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Kinetic Site of Protonation in Transition Metal Clusters and Its Possible Relationship to Large Kinetic Deuterium Isotope Effects in Hydrogen Transfer Processes

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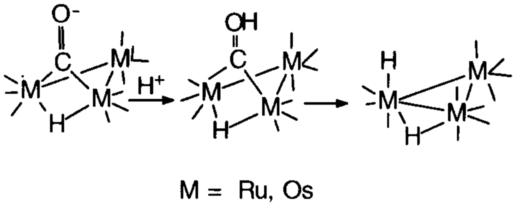
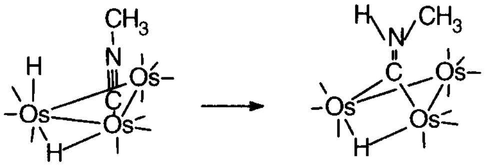
The protonation of $Ru_3(CO)_{10}(\mu\text{-}NO)^-$ (**1**) has been reexamined using CF_3CO_2X and CF_3SO_3X (X = H or D) in the temperature range of −80 to +25 °C using ^{13}C NMR techniques. For both acids, the kinetic site of protonation is the oxygen of the nitrosyl group, giving $Ru_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}NOH)$ (**2**). The rate of proton transfer to the metal core, to give $Ru_3(CO)_{10}(\mu\text{-}NO)(\mu\text{-}H)$ (**3**), is approximately the same for both the protic and deuterated cases. These results are contrasted with previous proton transfer studies of other metal clusters which exhibit anomalously large kinetic deuterium isotope effects, and it is tentatively concluded that these effects are associated with strictly intramolecular hydrogen transfer as opposed to the anion-assisted intermolecular process reported here. The carbonyl group ligand dynamics for **1**−**3** are reported.

Introduction

The organometallic literature contains many examples of proton transfer reactions which exhibit anomalously large kinetic deuterium isotope effects (KDIE).[1−5] In the particular case of metal clusters, these large KDIE are not thermodynamic in origin since large KDIE are observed for both ligand to metal and metal to ligand hydrogen transfer (eqs 1 and 2).[1,3] Considerable evidence has been presented that suggests that these hydrogen transfers are intramolecular and that proton barrier tunneling is responsible for the anomalously large KDIE observed.[1,3,5] Intermolecular proton transfer from monometallic hydrides to nitrogen bases has been studied in detail, and the KDIE observed are classical primary isotope effects whose magnitude, temperature dependence, and preexponential factor ratios do not indicate tunneling.[6,7] In the case of eqs 1 and 2, however, one cannot exclude the possibility that the presence of the acid's conjugate base (eq 1) or trace bases, such as water (eq 2), makes this apparently intramolecular process intermolecular (Scheme 1). The anomalously large KDIE could arise from hydrogen transfer mediated by the base in very tight hydrogen-bonded acid−base pairs.[8]

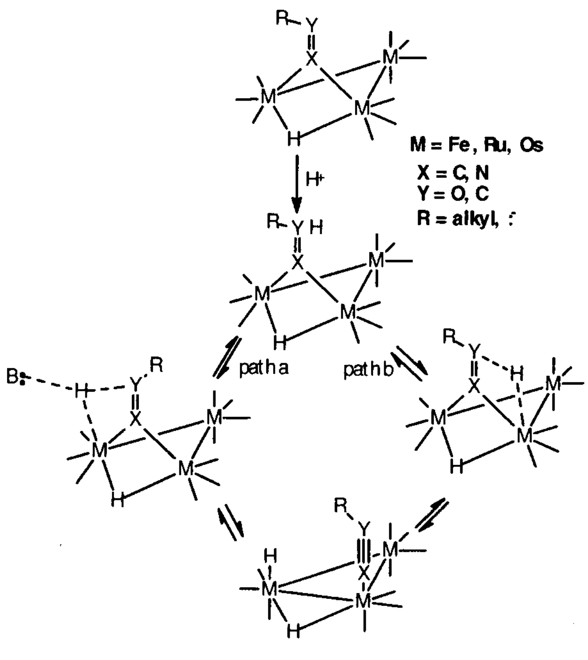


(1)



(2)

Scheme 1



Some time ago, Gladfelter and co-workers reported that protonation of $Ru_3(CO)_{10}(\mu\text{-}NO)^-$ (**1**) with CF_3SO_3H resulted in initial protonation at the nitrosyl oxygen

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[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1997.

[1] Rosenberg, E.; Pribich, D. *Organometallics* **1988**, *7*, 1741.

[2] Rosenberg, E. *Polyhedron* **1989**, *8*, 383.

[3] Anslyn, E. V.; Green, M.; Nicola, G.; Rosenberg, E. *Organometallics* **1991**, 10, 2600.

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[5] Rosenberg, E.; Hash, K. R.; Field, R. J. *Inorg. Chim. Acta*, in press.

[6] Norton, J. R.; Sullivan, J. M.; Edidin, R. T. *J. Am. Chem. Soc.* **1987**, *109*, 3945.

[7] Smith, K. T.; Tilset, M.; Kristjansdottir, S. S.; Norton, J. R. *Inorg. Chem.* **1995**, *34*, 6497.

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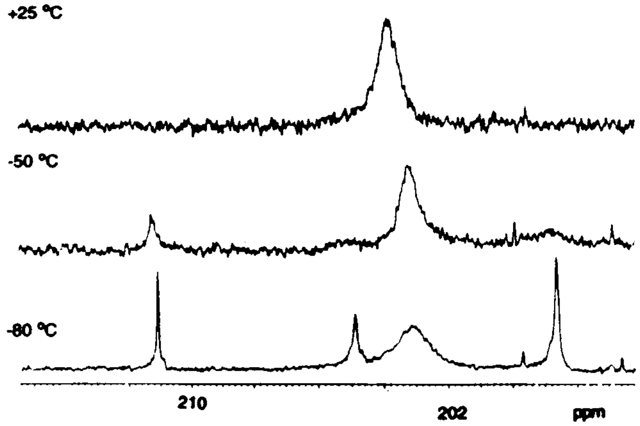
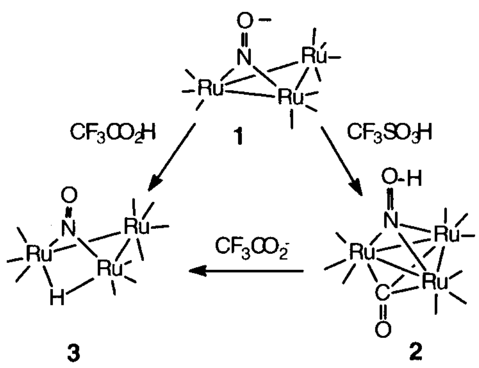


Figure 1. Variable-temperature ^{13}C NMR in the carbonyl region of **1** in CD_2Cl_2/CH_2Cl_2 at 100 MHz.

Scheme 2



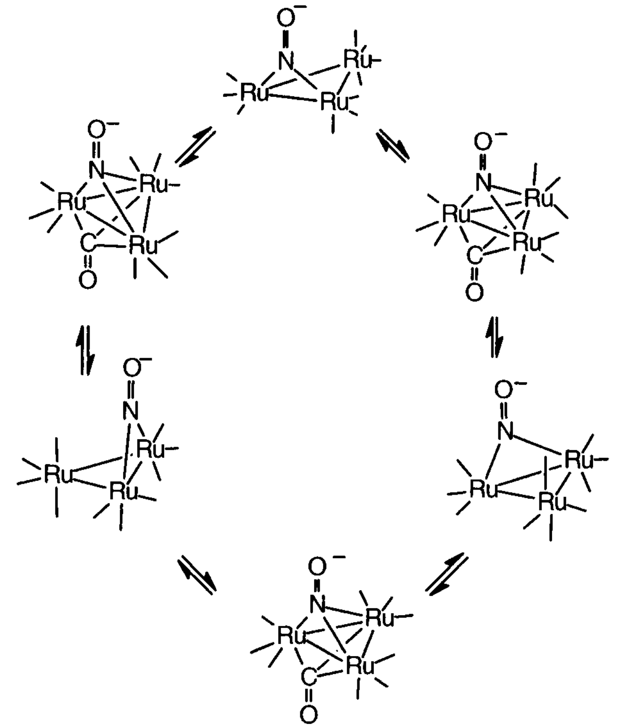
yielding $Ru_3(CO)_9(\mu_3\text{-}CO)(NOH)$ (Scheme 2, **2**).[9] Protonation with CF_3CO_2H on the other hand yielded $Ru_3(CO)_{10}(\mu\text{-}NO)(\mu\text{-}H)$ (Scheme 2, **3**).[9] Compound **2** is converted to **3** by the addition of $CF_3CO_2^-$ (Scheme 2). This system, therefore, provides an ideal test for determining whether the large KDIE previously observed (eqs 1 and 2) could arise via base-assisted intermolecular ligand to metal proton transfer. We have, therefore, reexamined the protonation of **1** with CF_3SO_3D and CF_3CO_2D in the temperature range from −80 to +25 °C using ^{13}C NMR techniques.

Results and Discussion

In order to follow the reaction of **1** with both protonated deuterated acids, we decided to monitor the conversion of **1** to **2** and the conversion of **2** to **3** by ^{13}C NMR on ^{13}CO-enriched samples of **1**. The variable-temperature (VT) ^{13}C NMR of **1**−**3** has not been previously reported, and so we began our investigations with a variable-temperature study of **1**.

The VT ^{13}C NMR of the carbonyl region of **1** is shown in Figure 1. At −80 °C, the spectrum consists of four resonances at 211.08, 204.89, 203.15, and 198.66 ppm in a relative intensity of 1:1:6:2. As the temperature is increased to +25 °C, these resonances coalesce to a single broad resonance at 203.25 ppm in reasonable agreement with the weighted average chemical shift of the resonances at −80 °C, 203.22 ppm. We can assign the broad resonance of relative intensity 6 at 203.15 ppm, to the two sets of three carbonyl groups bridged by the nitrosyl group, which are undergoing tripodal motion on the NMR time scale at −80 °C. The resonances at 211.08 and 204.89 ppm are interchangeably assigned to the inequivalent axial carbonyl groups on the $Ru(CO)_4$ moiety in **1**, while the resonance of relative intensity 2 at 198.66 ppm is assigned to the equivalent radial carbonyls on this ruthenium atom. The simplest mechanism for complete averaging of all the carbonyl environments would be for one of the axial carbonyls on the $Ru(CO)_4$ group and the nitrosyl ligand to adopt μ_3-bonding modes in the intermediate which reverts to **1** with the bridging nitrosyl on a different edge of the Ru_3 triangle and the $Ru(CO)_4$ group on a different Ru atom. Along with a sequential tripodal motion involving both axial carbonyls on the $Ru(CO)_4$ group and tripodal motion of the $Ru(CO)_3$ groups, this would interchange all carbonyl groups (Scheme 3).[10] We cannot exclude other more complex mechanisms involving intermetallic scrambling via μ-CO intermediates, but considering the ground state structure of **2**, this is the most likely process.

Scheme 3



Protonation of a ^{13}CO-enriched sample of **1** at ambient temperatures with CF_3SO_3H gives a ^{13}C NMR spectrum which shows two sharp resonances at 195.30 and 192.02 ppm in a relative intensity of 1:2 (Figure 2a) −80 °C. We can assign these resonances to the two pseudo-radial and one pseudo-axial terminal carbonyls in **2**.[9] A third very broad signal is barely detectable above the noise at 264.7 ppm, which we tentatively assign to the triply bridging carbonyl in **2**.[11] As the temperature is increased to +25 °C, the two upfield resonances merge and begin to sharpen to a single resonance at 193.38 ppm (Figure 2b). The weighted average of the two

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[9] Gladfelter, W. L.; Steven, R. E.; Guettler, R. D. *Inorg. Chem.* **1990**, *29*, 451.

[10] Rosenberg, E.; Espitia, D.; Hardcastle, K. I.; Kabir, S. E.; McPhillips, T.; Gobetto, R.; Milone, L.; Osella, D. *Organometallics* **1993**, *12*, 2390.

[11] The μ_3-CO in $Ru_3(CO)_9(\mu_3\text{-}CO)(CC(OMe)Me)$ is reported at 263 ppm (br), see: Sailor, M. J.; Brock, C. P.; Shriver, D. F. *J. Am. Chem. Soc.* **1987**, *109*, 6015.

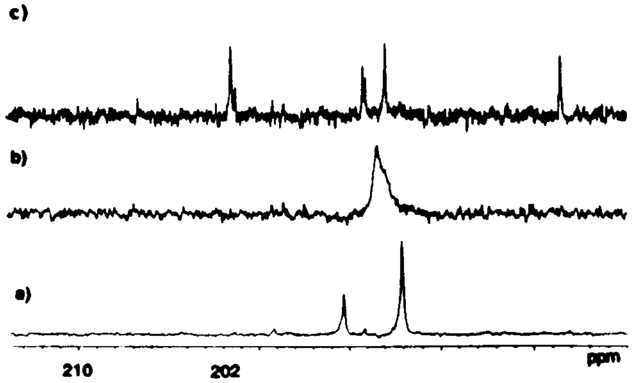

Figure 2. (a) ^{13}C NMR in the carbonyl region of **2** (**1** + 1 equiv of CF_3SO_3H) in CD_2Cl_2/CH_2Cl_2 at −80 °C at 100 MHz. (b) ^{13}C NMR of **2** at +25 °C. (c) ^{13}C NMR of **2** after addition of $PPNCF_3CO_2$ at +25 °C.

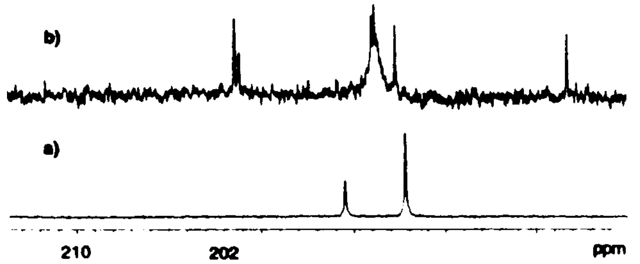

Figure 3. (a) ^{13}C NMR of **1** after the addition of 1 equiv CF_3CO_2X (X = H or D) at −80 °C. (b) ^{13}C NMR of **1** after the addition of 1 equiv of CF_3CO_2X (X = H or D) at −80 °C and warming to +10 °C, showing the partial conversion of **2** to **3**.

terminal carbonyl resonances is 193.11 ppm. When 0.4 equiv of $PPNCF_3CO_2$ is added to this solution at +25 °C, the color of the solution changes from reddish to amber. The ^{13}C NMR now reveals six resonances at 201.59, 201.35, 194.22, 194.09, 192.89, and 183.46 ppm in a relative intensity of approximately 2:1:1:2:2:2. This spectrum is consistent with the conversion of **2** to **3**,[9] with the latter being rigid on the NMR time scale (Figure 2c). This spectrum is identical to one obtained by the addition of 1 equiv of CF_3COOH to **1** at 25 °C. When the $PPNCF_3CO_2$ is injected at −80 °C, no conversion of **2** to **3** is noted until the sample is warmed to above +10 °C. When CF_3SO_3D is used, the addition of $PPNCF_3CO_2$ results in the same overall changes in the ^{13}C NMR, except for some disappearance of the multiplicity or broadness of the carbonyl resonances in **3** at 201.59, 192.94, and 183.46 ppm, which is attributable to the absence of partially-resolved proton couplings with the bridging hydride in the deuterated analog.

When a ^{13}CO-enriched sample of **1** is treated with 1 equiv of CF_3COOH or CF_3COOD at −80 °C, ^{13}C NMR reveals a spectrum identical to that observed when **1** is protonated at +25 °C with CF_3SO_3H, assignable to **2** (Figure 3a). No change in the spectrum is observed for both the protonated or deuterated cases up to +10 °C, at which point partial conversion from **2** to **3** is observed (Figure 3b). On further warming to +25 °C, conversion to **3** is complete in about the same time for the protonated and deuterated cases. Thus, protonation at low temperatures with CF_3CO_2X (X = H or D) leads to initial protonation at the nitrosyl oxygen. Low-temperature protonation of $Ru_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}H)^-$ with CF_3CO_2H has also been reported but O-protonation was not observed as was the case for CF_3SO_3H or FSO_3H.[1,12] These results suggest that initial protonation at oxygen may be the kinetic product for $HRu_3(CO)_{11}^-$ with CF_3CO_2H as well but that transfer to the metal core is even faster than for **2** at the temperature examined (approximately −40 °C).

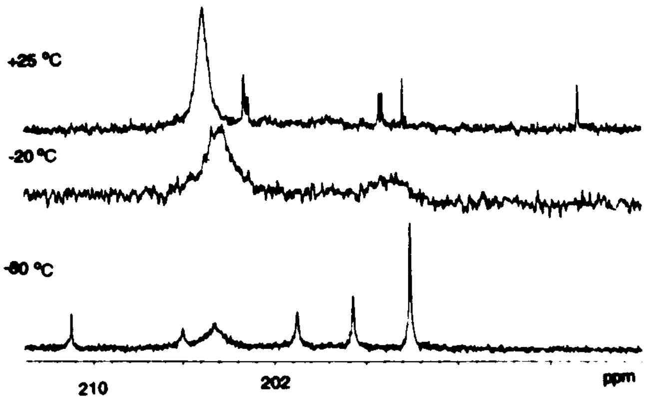

Figure 4. Variable-temperature ^{13}C NMR of **1** in the carbonyl region after being treated with 0.3 equiv of CF_3CO_2H at 100 MHz in CD_2Cl_2/CH_2Cl_2.

When a ^{13}CO-enriched sample of **1** was treated with 0.3 equiv of CF_3COOH at −80 °C, the ^{13}C NMR spectrum reveals only resonances assignable to **1** and **2** (Figure 4). As the solution is warmed to +25 °C, the resonances associated with **1** and **2** appear to average independently. At 25 °C, **2** is completely converted to **3** and the resonances associated with **3** are sharp (Figure 4). Thus, exchange between **1** and **3** is slow on the NMR time scale at 25 °C. In a separate experiment, an excess of CF_3SO_3H was added to ^{13}CO-enriched **1** at 25 °C and then the ^{13}C NMR was recorded at −80 °C. The spectrum revealed resonances associated with both **2** and **3**. On warming to room temperature, the resonances associated with **3** remained relatively sharp while those associated with **2** broadened, as reported above. There was, however, considerable decomposition during the period that this sample was monitored by ^{13}C NMR, presumably due to secondary protonations in the presence of excess CF_3SO_3H. This result does indicate that in the presence of excess triflate, conversion of **2** to **3** is possible, although more slowly than for the more basic trifluoroacetate. Apparently, direct exchange between **2** and **3** is also slow in the NMR time scale.

Conclusions

The results reported clearly show that the site protonation is the oxygen of the nitrosyl group for both CF_3SO_3H and CF_3COOH. On the basis of these experiments, we cannot say, for certain, that there is or is not an appreciable KDIE associated with the anion-assisted conversion of **2** to **3** since this transformation was too rapid to follow by the methods employed here. The anomalously large KDIE observed for the much slower ligand to metal proton transfers in $M_3(CO)_{10}(\mu\text{-}COH)$ (eq 1) are not observed for this conversion but could be imbedded in this more rapid process. However, it should also be noted that for eq 2, the addition of base dramatically increases the rate of metal to ligand

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[12] Nevinger, L. R.; Keister, J. B. *Organometallics* **1990**, *9*, 1900.

hydrogen transfer and decreases the large KDIE from 27 to 1.2 at 32 °C for comparable amounts of base to those used here (~0.5 equiv). This leads us to suggest that the anomalously large KDIE are associated with the intramolecular processes depicted in eqs 1 and 2. This conclusion is only tentative and must await confirmation by studies using more rapid kinetic techniques. These preliminary studies have established that, in general, the intermolecular base-assisted proton transfer (path a, Scheme 1) is a much more rapid process than the intramolecular one (path b, Scheme 1). Finally, the greater fluxionality of **1** and **2** relative to **3** is common for anionic and/or face-capped trimetallic clusters relative to their neutral doubly edge-bridged analogs.[11,13]

Experimental Section

Materials. Compound **1**[9] and PPNCF$_3$CO$_2$[14] were synthesized according to literature procedures. Trifluoroacetic acid, triflic acid, deuterated trifluoroacetic acid, deuterated triflic acid, and methylene chloride-d_2 were purchased from Aldrich Chemicals and used as received. Methylene chloride was distilled from calcium hydride before use. Enriched Ru$_3$(CO)$_{12}$ was obtained by exposing 0.5 g of Ru$_3$(CO)$_{12}$ in 250 mL of heptane to 0.5 atm of 90% ^{13}CO (Monsanto) at 80−90 °C for 2−3 days.

Instrumentation. ^{1}H and ^{13}C NMR spectra were obtained on a Varian Unity Plus 400 NMR spectrometer at 400 and 100 MHz, respectively.

Sample Preparation and Monitoring Procedures. Samples of ^{13}CO-enriched **1** (40−50 mg) were dissolved in 2.5 mL of a 1:4 mixture of CD$_2$Cl$_2$:CH$_2$Cl$_2$ under inert atmosphere in a 5 or 10 mm resealable NMR tube (J. S. Young). The addition of 1 equiv of CF$_3$SO$_3$X (X = H or D) was carried out in a Braun drybox at ambient temperatures. The samples were then placed in the NMR spectrometer and the temperature varied from −80 to +25 °C to obtain the VT ^{1}H or ^{13}C NMR of **2**. In a separate run, the sample was made up in a septum-capped 10 mm NMR tube cooled to −80 °C in the NMR spectrometer and then quickly injected with 0.4 equiv of PPNCF$_3$CO$_2$, inverted once, and reinserted into the NMR probe at −80 °C. Spectra were then recorded at −80, −50, −20, +10, and +25 °C. Accumulation times were 7 min and temperature equilibration times were 15 min. No significant conversion of **2** to **3** was observed until +10 °C. Under these conditions, no difference in the rate of conversion of **2** to **3** was noted for the protonated and deuterated cases. When PPNCF$_3$CO$_2$ was added to solutions of **2** at ambient temperature, conversion to **3** was instantaneous. The low-temperature protonation of **1** with CF$_3$COOX (X = H or D) was performed by cooling solutions of **1** prepared in septum-sealed 10 mm NMR tubes as above, cooled to −80 °C, and then rapidly injected with equiv of CF$_3$CO$_2$X (X = H or D). The tube was inverted once and then immediately reinserted into the spectrometer at −80 °C. The ^{13}C NMR spectra were then obtained at −80, −50, −20, +10, and +25 °C. Conversion of **2** to **3** was noted to commence at +10 °C, and no difference between the protonated and deuterated cases was observed. Protonation of **1** with CF$_3$CO$_2$X (X = H or D) leads directly to **3,** as previously reported.[9]

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