Gas-Phase Ligand Exchange in a Square-Planar Rhodium(I) Complex Proceeding by Dissociative Exchange: ESI FT-ICR MS and DFT Evidence

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Although the kinetics of square-planar d^8 ligand-substitution reactions have been explored extensively in solution, no such studies of gas-phase systems have been reported. Measurement of gas-phase ligand exchange offers the advantage that the exchange mechanism is readily determined in the absence of solvent effects. The complex *trans*-$Rh(PPh_3)_2CO(4\text{-picoline})^+$ substitutes pyridine for its 4-picoline ligand readily in the gas phase but also loses CO during the reaction. The double-resonance experiments show that its primary substitution pathway proceeds dissociatively, unlike almost all solution ligand substitutions for Pt(II) and Pd(II). The density functional calculations reveal that the bond energies of Rh-4-picoline, Rh-pyridine, and Rh−CO are similar enough that CO loss might be expected. In support of the dissociative mechanism, the calculations also show five-coordinate intermediates for the associative pathway to be relatively high in energy.

Introduction

Square-planar ligand-substitution reactions comprise a well-investigated class of processes for Pt(II) and, to a lesser extent, Pd(II), Ni(II), and Au(III) metal centers.[1,2] Detailed studies into their mechanisms have shown why chemotherapeutics based upon *cis*-$Pt(NH_3)_2Cl_2$ are efficacious.[3−6] Although Pt(II) ligand-substitution reactions are reasonably well understood, little information is available for those of Rh(I) systems,[7−13] despite rhodium's prowess in homogeneous catalysis of organic reactions.[14] Square-planar Rh(I) complexes generally undergo ligand substitution very rapidly,[1] so that most analytical methods commonly used for kinetics are inappropriate. Gas-phase kinetics studies employing very fast techniques may provide insights applicable to solid catalysts containing site-isolated Rh(I) or other square-planar d^8 moieties for gas-phase reactions[12] as well as to reactions in solution.

In most Pt(II) and Pd(II) square-planar systems, ligand exchange in solution occurs by associative interchange. A five-coordinate intermediate forms first, followed by departure of the leaving ligand. There are rare exceptions to this mechanism, notably $Pt(H_2O)_4{}^{2+}$ exchanging a water for halide. That reaction proceeds by dissociative interchange: the $Pt(H_2O)_4{}^{2+}$complex loses water to give $Pt(H_2O)_3{}^{2+}$ and then binds the

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incoming halide to form $Pt(H_2O)_3X^+$.[15,16] Additionally, an Ir(I) Vaska system undergoes ligand dissociation in phosphine-ligand redistribution reactions.[17,18]

With Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS),[19] gas-phase ion−molecule reaction rate constants and equilibria are readily determined.[20−25] Most prior FT-ICR MS analysis of gas-phase metal ion−molecule reactions has been based on ions generated by electron ionization of volatile metal complexes or laser desorption/ionization to generate metal ions directly.[24−38] Here, electrospray ionization serves to transport ionic complexes intact into the gas phase.

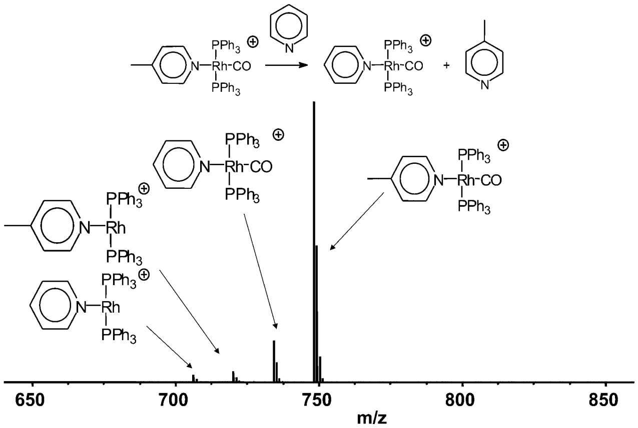

Figure 1. Gas-phase ligand exchange of pyridine for 4-picoline in $[Rh(PPh_3)_2CO(4pic)]^+$. The complex shows ready exchange of pyridine for 4-picoline but also shows some loss of the CO ligand. DFT calculations (see text) show that the Rh−ligand bond energies among $Rh-NC_5H_4-CH_3$, $Rh-NC_5H_5$, and Rh−CO are sufficiently similar to account for the observed CO loss.

In this paper, we apply FT-ICR MS/MS experiments and density functional theory (DFT) to determine and explain the gas-phase ligand exchange between *trans*-$Rh(PPh_3)_2CO(4\text{-picoline})^+$ and pyridine. The experiments definitively establish the predominant ligand exchange reaction pathway between *trans*-$Rh(PPh_3)_2CO(_4\text{-picoline})^+$ and pyridine as dissociative, not associative, in nature. The result comes as a surprise, considering that most other such ligand substitutions, at least in solution, are associative. Carbon monoxide loss is also observed, and DFT calculations corroborate that unexpected reaction pathway.

Results and Discussion

Experimental Results. Figure 1 shows the mass spectrum following the reaction of $[Rh(PPh_3)_2CO(4pic)]^+$ with pyridine for 10 s in the ICR cell. Although exchange of pyridine for 4-picoline is the primary process, a competing CO loss also occurs. This result prompted the MS/MS experiments to determine the ligand exchange mechanistic route.

Figure 2 shows an FT-ICR mass spectrum obtained as in Figure 1, but with constant irradiation at 174.24 kHz so as to eject continuously the five-coordinate $[Rh(PPh_3)_2CO(pyr)(4pic)]^+$ ions (i.e., the intermediate in the reactive collision pathway). Thus, $[Rh(PPh_3)_2CO(pyr)(4pic)]^+$ ions are removed as soon as they are formed,

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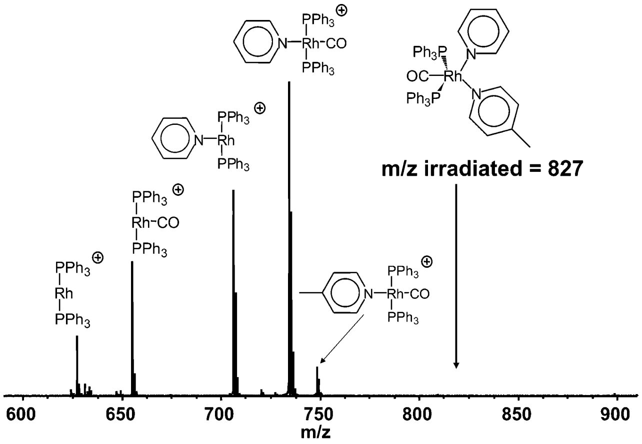

Figure 2. FT-ICR MS/MS experiment to test the associative reactive collision pathway. The putative five-coordinate intermediate is ejected continuously during the reaction period, removing it as a source of additional reactions. The rf irradiation evidently heats the complex sufficiently to form products other than the exchange products shown in Figure 1.

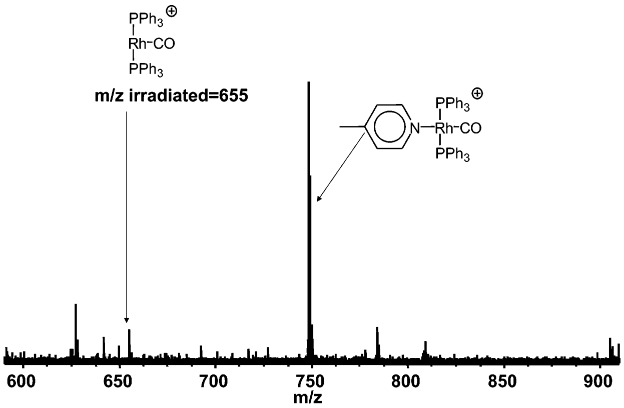

Figure 3. FT-ICR MS/MS experiment to test the dissociative collision pathway. The mass spectrum indicates that this ion must be the predominant intermediate, because its continuous ejection results in the disappearance of the main exchange product ions of Figure 1.

so that any product ions from that pathway will also be eliminated. Because the ion cyclotron frequency difference between the $[Rh(PPh_3)_2CO(4pic)]^+$ and $[Rh(PPh_3)_2CO(pyr)(4pic)]^+$ is large, the observed FT-ICR spectrum should not be significantly affected by off-resonance excitation.[39] Figure 2 shows that the primary product is still that from exchange of pyridine for 4-picoline. CO ligand loss is again the second most abundant product ion, followed by three-coordinate $[Rh(PPh_3)_2CO]^+$. Two-coordinate $[Rh(PPh_3)_2]^+$ is also observed. The latter product has been observed in other experiments and is unreactive toward H_2 or D_2 addition in the gas phase.[40]

Dramatically different behavior results from continuous ejection of $[Rh(PPh_3)_2CO]^+$ (Figure 3). All of the previously observed product ions of Figure 1 are gone, leaving less than 5% of $[Rh(PPh_3)_2CO(4pic)]^+$ (the unreacted original complex) and $[Rh(PPh_3)_2CO]^+$ (the ejected ions), indicating depletion of the ions of a necessary intermediate. The results of Figure 4 strongly point to a dissociative process, for which $[Rh(PPh_3)_2CO]^+$ is the intermediate species.

The above results can be rationalized in the following way: if the reaction in the gas phase proceeded by an associative mechanism, the intuitively likely path, then ejection of the five-coordinate intermediate would prevent formation of the substitution product. However, ejecting the putative five-coordinate intermediate does not affect the outcome of the reaction, because the substitution product is present in the spectrum along with other reaction products. The other products are observed in the absence of double resonance (data not shown). In contrast, ejection of the three-coordinate species effectively eliminates products. The three-coordinate intermediate must thus be long-lived in this gas-phase reaction.

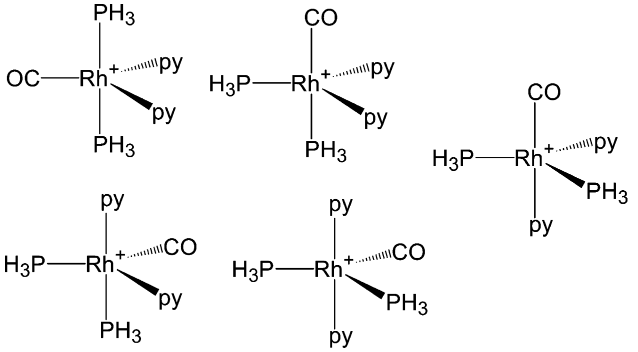

Figure 4. Trigonal-pyramidal isomers of $[Rh(PH_3)_2CO(pyr)_2]^+$ examined by DFT calculations. This ion was chosen instead of $[Rh(PPh_3)_2CO(4pic)(pyr)]^+$ to reduce the number of possible isomers for the system.

The reactant ions could in principle be heated by off-resonance excitation. The collision energy varies as the inverse square of the frequency offset between the sustained off-resonance irradiation (SORI) irradiation frequency and the ion cyclotron frequency.[39] In this case, that frequency difference is several kilohertz, so that SORI excitation of the reactant ion is negligible.

Another possible reaction path is associative interchange (S_N2). If the intermediate five-coordinate complex is short-lived, then it may not be ejected during the first experiment. However, given that no products form when the three-coordinate intermediate is ejected, the S_N2 path does not appear to contribute significantly to the reaction overall. If it did, substitution products should still be observed on ejection of the three-coordinate intermediate.

The above results, while definitive, are somewhat surprising, given that solution-phase square-planar substitution reactions typically proceed by an associative mechanism as the major pathway. Some square-planar substitutions in solution do show dissociative mechanisms: e.g., $Pt(H_2O)_4{}^{2+}$ in dimethyl sulfoxide and palladium iminoethylene bis(ethyleneamine) halides.[15,16]

Computational Results. Bond energies were calculated from the B3LYP/CSDZ* data in Table 1. As expected, the Rh–N bond energy is calculated by DFT to be slightly larger for the four-coordinate 4-picoline complex (BDE = 52 kcal/mol) than for its pyridine analogue (BDE = 50 kcal/mol). For both complexes, the Rh–CO bond energy is 52 kcal/mol. The shorter Rh–N bond for $[Rh(PH_3)_2(CO)(4pic)]^+$ compared to the pyridine analogue is consistent with the results of a survey of the Cambridge Structural Database that show a "reduced" (i.e., $MN_{X\text{-}ray} - r_{covalent}(M) = MN_{red}$) bond length of 0.907 Å ($n = 214$) for 4-picoline complexes versus $MN_{red} = 0.921$ Å for pyridine complexes ($n = 2196$).

Table 1. Calculated B3LYP/CSDZ* Energetics and Geometries

species	DFT calcd energy (au)	bond dist (Å)	bond angle (deg)
CO	−113.3069	1.14	
pyridine	−248.2796	1.34 (C−N) 1.40 (C−C)	
4-picoline	−287.5984	1.34 (C−N) 1.40 (C(sp^2)−C(sp^2)) 1.51 (C(sp^2)−C(sp^3))	
$[Rh(PH_3)_2CO]^+$	−908.9449	2.38 (Rh−P) 1.82 (Rh−C) 1.15 (CO)	177 (P−Rh−P) 92 (P−Rh−C)
$[Rh(PH_3)_2(py)]^+$	−1043.9137	2.37 (Rh−P) 2.02 (Rh−N)	177 (P−Rh−P) 91 (P−Rh−N)
$[Rh(PH_3)_2(4pic)]^+$	−1083.2359	2.36 (Rh−P) 2.02 (Rh−N)	178 (P−Rh−P) 91 (P−Rh−N)
$[Rh(PH_3)_2CO(py)]^+$	−1157.3039	2.37 (Rh−P) 2.17 (Rh−N) 1.87 (Rh−C)	177 (P−Rh−P) 180 (C−Rh−N)
$[Rh(PH_3)_2CO(4pic)]^+$	−1196.6260	2.36 (Rh−P) 2.16 (Rh−N) 1.87 (Rh−C)	178 (P−Rh−P) 180 (C−Rh−N)
$[Rh(PH_3)_2CO(py)_2]^{+\,a}$	−1405.5976	2.36 (Rh−P) 2.16 (Rh−N) 1.87 (Rh−C)	192 (C−Rh−P) 88 (N−Rh−P) 176 (P−Rh−P) 179 (N−Rh−C)

[a] Values reported for lowest energy isomer.

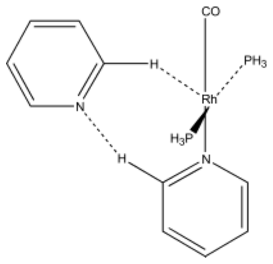

Figure 5. Structure of the most stable five-coordinate intermediate analyzed by DFT. The DFT calculations indicate that this isomer possesses an agostic interaction between the pyridine H and the Rh(I) center, thereby stabilizing the structure.

Hence, in the gas-phase experiments it is quite plausible that CO, py, and 4-picoline dissociation are competing processes, as observed experimentally.

To address the nature of the exchange of pyridine and 4-picoline, i.e., whether it takes place by an associative or dissociative mechanism, calculations were carried out on $[Rh(py)_2(CO)(PH_3)_2]^+$. A second pyridine was used instead of a 4-picoline ligand, due to the similarity of their bonding and to reduce the number of geometric isomers. The five families of geometric isomers investigated are shown in Figure 4. Several conformations arising from rotation about the Rh−N bonds were studied for each at the B3LYP/CSDZ* level of theory. Complexes were started in a trigonal-bipyramidal arrangement.

Upon geometry optimization from the $[Rh(py)_2(CO)(PH_3)_2]^+$ starting points, no bona fide five-coordinate intermediates are found. Indeed, the lowest energy structure appears to be an ion−dipole complex of pyridine and *trans*-$[Rh(PH_3)_2(CO)(py)]^+$ with weak agostic Rh- - -H_{ortho} interactions and an N_{py}- - -H hydrogen bond (see Figure 5). This species is 9 kcal/mol lower in energy than separated pyridine and *trans*-$[Rh(PH_3)_2(CO)(py)]^+$. The lack of a true five-coordinate $[Rh(PPH_3)_2CO(py)_2]^+$ gives further credence to the proposed dissociative exchange pathway's predominance.

Experimental Section

Sample Preparation and Mass Spectrometry. Pyridine (py) and 4-picoline (4pic) (4-methylpyridine) were purchased from Aldrich Chemical (St. Louis, MO) and were used without further purification. $[Rh(PPh_3)_2(CO)(4pic)]BF_4$ was prepared as follows. $Rh(PPh_3)_2(CO)(OH_2)]BF_4{\cdot}2H_2O$[41] (121 mg, 0.152 mmol) and 4pic (0.30 g, 3.2 mmol) were combined aerobically in 5 mL of CH_2Cl_2. The resulting solution was stirred for 2 min; then 50 mL of diethyl ether was dripped in slowly to afford a microcrystalline lemon yellow solid, which was filtered and washed with three 5 mL portions of ether. After thorough air drying, the solid was heated at 80 °C/50 mTorr for 4 h. The yield was 105.3 mg (82.9%). Its spectroscopic properties matched those of previously characterized complexes.[41−43] A 10 mg portion of $[Rh(PPh_3)_2(4pic)CO]BF_4$ was dissolved in 1 mL of acetonitrile and then diluted 100-fold. The dilute solution was infused directly into the ESI source at 500 nL/min. The emitter voltage was set to +2.0 kV and the tube lens set to +0.370 kV. Ions were accumulated for 0.75 s in an external-accumulation octapole ion trap.[44] Accumulated ions were then transported to the open cylindrical cell of the home-built 9.4 T ESI FT-ICR mass spectrometer.[44,45] The accumulation and transport octapoles were set to 1.5 MHz at 153 V_{p-p}. Experimental data were collected with a MIDAS 160 data station.[46,47] Time domain transients were collected as 9 coadded 2 Mword files. The accumulated time-domain transients were zero-filled once, Hamming apodized, fast Fourier transformed, magnitude calculated, and then frequency-to-*m*/*z* converted.[48,49] The theoretical masses and isotope distributions for complexes were calculated with Isopro 3.1.[50]

MS/MS experiments were performed by stored waveform inverse Fourier transform (SWIFT) isolation of the $[Rh(PPh_3)_2CO(4pic)]^+$ complex ion under constant pyridine pressure (50 nTorr ion gauge reading) and then irradiation of the trapped

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ions at 220.24 and 174.24 kHz (the ion cyclotron resonance frequencies of $[Rh(PPh_3)_2CO]^+$ and $[Rh(PPh_3)_2CO(pyr)(4pic)]^+$) on the excitation electrodes in two separate experiments.[51-53] $[Rh(PPh_3)_2CO]^+$ and $[Rh(PPh_3)_2CO(pyr)(4pic)]^+$ ions are thus ejected as soon as they form. The reaction/irradiation period was sustained for 10 s. The product ions were frequency-sweep excited to generate the time domain transient and processed to magnitude mode mass spectra as described above.

Computational Methods. Calculations were performed with the Jaguar package.[54] The B3LYP hybrid functional[55] was used in conjunction with the CSDZ* effective core potential (ECPs)/basis set scheme.[56] The latter entails the use of the Stevens ECPs and attendant valence basis sets for Rh and P and the 6-31G* basis set for C, O, and N. The -31G basis set is employed for H. All calculations were performed within a restricted formalism on closed-shell singlets. Energetic and metric data are organized in Table 1.

Conclusion

Our experimental results show that, at least for $[Rh(PPh_3)_2CO(4pic)]^+$, the ligand substitution pathway is dissociative, not associative. The DFT results show that CO loss can be a competing process in the substitution. No bona fide five-coordinative intermediate is found by DFT calculations, suggesting such an intermediate is high in energy.

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Supporting Information Available: A table of Cartesian coordinates for B3LYP/CSDZ* optimized geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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