Inorg. Chem. **1999,** *38,* 6206−6211

Kinetic and Thermodynamic Studies of Reaction of $\bullet Cr(CO)_3C_5Me_5$, $HCr(CO)_3C_5Me_5$, and $PhSCr(CO)_3C_5Me_5$ with $\bullet NO$. Reductive Elimination of Thermodynamically Unstable Molecules HNO and RSNO Driven by Formation of the Strong Cr−NO Bond

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Received July 14, 1999

Reaction of $H\text{-}Cr(CO)_3C_5Me_5$ with $\bullet NO$ at 1−2 atm pressure in toluene solution yields $Cr(NO)(CO)_2C_5Me_5$ as the sole metal-containing product in addition to N_2O and HNO_2 as the principle nitrogen-containing products. N_2O and HNO_2 are attributed to decomposition of the initial product HNO. Kinetic studies yield the rate law $d[P]/dt = -k^{2nd\ order}[HCr(CO)_3C_5Me_5][\bullet NO]$; $k^{2nd\ order} = 0.14\ M^{-1}\ s^{-1}$ at 10 °C, with $\Delta H^{\ddagger} = 11.7 \pm 1.5$ kcal/mol and $\Delta S^{\ddagger} = -16.3 \pm 3.5$ cal/(mol deg). The rate of reaction is not inhibited by CO. The kinetic isotope effect for reaction of $D\text{-}Cr(CO)_3C_5Me_5$ is $k_H/k_D = 1.7$. These observations are consistent with a first step involving direct H (D) atom transfer from the metal hydride to $\bullet NO$, forming HNO. Also supporting this mechanism is the ∼150-times slower reaction of $H\text{-}Mo(CO)_3C_5Me_5$ and failure to observe reaction for $H\text{-}W(CO)_3C_5Me_5$ in keeping with metal−hydrogen bond strengths $Cr < Mo < W$. Reaction of $PhS\text{-}Cr(CO)_3C_5Me_5$ with NO at 1−2 atm pressure in toluene solution also forms $Cr(NO)(CO)_2C_5Me_5$ as the sole metal-containing product. The initial product is the unstable nitrosothiol PhS-NO. Kinetic studies yield the rate law $d[P]/dt = -k^{1st\ order}[PhS\text{-}Cr(CO)_3C_5Me_5]$; $k^{1st\ order} = 3.1 \pm 0.3 \times 10^{-3}\ s^{-1}$ at 10 °C, with $\Delta H^{\ddagger} = 21.6 \pm 1.2$ kcal/mol, $\Delta S^{\ddagger} = +3.9 \pm 1.5$ cal/(mol deg). The rate of reaction is independent of both NO and CO pressure. The transition state in the first-order process is proposed to involve migration of bound thiolate to coordinated CO, forming $Cr(CO)_2(\eta^2\text{-}C(=O)SPh)C_5Me_5$. The enthalpy of reaction of $\bullet Cr(CO)_3C_5Me_5$ and NO yielding $Cr(NO)(CO)_2C_5Me_5$ and CO has been measured by solution calorimetry: $\Delta H° = -33.2 \pm 1.8$ kcal/mol. The Cr−NO bond strength is estimated as ∼70 kcal/mol and provides the net thermodynamic driving force for the proposed elimination of the unstable molecules HNO and PhSNO.

Introduction

The chemistry of metal-nitrosyl complexes has been intensively investigated in recent years.[1,2] Despite a wealth of synthetic and structural observations, kinetic and thermodynamic studies of this simple radical analogue of CO are rare. The authors can find no reliable thermodynamic data regarding the M−NO bond strength for organometallic complexes in solution.

Nitric oxide is a "weak" radical in the sense that its bond strength to hydrogen (∼50 kcal/mol[3]) is low enough to make it thermodynamically unstable with respect to eq 1. We have

$$2(H\text{-}NO) \rightarrow H_2 + 2\bullet NO \tag{1}$$

recently investigated reactions of the stable chromium-centered radical $\bullet Cr(CO)_3C_5Me_5$ (= •Cr) with phenyl disulfide[4] as shown in eq 2. The first step in reaction 2 was proposed to involve

$$\bullet Cr + PhS\text{-}SPh \rightleftharpoons Cr\text{-}SPh + \bullet SPh + \bullet Cr \rightarrow Cr\text{-}SPh \tag{2}$$

reversible generation of the •SPh radical in a thermodynamically uphill reaction. The activation energy for the first step, ∼10 kcal/mol, was found to be only ∼2 kcal/mol above the calculated thermodynamic estimate on the basis of measured bond dissociation energies.[4] In addition, the •SPh radicals generated in reaction 2 were shown[4,5] to rapidly abstract an H atom (eq 3).

$$\bullet SPh + H\text{-}Cr \rightarrow H\text{-}SPh + \bullet Cr \tag{3}$$

The bond strengths to hydrogen for Cr-H (62 kcal/mol)[6] and H-SPh (79 kcal/mol)[7] can be used as a scale for the "strength" of the corresponding radicals •Cr and •SPh. The "weak" natures of the •NO, •Cr, and •SPh radicals are also reflected in the low enthalpies of dimerization [$\bullet NO^{8} \leq 4$, $\bullet Cr^{9} = 15$, $\bullet SPh^{10} = 43$ kcal/mol] as shown in eq 4. Interest in radical reactions involving

$$\bullet A + \bullet A \rightarrow A{-}A \tag{4}$$

such weak radicals[11] and bound substrates prompted us to

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[1] Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: New York, 1992.

[2] Lancaster, J. *Nitric Oxide, Principles and Actions*; Academic Press: Limited, London, 1996.

[3] The H−NO bond strength of 50 kcal/mol is calculated on the basis of the best existing experimental data (ref 3a). Recent high level theoretical calculations suggest a value of it ∼48 kcal/mol (ref 3b). In the authors' view, a solution phase estimate of 50 ± 4 kcal/mol seems reasonable. Discussion of decomposition pathways of HNO can be found in ref 3c. (a) Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N.; *J. Chem. Phys. Ref. Data* **1985**, *14*, Supplement 1. (b) Lee, T. J.; Dateo, C. E. *J. Chem. Phys.* **1995**, *103*, 9110. (c) Bunte, S. W.; Rice, B. M.; Chabalowski, C. F. *J. Phys. Chem. A* **1997**, *101*, 9430. (d) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley and Sons: New York, 1997.

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[5] The rate of reaction of phenyl thiyl radicals and $H\text{-}Mo(CO)_3C_5H_5$ is one of the fastest H atom transfers to this radical that have been measured: Franz, J. Private communication.

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10.1021/ic990829i CCC: $18.00

investigate reactions of nitric oxide. The concomitant formation of strong metal−nitrosyl bonds is the driving force in its reactivity. This paper reports the first in a series of kinetic and thermodynamic study of reactions of •NO and group VI metal complexes.[12]

Experimental Section

All manipulations were carried out using standard Schlenk tube/inert atmosphere techniques. Toluene was purified by distillation from sodium/benzophenone ketyl under argon. Methylene chloride was purified by distillation from phosphorus pentoxide under argon. Research grade H_2 , CO, and •NO were obtained from Matheson gas; ^{13}CO and D_2 [99% isotopic purity] were obtained from Isotec. The complexes $RS\text{-}Cr(CO)_3C_5Me_5$ were prepared as reported in the literature.[4,26]

Rate of Reaction of •NO and H-Cr(CO)$_3$C$_5$Me$_5$. Nitric oxide was passed through coiled copper tubing held at −78 °C in a dry ice/acetone trap to remove $•NO_2/N_2O_4$ and used to fill a 1 L stainless gas cylinder fitted with a calibrated pressure transducer obtained from Omega Scientific. The previously evacuated container was filled to a total absolute pressure of ∼3 atm. A thermostated glass reactor at 10.0 °C in the FT-IR microscope/reactor system[11] was evacuated and filled with nitric oxide three times and then loaded with 25 mL of freshly distilled toluene. Reaction was initiated by syringe addition of 2.0 mL of a toluene solution of $HCr(CO)_3C_5Me_5$, yielding a starting concentration of $HCr(CO)_3C_5Me_5$ of 0.0058 M. Pressure and temperature were recorded continuously throughout the reaction. The reaction was conveniently monitored by following the decay of peaks at 1996 and 1913 cm^{-1} due to $HCr(CO)_3C_5Me_5$ or production of $C_5Me_5Cr(CO)_2(NO)$ with peaks at 2000, 1930, and 1684 cm^{-1}. Production of N_2O was monitored by its band at 2219 cm^{-1}, and HNO_2 was monitored by its band at 3443 cm^{-1}. Samples of N_2O and HNO_2 prepared by thermal decomposition of NH_4NO_3 and acidification of $NaNO_2$ with anhydrous HCl were observed to match our band assignments in toluene solution in our reactor system. Study of the rate of reaction as a function of added CO pressure [up to 2 atm] showed no influence on rate of reaction. Plots of ln[$HCr(CO)_3C_5Me_5$] versus time were linear for 2−4 half-lives. Rates of reaction shown in Table 1 in the Supporting Information typically had experimental errors of ∼10%. The rate of reaction of $DCr(CO)_3C_5Me_5$ was shown to be 1.7 ± 0.2 times slower than that measured for $HCr(CO)_3C_5Me_5$.Rates of Reactions of $H\text{-}Mo(CO)_3C_5Me_5$ and $H\text{-}W(CO)_3C_5Me_5$ with •NO.

Rates of Reactions of H-Mo(CO)$_3$C$_5$Me$_5$ and H-W(CO)$_3$C$_5$Me$_5$ with •NO. The rates of reaction of $H\text{-}Mo(CO)_3C_5Me_5$ and $H\text{-}W(CO)_3C_5Me_5$ were studied under identical conditions and in the same reactor system described above for $H\text{-}Cr(CO)_3C_5Me_5$. The rate of reaction of $H\text{-}Mo(CO)_3C_5Me_5$ was initially studied at 10 °C, where it underwent no apparent reaction. Study of the rate of reaction at 30 °C led to observed production of $Mo(NO)(CO)_2C_5Me_5$ by a first-order process with a rate of reaction ∼150 times slower than that observed for reaction of the chromium hydride under these conditions. Nitrous oxide was produced as the reaction proceeded, as monitored by its characteristic band at 2219 cm^{-1}. Reaction of $H\text{-}W(CO)_3C_5Me_5$ with •NO was also studied at 30 °C and a nitric oxide pressure of 2.8 atm over a 30 min period. No reaction was observed to take place under these conditions.

Rate of Reaction of •NO and PhS-Cr(CO)$_3$C$_5$Me$_5$. Data for this reaction were obtained in a manner strictly analogous to that described above for $H\text{-}Cr(CO)_3C_5Me_5$. Reaction rates measured based on decay of $PhS\text{-}Cr(CO)_3C_5Me_5$ at 2008, 1954, 1920 (sh) cm^{-1} or growth of peaks due to $C_5Me_5Cr(CO)_2(NO)$ were identical. First-order plots were found to be linear for 2−4 half-lives. A broad band at 1565 cm^{-1} in the FT-IR spectrum was observed to rise during reaction and undergo slow decay and is assigned to PhSNO. A reaction done in C_6D_6 [also distilled from Na/benzophenone] allowed better observation of this peak. Due to the fact that this peak rose to a maximum value and began to decay prior to the completion of the experiment, no kinetic analysis was performed regarding generation of PhSNO. Reactions done using a gas mixture of 1 atm nitric oxide and 2 atm carbon monoxide occurred at the same rate as reactions using a gas mixture of 1 atm nitric oxide and 2 atm argon pressure.

Reaction of •NO and HS-Cr(CO)$_3$C$_5$Me$_5$. The rate of reaction of $HS\text{-}Cr(CO)_3C_5Me_5$ with •NO was studied at 10 °C using techniques

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(8) The value for the enthalpy of dimerization of nitric oxide is taken from ref 18. It is of interest to estimate enthalpies of bond formation for mixed species assuming a low metathesis enthalpy $A-A + B-B \rightarrow 2\ A-B$. Using these data produces the following yields estimates for the radical pairs: $C_5Me_5(CO)_3Cr\text{-}SPh = 29$, $PhS\text{-}NO = 23.5$, and $C_5Me_5(CO)_3Cr\text{-}NO = 9.5$ kcal/mol. The value for Cr-SPh is lower than the measured value of 35 kcal/mol, and values for the other two estimated bond strengths are not known.

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(10) This value for the sulfur−sulfur bond strength is derived on the basis of literature values for the enthalpy of hydrogenation of phenyl disulfide as discussed in detail in ref 4.

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(15) Reaction of HCl with $OsCl(CO)(NO)(PPh_3)_2$ yields a stability complex of HNO, $OsCl_2(CO)(HNO)(PPh_3)_2$, the crystal structure of which has been determined: Wilson, R. D.; Ibers, J. A. *Inorg. Chem.* **1979**, *18*, 336.

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(17) Such radical combinations are typically very fast. For example, the second-order rate constant for $2•Cr(CO)_3C_5Me_5 \rightarrow C_5Me_5(CO)_3Cr\text{-}Cr(CO)_3C_5Me_5$ has been determined to be $1.7 \times 10^7\ M^{-1}\ s^{-1}$ at 228 K in CH_2Cl_2: T. C.; Geiger, W. E.; Baird, M. C. *Organometallics* **1994**, *13*, 4494.

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(20) It should be noted that the activation parameters are calculated using rate constants with all species in toluene solution. The enthalpy and entropy of a solution of nitric oxide in toluene are −0.5 kcal/mol and −15.2 cal/(mol deg), respectively.[13] The entropy of activation based on reaction of nitric oxide gas would be substantially more negative [ca. −31.5 cal/(mole deg)], while the enthalpy of activation is little changed.

(21) This system would be expected to exhibit an inverse equilibrium isotope effect because $\nu_{M-H} < \nu_{H-NO}$. However, if the reaction transition state depends on breaking the M−H versus M−D bond in an early transition state prior to establishment of the H−NO bond, a normal kinetic isotope effect is expected. For an excellent discussion of isotope effects in related transfers see: Bullock, R. M. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH Publishers: New York, 1992; p 263.

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(25) (a) There is little evidence in related chemistry of this system that ring slippage to form coordinatively unsaturated (η^3 Cp*)Cr(CO)$_3$X is a low energy pathway, but this cannot be entirely discounted. Work aimed at testing this and other mechanistic possibilities is planned. (b) A referee has pointed out that the proposed intermediates in these reactions might be trapped by other species in addition to nitric oxide. Experiments to test this using suitable trapping agents are also planned. The proposed reaction pathways have reasonable support but are tentative, as in all mechanistic work.

(26) Bauer, A.; Capps, K. B.; Wixmerten, B.; Abboud, K. A.; Hoff, C. D.; *Inorg. Chem.* **1999**, *38*, 2136.

identical to those described above. The rate of reaction was found to be first order in HS-$Cr(CO)_3C_5Me_5$. The observed first-order rate constant at two pressures of nitric oxide were measured: $k = 5.2 \times 10^{-4}$ s^{-1} at 2.35 atm nitric oxide and $k = 5.3 \times 10^{-4}$ s^{-1} at 1.26 atm nitric oxide, indicating zero-order dependence on nitric oxide. FT-IR spectral changes confirmed that $Cr(NO)(CO)_2C_5Me_5$ was the sole metal-containing product in the reaction. No sign of production of N_2O was seen on the time scale of the experiment.

Enthalpy of Reaction of •NO and •$Cr(CO)_3C_5Me_5$. The enthalpy of reaction in toluene solution of •$Cr(CO)_3C_5Me_5$ was measured using a high-pressure Calvet cell at a pressure of 2.5 atm nitric oxide (10 measurements) and in a Guild solution calorimeter at 1.0 atm (5 measurements). The average value of −33.0 ± 1.8 kcal/mol is the average of both types of measurements and corresponds to the enthalpy of reaction with all species in solution. Because of the highly exothermic nature of reactions of trace oxygen with both the metal radical and nitric oxide, these measurements required additional purification of nitric oxide by exposing it to a solution of the metal radical to ensure nitrogen dioxide was not present during the calorimetric runs. Spectroscopic analysis by FT-IR of the reactions done in toluene and NMR analysis of two experiments done in deuteriobenzene confirmed the clean conversion of •$Cr(CO)_3C_5Me_5$ to $Cr(NO)(CO)_3C_5Me_5$.

Reaction of ^{12}CO with $Cr(NO)(^{13}CO)_2C_5Me_5$. The complex $Cr(NO)(^{13}CO)_2C_5Me_5$ was prepared by stirring a solution of 0.3 g of •$Cr(CO)_3C_5Me_5$ in 60 mL of toluene under at a pressure of 2 atm ^{13}CO for 30 min. Injection of 50 mL of nitric oxide gas using a high-pressure stainless steel syringe obtained from Harvard Scientific to this solution and continued stirring resulted in quantitative conversion of the labeled radical complex to $Cr(NO)(^{13}CO)_2C_5Me_5$ as determined by FT-IR spectroscopy: the bands of $C_5Me_5Cr(CO)_2(NO)$ at 2000, 1930, and 1684 cm^{-1} are shifted to 1958, 1887, and 1682 cm^{-1} for the labeled complex. This solution was transferred under argon to a high-pressure sample cylinder directly attached to a high-pressure FT-IR cell obtained from Harrick Scientific. The cell was filled with 14 atm of ^{12}CO and heated over a period of about 2 h to 60 °C. No detectable change or incorporation of ^{12}CO occurred during this time. The cell was allowed to cool and left overnight. A spectrum run the next day also showed no apparent incorporation of ^{12}CO.

Results and Discussion

There is little literature data available to indicate the reaction products of metal hydrides and nitric oxide beyond the fact that metal nitrosyls can be formed.[14,15] This work was begun to see if •NO was capable of direct attack on the metal−hydrogen bond of the complexes H-$M(CO)_3C_5Me_5$ (M = Cr, Mo, W).

Kinetic Study of Reaction of •NO and H-$Cr(CO)_3C_5Me_5$. In toluene solution under pseudo-first-order conditions of 1.18−2.81 atm of NO, reaction of the chromium hydride occurs cleanly as monitored by FT-IR spectroscopy (eq 5). The fate

$$\text{H-Cr(CO)}_3\text{C}_5\text{Me}_5 + 2\bullet\text{NO} \rightarrow \text{Cr(NO)(CO)}_2\text{C}_5\text{Me}_5 + \text{CO} + \text{“H-NO”} \quad (5)$$

of the chromium complex is unequivocally followed by the characteristic ν_{CO} and ν_{NO} bands as shown in Figure 1. Production of nitrosyl hydride[3] (“HNO”) is based on detection of its decomposition products N_2O and HNO_2 by FT-IR spectroscopy. Information concerning the decomposition of HNO is available in the gas phase and under various conditions in aqueous solution.[3] The authors were unable to find literature data on its decomposition in toluene solution under a pressure of •NO. A reasonable expectation based upon observations in the literature is shown in eq 6. The presence of N_2O is readily

$$\text{HNO} + 2\bullet\text{NO} \rightarrow \text{N}_2\text{O} + \text{HNO}_2 \quad (6)$$

established by its characteristic IR absorption[3d] at 2219 cm^{-1} in toluene solution, and HNO_2 was identified on the basis of a broad band at 3442 cm^{-1} in toluene. As described in the Experimental Section, prepared samples of N_2O and HNO_2 matched the experimental peaks in the kinetic runs. As shown in Figure 1 in the Supporting Information, under pseudo-first-order conditions in [•NO], first-order plots of decay of [$HCr(CO)_3C_5Me_5$], buildup of [$Cr(NO)(CO)_2C_5Me_5$], and buildup of [N_2O] are nearly parallel. The similar rates of decay of the metal hydride and buildup of nitrous oxide and metal nitrosyl complex do not prove that the reaction is occurring through intermediate HNO formation but do support that generation of N_2O is linked to reaction of the hydride. The broad band at 3442 cm^{-1} assigned to HNO_2 was shifted to 2550 cm^{-1} when D-$Cr(CO)_3C_5Me_5$ was studied, indicating that DNO_2 was formed by interaction with the hydride and not solvent or a contaminant such as trace water.

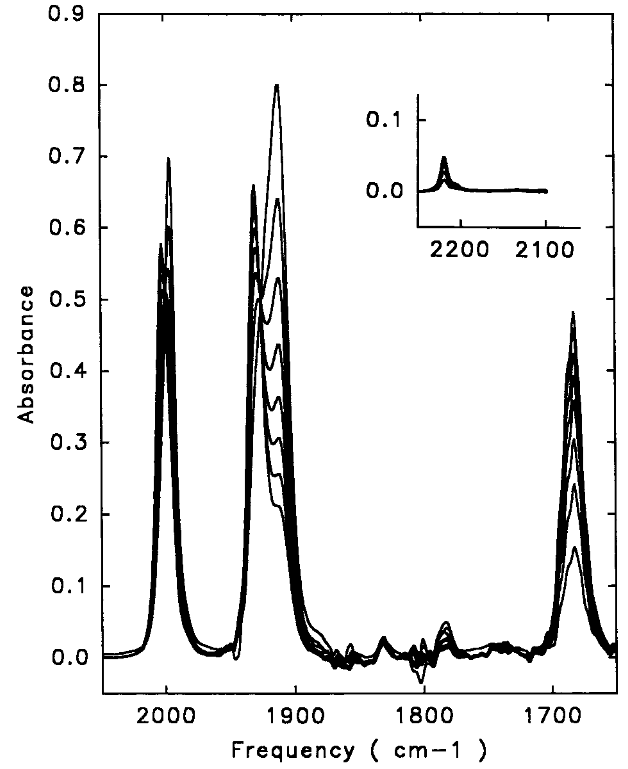

Figure 1. Infrared spectroscopic data for reaction of H-$Cr(CO)_3C_5Me_5$ (peaks decreasing at 1996 and 1912 cm^{-1}) and •NO in toluene solution at 20 °C at 2.17 atm, with •NO pressure producing $Cr(NO)(CO)_2C_5Me_5$ (peaks increasing at 2001, 1929, and 1682 cm^{-1}). Inset peak is band at 2019 cm^{-1} due to increase in N_2O.

As shown in Table 1 in the Supporting Information, the rate of reaction was found to be first order in •NO pressure over the 1.18−2.81 atm pressure range studied. The values of the second-order rate constants derived from these data are 7.7×10^{-4} (0 °C), 1.69×10^{-3} (10 °C), and 3.50×10^{-3} (20 °C) atm^{-1} s^{-1} . The rates of reaction with all species in toluene solution were calculated using published data on the solubility of nitric oxide in toluene,[13] yielding derived second-order rate constants based on reaction of nitric oxide in solution: 6.3×10^{-2} (0 °C), 1.37×10^{-1} (10 °C), and 2.85×10^{-1} (20 °C) M^{-1} s^{-1} . Activation parameters derived from these data (for all species in solution)[20] are $\Delta H^{\ddagger} = 11.7 \pm 1.5$ kcal/mol and $\Delta S^{\ddagger} = -16.3 \pm 3.5$ cal/(mol deg).

The rate of reaction was found to be unchanged when 2−3 atm of CO pressure were added, discounting reaction mechanisms based on reversible loss of CO. The rate of reaction of D-$Cr(CO)_3C_5Me_5$ was found to be 1.7 times slower than that of H-$Cr(CO)_3C_5Me_5$, giving further evidence that the transition state involves breaking the metal−hydrogen bond. This normal kinetic isotope effect for a reaction expected to have an inverse equilibrium isotope effect implies an early transition state for the H atom transfer reaction.[21]

The activation parameters are in reasonable agreement with a mechanism involving rate-limiting H atom transfer from chromium to nitric oxide as shown in eq 7, followed by rapid trapping of the chromium radical as shown in eq 8.

$$\text{H-M(CO)}_3\text{C}_5\text{Me}_5 + \bullet\text{NO} \rightarrow \bullet\text{M(CO)}_3\text{C}_5\text{Me}_5 + \text{H-NO} \quad (7)$$

$$\bullet\text{M(CO)}_3\text{C}_5\text{Me}_5 + \bullet\text{NO} \rightarrow \text{M(NO)(CO)}_2\text{C}_5\text{Me}_5 + \text{CO} \quad (8)$$

Available data on M−H bond strengths for these complexes (Cr = 62, Mo = 65, W = 73 kcal/mol)[6,16] indicate that H atom transfer shown in eq 7 would be uphill by 12, 15, and 23 kcal/mol for Cr, Mo, and W, respectively. Any metal radical generated in eq 7 would be expected to combine rapidly with nitric oxide[17] (eq 8).

Reactions involving •NO always present the possibility that $\bullet NO_2$ may be involved instead. This more powerful radical, capable even of removing a hydrogen atom from R−H, is readily formed when •NO is exposed to O_2 or from the well-known disproportionation reaction[18] (eq 9). Whereas reaction

$$3\bullet\text{NO} \rightleftharpoons \text{N}_2\text{O} + \bullet\text{NO}_2 \quad (9)$$

7 is endothermic, reaction 10 is readily calculated to be exothermic for all of the metal hydrides (eq 10).

$$\text{H-M(CO)}_3\text{C}_5\text{Me}_5 + \bullet\text{NO}_2 \rightarrow \bullet\text{M(CO)}_3\text{C}_5\text{Me}_5 + \text{H-NO}_2 \quad (10)$$

The sequence of reactions 9 and 10 followed by 8 presents an alternative pathway for which generation of $\bullet NO_2$ in eq 9 would be rate-limiting. Reactions in which $\bullet NO_2$ may build up either from slow infusion of oxygen or metal-catalyzed disproportionation[19] may lead to false conclusions regarding apparent reactivity of metal hydrides if care is not taken to exclude this possibility. The measured value for the enthalpy of activation, ∼12 kcal/mol, is identical to estimates made earlier on the basis of bond strength data. A small overbarrier of 1−4 kcal/mol is expected for radical reactions of this type. The close agreement between the calculated energy difference based on bond strength data and the observed enthalpy of activation is likely attributable to experimental errors on the order of 2−3 kcal/mol in each of these bond strength estimates.[3,6]

Rate-determining H atom transfer from metal to nitric oxide is also supported by investigation of reactions of the analogous molybdenum and tungsten hydrides. As discussed earlier, molybdenum and tungsten hydride complexes are predicted to have activation energies (based on the metal−hydrogen bond dissociation energies) 3 and 11 kcal/mol, respectively, higher than that for chromium if the mechanism involves breaking the M−H bond as a rate-determining step. Qualitative studies showed that under comparable conditions the molybdenum hydride reacted ∼150 times slower than the chromium hydride and the tungsten hydride did not react to any extent. The fact that the tungsten hydride did not react to any detectable amount shows that under the conditions utilized reactions based on $\bullet NO_2$ are probably not responsible. Although no mechanism can be completely proven, eqs 7 and 8 are the simplest reaction scheme accounting for all of the observations described above.[25]

Kinetic Study of Reaction of •NO and PhS-Cr(CO)$_3$C$_5$Me$_5$. Reaction of PhS-Cr(CO)$_3$C$_5$Me$_5$ with •NO at 1−2 atm pressure in toluene solution also forms Cr(NO)(CO)$_2$C$_5$Me$_5$ as the sole metal-containing product, and the unstable nitrosothiol PhS-NO is also proposed to be formed as an initial product (eq 11).

$$\text{PhS-Cr(CO)}_3\text{C}_5\text{Me}_5 + 2\bullet\text{NO} \rightarrow \text{Cr(NO)(CO)}_2\text{C}_5\text{Me}_5 + \text{PhS-NO} \quad (11)$$

Nitrosothiols[22] are known to decompose according to eq 12.

$$2\text{RS-NO} \rightarrow \text{RS-SR} + 2\bullet\text{NO} \quad (12)$$

Characterization of PhS-NO is based on the observed FT-IR band at 1565 cm^{-1}, assigned for $\nu_{\text{PhS-NO}}$,[23] which grew in and then decayed during the course of reaction.

The rate of reaction 11 was studied under pseudo-first-order conditions of constant pressure of •NO. Spectroscopic data showed clean and quantitative conversion of PhSCr(CO)$_3$C$_5$Me$_5$ to Cr(NO)(CO)$_2$C$_5$Me$_5$. Plots of ln[PhSCr(CO)$_3$C$_5$Me$_5$] versus time were linear through at least three half-lives. As shown in Table 2 in the Supporting Information, the rate of reaction was found to be **independent** of the pressure of •NO when studied between 1.0 and 2.84 atm. Values for the first-order rate constant of 8.0×10^{-4} (10 °C), 3.1×10^{-3} (20 °C), and 1.1×10^{-2} (30 °C) s^{-1} yield calculated activation parameters of $\Delta H^{\ddagger} = 21.6 \pm 1.2$ kcal/mol and $\Delta S^{\ddagger} = +3.9 \pm 1.5$ cal/(mol deg). The rate of reaction was shown to be independent of added CO pressure; reactions performed at a total pressure of 3 atm (1 atm •NO and 2 atm CO) yielded the same first-order rate constant as those done under 3 atm (1 atm •NO and 2 atm Ar).

The fact that the rate of reaction was independent of both •NO and CO suggested two possible mechanisms. The first is rate-determining fragmentation of the starting materials to radicals by complete cleavage of the Cr−SPh bond[4] (eq 13).

$$\text{PhS-Cr(CO)}_3\text{C}_5\text{Me}_5 \rightarrow \text{PhS}\bullet + \bullet\text{Cr(CO)}_3\text{C}_5\text{Me}_5 \quad (13)$$
$$\Delta H = +\ 35\ \text{kcal/mol}$$

Rapid trapping of the two radicals (eq 13) by •NO would yield products. However, the activation parameters listed above do not support this mechanism. The reported value for the Cr−SPh bond of 35 kcal/mol[4] is too high to support full dissociation to radicals. In addition, the entropy of activation would be expected to be more positive for a dissociative mechanism.

Any other mechanism independent of [•NO] and not involving either dissociation of CO (ruled out because the rate of reaction is independent of added CO) or •SPh (ruled out because the enthalpy of activation is too low) must be a rate-limiting rearrangement of the metal complex. Rate-determining migration of alkyls to coordinated carbon monoxide have been shown to yield rate laws for reaction 14 which are independent of [L]:[24]

$$\text{R-Mo(CO)}_3\text{Cp} \xrightarrow{\text{rds}} \text{Mo(CO)}_2(\eta^2\text{-C(=O)R)Cp} + \text{L} \xrightarrow{\text{fast}} \text{R-C(O)Mo(CO)}_2\text{(L)Cp} \quad (14)$$

Analogous reactivity with phenyl thiyl migration and •NO as the incoming ligand is shown in eq 15. Thermochemical data

$$\mathrm{PhS\text{-}Cr(CO)_3C_5Me_5} \xrightarrow{\text{rds}} \mathrm{Cr(CO)_2(\eta^2\text{-}C(=O)SPh)C_5Me_5} \qquad (15)$$

$$\Big\downarrow \text{fast} \quad \bullet\mathrm{NO}$$

$$\mathrm{Cr(\bullet NO)(CO)_2(\eta^1\text{-}C(=O)SPh)C_5Me_5}$$

$$\Big\downarrow \text{fast}$$

$$\mathrm{Cr(NO)(CO)_2C_5Me_5 + CO + PhS\bullet} \quad \underset{\bullet\mathrm{NO}}{\xrightarrow{\text{fast}}} \mathrm{PhS\text{-}NO}$$

(subtraction of eq 18 reported below from eq 13) indicate that $\Delta H° \approx 2$ kcal/mol for reaction 16. Because it can be estimated[24]

$$\mathrm{PhS\text{-}Cr(CO)_3C_5Me_5} + \bullet\mathrm{NO} \rightarrow \mathrm{PhS\bullet} + \mathrm{CO} + \mathrm{Cr(NO)(CO)_2C_5Me_5} \quad (16)$$

that $\Delta S° \approx 30$ cal/(mol deg) for reaction 16, any net process leading to it should have $\Delta G° \leq 0$. Other possibilities with literature precedent, namely, involvement of the Cp* ligand either in migration of the •SPh radical to the ring or in η^5 to η^3 "ring slippage", are viewed by the authors as less likely.[25]

Kinetic Study of Reaction of •NO and HS-Cr(CO)$_3$C$_5$Me$_5$. Recently the sulfhydryl complexes HS-M(CO)$_3$C$_5$Me$_5$ have been prepared in our laboratory.[26] Reaction of •NO with H-S-Cr(CO)$_3$C$_5$Me$_5$ was investigated to see if reaction might occur by attack at the sulfur−hydrogen bond (eq 17). It was thought that

$$\bullet\mathrm{NO} + \mathrm{H\text{-}S\text{-}Cr(CO)_3C_5Me_5} \xrightarrow{?} \mathrm{H\text{-}NO} + \bullet\mathrm{S\text{-}Cr(CO)_3C_5Me_5} \quad (17)$$

reaction 17 might be feasible if the H−S bond strength in the sulfhydryl complex was reduced as a result of stability of the •S-Cr(CO)$_3$C$_5$Me$_5$ radical.[26] However, no evidence for reaction 17 was found: (i) the rate of reaction was zero-order in •NO pressure and hence resembles reaction of PhS-Cr(CO)$_3$C$_5$Me$_5$ instead of H-Cr(CO)$_3$C$_5$Me$_5$, and (ii) decomposition products expected from reaction 17 [N$_2$O and HNO$_2$ from HNO or chromium sulfido products from •S-Cr(CO)$_3$C$_5$Me$_5$] were not detected. Reaction proceeded cleanly to give Cr(NO)(CO)$_2$C$_5$Me$_5$ as the only metal-containing product. Reaction of HS-Cr(CO)$_3$C$_5$Me$_5$ was found to be slower than that of PhS-Cr(CO)$_3$C$_5$Me$_5$, in keeping with the fact that the Cr−SPh bond is weaker than the Cr−SH[4,26] bond, which would presumably present a higher barrier to migration.

Enthalpy of Reaction of •NO and •Cr(CO)$_3$C$_5$Me$_5$. The enthalpy of reaction 18 was measured in toluene solution at 30 °C:

$$\bullet\mathrm{NO} + \bullet\mathrm{Cr(CO)_3C_5Me_5} \rightarrow \mathrm{Cr(NO)(CO)_2C_5Me_5} + \mathrm{CO} \qquad \Delta H° = -33.0 \pm 1.8\ \text{kcal/mol} \quad (18)$$

Reaction 18 includes loss of CO as well as coordination of •NO. The Cr−CO bond strength in Cr(CO)$_6$ is 36.8 kcal/mol.[27] Assuming this bond strength can be transferred[28] to •Cr(CO)$_3$C$_5$Me$_5$, the total Cr−NO bond strength is estimated to be 70 kcal/mol for loss of •NO as a net three-electron donor (eq 19). This

$$\mathrm{Cr(NO)(CO)_2C_5Me_5} \rightarrow \bullet\mathrm{NO} + \bullet\mathrm{Cr(CO)_2C_5Me_5} \qquad \Delta H = +70\ \text{kcal/mol} \quad (19)$$

value provides a "benchmark" for how strong thermodynamically disfavored loss of •NO is when bound to a low valent saturated complex. As discussed above, the exothermic nature of reaction 18 provides the driving force for the calculated thermoneutral production of phenyl thiyl radicals according to reaction 16. Additional work is in progress to further define the thermodynamic activating power of •NO.[29]

Rate of Reaction of ^{12}CO with Cr(NO)(^{13}CO)$_2$C$_5$Me$_5$. These studies were begun to try to obtain some estimate the enthalpy of binding of •NO as a one-electron versus three-electron donor. The measured net enthalpy of reaction 18 (−33 kcal/mol) can be considered the sum of the two steps shown in eq 20. The first step shown in eq 20 is formation of a radical

$$\mathrm{ON\bullet} + \bullet\mathrm{Cr(CO)_3C_5Me_5} \xrightarrow{\text{(i)}} \mathrm{ON\bullet\cdots\bullet Cr(CO)_3C_5Me_5} \xrightarrow{\text{(ii)}} \mathrm{Cr(NO)(CO)_2C_5Me_5} + \mathrm{CO} \quad (20)$$

pair or bent nitrosyl complex in which •NO is effectively a one-electron donor. The second step is loss of a CO ligand and conversion to a bent nitrosyl complex that is effectively a three electron donor. Kinetic data for either the forward or reverse steps in reaction 20 could provide information about how the −33 kcal/mol is partitioned between steps i and ii.

There is considerable evidence, particularly for phosphine substitution, that conversion of linear NO complexes to bent facilitates ligand substituion.[1] The reverse of step ii for eq 20 would provide a mechanism for exchange of isotopically labeled CO. The labeled complex Cr(NO)(^{13}CO)$_2$C$_5$Me$_5$ was prepared, and the rate of reaction 21 investigated. Heating the reactants

$$\mathrm{Cr(NO)(^{13}CO)_2C_5Me} + {}^{12}\mathrm{CO} \rightarrow \mathrm{Cr(NO)(^{12}CO)_2C_5Me_5} + {}^{13}\mathrm{CO} \quad (21)$$

from room temperature to 60 °C under a pressure of 15 atm ^{12}CO resulted in no detectable substitution over a period of 2 h. These data imply a substantial barrier to the reverse of the second step in eq 20. All attempts on our part to detect the proposed intermediate ON•···•Cr(CO)$_3$C$_5$Me$_5$ have been unsuccessful to date and indicate vary low barriers to reaction 20 in the forward direction.[29] These two observations imply that the majority of the −33 kcal/mol is "spent" on the second reaction and that the enthalpy of forming the initial adduct is small. Additional work in progress is aimed at better understanding of the thermochemistry of •NO coordination.

Conclusion

Reaction of •NO and H-Cr(CO)$_3$C$_5$Me$_5$, RS−Cr(CO)$_3$C$_5$Me$_5$, and •Cr(CO)$_3$C$_5$Me$_5$ have been studied. Combination of the two radicals leads rapidly to Cr(NO)(CO)$_2$C$_5$Me$_5$ and is exothermic by 33 ± 1.8 kcal/mol. The Cr−NO bond strength of ~70 kcal/mol is one of the highest ligand-to-metal bonds measured to date for a first row metal.[30]

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(27) Smith, G. P. *Polyhedron* **1988**, *7*, 1605.

(28) There is always risk involved in assuming that bonds strengths in one complex can be transferred to another. The formal oxidation state of Cr in •Cr(CO)$_3$C$_5$Me$_5$ is +1 compared to Cr(CO)$_6$ where the formal oxidation state is 0. Higher oxidation states normally result in weaker M-CO bonds, but the strong donating power of the Cp* ligand offsets that such that the average CO stretching frequencies of the A and E bands of •Cr(CO)$_3$C$_5$Me$_5$ (1994 and 1886 cm^{-1}) are lower than the observed A band of Cr(CO)$_6$ (1980 cm^{-1}). In short, the authors feel that the bond strengths are comparable for the two low valent complexes discussed here.

(29) At temperatures as low as − 30 °C, even under CO atmosphere, no intermediate such as Cr(NO)(CO)$_3$C$_5$Me$_5$ could be detected. The sampling time in these experiments was 10 s. Work in progress is aimed at repeating this measurement on the millisecond time scale.

(30) Hoff, C. D. *Prog. Inorg. Chem.* **1992**, *40*, 503.

Ultimately it is this driving force that is responsible for generation of the unstable molecules HNO and RSNO when nitric oxide reacts with the chromium hydride and thiolate complexes. The mechanisms of these two apparently similar reductive eliminations are in fact quite different. Reaction of H-Cr(CO)$_3$C$_5$Me$_5$ is proposed to proceed by rate-limiting H atom transfer from chromium to nitric oxide, whereas reaction of RS-Cr(CO)$_3$C$_5$Me$_5$ was shown to proceed by a rate-limiting intramolecular rearrangement of the chromium thiolate, possibly through a complex such as Cr(CO)$_2$ (η^2-C(=O)SPh)C$_5$Me$_5$. In neither of these reactions does interaction of nitric oxide with the metal atom play an initial decisive role. Reaction of the hydride is viewed as abstraction of an H atom in which •NO reacts simply as a weak radical in the first step. In reaction of RS-Cr(CO)$_3$C$_5$Me$_5$, the apparent role of •NO is to trap a reactive intermediate formed in the first step of the reaction, which is viewed as an intramolecular rearrangement. It is in the final steps of these reactions that the unique character of •NO as a ligand is displayed. For the saturated complexes, H-Cr(CO)$_3$C$_5$Me$_5$ and RS-Cr(CO)$_3$C$_5$Me$_5$, the observed reactions are relatively slow, especially when compared to the rate of reaction of •Cr(CO)$_3$C$_5$Me$_5$. Additional work is in progress to further explore thermodynamic and kinetic aspects of how •NO interacts with complexes of the group VI metals.

Acknowledgment. Support of this work by the Petroleum Research Fund administered by the American Chemical Society and the National Science Foundation is gratefully acknowledged. A. B. thanks the Deutsche Forschungsgemeinschaft (DFG) for the granted postdoctoral fellowship.

Supporting Information Available: Experimental data and calculated rate constants for reactions of PhS-Cr(CO)$_3$C$_5$Me$_5$ and H-Cr(CO)$_3$C$_5$Me$_5$ with •NO and first-order plots of decay of [HCr(CO)$_3$C$_5$Me$_5$], buildup of [Cr(NO)(CO)$_2$C$_5$Me$_5$], and buildup of [N$_2$O]. This material is available free of charge via the Internet at http://pubs.acs.org.

IC990829I