that the two observed intermediates correspond to unsolvated or weakly solvated Tp*Rh(CO) and to strongly solvated Tp*Rh(CO)(alkane). Although the time constant for the observed rearrangement (200 ps) is similar to that observed for the rearrangement of $Cr(CO)_5(ROH)$ (agostic) to $Cr(CO)_5$(OHR) (O-bound),[4−6] the observed ν_{CO} shift between Cp*Rh(CO) in Kr and in cyclohexane is only 1 cm^{-1}.[7] Second, the observed difference might be due to an initially formed triplet (singlet) that then decays to a more stable singlet (triplet). However, one would expect that for Rh, a metal with fairly large spin−orbit coupling, the decay to the lowest-energy spin state might be faster than 200 ps. Our explanation, that the two observed intermediates are (η^3-Tp*)Rh(CO) and (η^2-Tp*)Rh(CO), provides a simple way to remove these objections. The initially formed (η^3-Tp*)Rh(CO), unsolvated **1** or weakly solvated **2**, vibrationally relaxes to the first observed intermediate. Then with a time constant similar to that for the rearrangement of the $Cr(CO)_5(ROH)$, the first intermediate decays to the more stable (η^2-Tp*)Rh(CO)S (**3**) where S indicates a specific agostically bound solvent. Although at these short time scales other intermediates could be involved, the η^3-to-η^2 rearrangement provides a simple rationale for all of the observed intermediates in the photolysis of (Tp*)Rh($CO)_2$ in the presence of alkanes.

Recently, published theoretical work[8] on the rearrangement of (η^3-Tp)M(CO)(η^2-CH_2CH_2) to (η^2-Tp)M(CO)(η^2-CH_2CH_2) (M = Rh, Ir) shows that both the η^3-Tp and the η^2-Tp ethane complexes are stable species connected by a small barrier. The subsequent reaction of these species to the oxidative-addition product (η^3-Tp)M(CO)(H)($CHCH_2$) proceeds through a single transition state from both of the ethane isomers. Calculations are being carried out on (Tp)Rh(CO)(CH_4) to determine if isomers and transition states are similarly connected.

Note Added in Proof. Recent experimental work confirms our prediction of the identity of the two observed intermediates (Bromberg, S. E.; Yang, H.; Asplund, M. C.; Lian, T.; McNamara, B. K.; Kotz, K. T.; Yeston, J. S.; Wilkens, M.; Frei, H.; Bergman, R. G.; Harris, C. B. *Science* **1997**, *278*, 260).

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