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Reversible Exchange of (η^5-Cyclopentadienyl)(dinitrosoalkane)cobalt Complexes with Alkenes. Kinetic and Spectroscopic Evidence for $C_5H_5Co(NO)_2$ as a Reactive Intermediate

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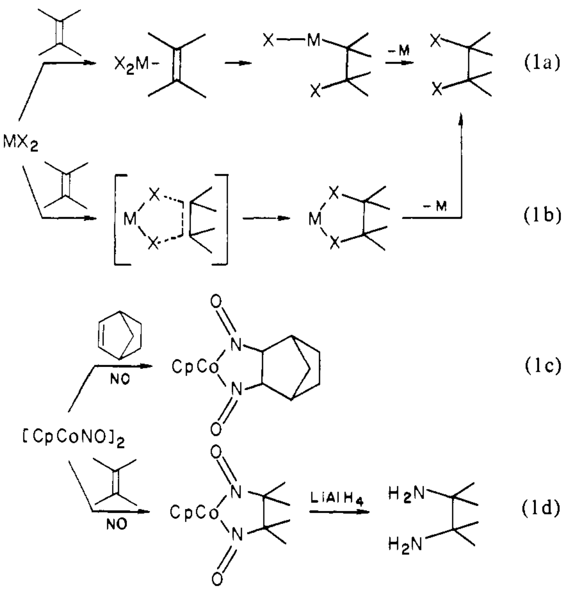
Abstract: Heating (η^5-cyclopentadienyl)(2,3-dimethyl-2,3-dinitrosobutane)cobalt (**1**), prepared from $[CpCoNO]_2$, NO, and 2,3-dimethyl-2-butene, with *cis-endo*-5,6-dicarbomethoxynorbornene (**2b**) in aromatic solvents converted it quantitatively into 2,3-dimethyl-2-butene (**4**) and **3b** (the adduct formed from **2b** and $[CpCoNO]_2$/NO). The reaction was first order in [**1**] with $k_{obsd} = (4.3 \pm 0.3) \times 10^{-4}\ s^{-1}$ at 75 °C, $E_a = 29.4 \pm 0.4$ kcal/mol, and $A = 1.3 \times 10^{15}\ s^{-1}$. Addition of alkene **4** inhibited the reaction in a linear fashion, consistent with a mechanism involving reversible dissociation of **1** into 2,3-dimethyl-2-butene and $CpCo(NO)_2$, followed by reaction of this dinitrosyl with **2b**, as shown in Scheme I. This olefin exchange occurs stereospecifically since complexes **5** and **7** exclusively regenerate (*E*)- and (*Z*)-3-methyl-2-pentene, respectively. Complex **1** also undergoes olefin exchange upon photolysis in the presence of **2b** with $\Phi_{300} = 1.12 \times 10^{-3}$. Treatment of $[CpCoNO]_2$ with nitric oxide generates a new species which is stable in solution at room temperature. This material is too reactive to allow isolation, but its solutions can be studied spectroscopically. It exhibits two bands in the IR (1609 and 1690 cm^{-1}) and a single resonance in the proton NMR (δ 4.22); in the UV it absorbs at λ_{max} 255 nm. Adding alkene to a solution of this material rapidly produces cobalt dinitrosoalkanes (Scheme III), identical with those formed on reaction of alkenes with $[CpCoNO]_2$/NO. On the basis of these observations this reactive species is proposed to be $CpCo(NO)_2$ (**10**). The kinetics of the reaction between **10** and alkenes have been studied by using rapid-scan UV-visible spectrophotometry. These experiments have shown that the rate is second order overall, first order in both dinitrosyl and alkene, and the bimolecular rate constants for a series of olefins are reported. An electronically modified derivative of **10**, $(CO_2Me)C_5H_4Co(NO)_2$ (**16**), was prepared from the corresponding dimer **15** and nitric oxide. This complex was noticeably more stable than its parent counterpart but was still too reactive to isolate.

Many homogeneous reactions are now known in which organotransition-metal complexes are used to transform alkenes into other organic materials. Some of these, such as hydroformylation and hydrocarboxylation, are major industrial processes;[1a] others are stoichiometric reactions useful in organic synthesis.[1b]

These reactions are among the most well studied of any in organometallic chemistry. The large majority proceed by a classical type of mechanism: π coordination of the alkene to the metal center, followed by an insertion and then a ligand-release reaction (eq 1a). However, a second type of mechanism has been identified in a smaller number of cases. Here the reactive ligands, activated in a more "remote" sense by the metal bound to them, react directly with an alkene (eq 1b). Osmium tetroxide oxidation and some related transformations[2] have been considered examples of this type of process. Such reactions have a number of practical advantages, the most important being attenuation of steric problems associated with direct approach to the metal center, more efficient complexation of electron-rich alkenes, and high retention of stereochemistry at the alkene.



It occurred to us that more examples of this second type of alkene activation, where X might by any number of electronegative σ-bound ligands, should be accessible. A reaction involving the formation of 1,2-dinitrosoalkane complexes from $[CpCoNO]_2$, nitric oxide, and bicyclo[2.2.1]hept-2-enes, which appeared to us to be an example of such a transformation, was reported several years ago[3a,b] by Brunner and his co-workers (eq 1c). This was especially intriguing because it involved C-N bond formation, a type of alkene functionalization which is rather rare, and also utilized metal nitrosyl complexes, whose inorganic and organometallic chemistry has been extensively studied. However, at the start of this work little was known about the mechanism of this reaction, or whether it could be generalized to a wide range of alkenes.

We therefore set out to investigate the scope and mechanism of this process. We found that the reaction proceeded well with a wide range of alkenes, even those which were substituted with several electron-donating alkyl groups. The dinitrosoalkanes formed in these reactions were in some cases isolable and in all cases could be reduced with $LiAlH_4$, providing a general method for converting alkenes into vicinal, primary diamines. This diamination method was communicated in 1980.[3c] The details of

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(1) For reviews, see (a) Parshall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980. (b) Alper, H., Ed. "Transition Metal Organometallics in Organic Synthesis"; Academic Press: New York, 1978.

(2) (a) Schroeder, M. *Chem. Rev.* **1980**, *80*, 187. (b) Chong, A. O.; Oshima, K.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 3420. For some recent comments on the OsO_4/alkane mechanism, see: (c) Schröder, M.; Constable, E. C. *J. Chem. Soc., Chem. Commun.* **1982**, 734. (d) Casey, C. P. *Ibid.* **1983**, 126.

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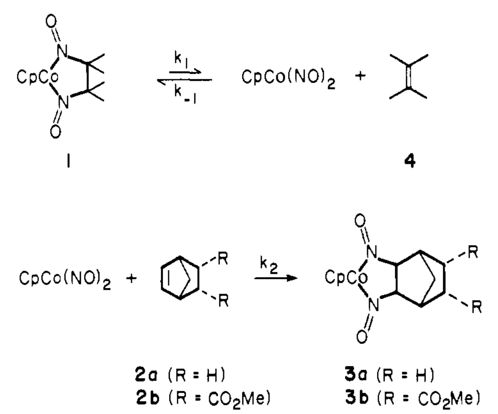
Scheme I

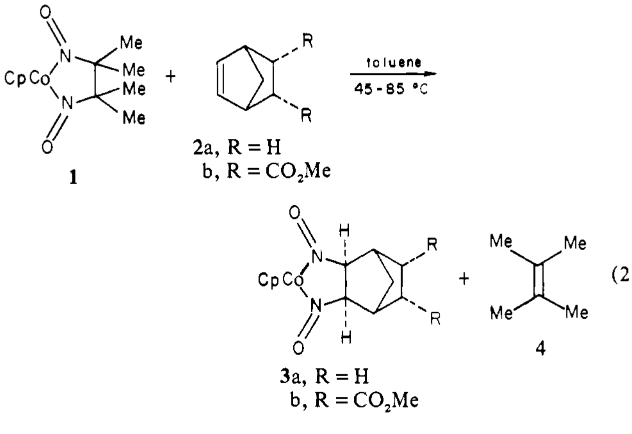


the diamination, the isolation and characterization of several dinitrosoalkane adducts, and a demonstration that dinitrosoalkane adduct formation is stereospecific are described in a separate paper.[3d]

During the course of this work, we discovered that the nitrosoalkane complexes are capable of exchanging olefin fragments both thermally and photochemically—that is, that the addition reaction illustrated in eq 1b is experimentally reversible, and so the C_2 fragments in the dinitrosoalkane adducts will undergo exchange with other alkenes. We report here a detailed study of the mechanism of this unique exchange reaction and evidence that it proceeds through the intermediacy of CpCo(NO)$_2$. In addition, we have found a method for generating solutions of the reactive species CpCo(NO)$_2$ and directly measuring the rate of its reactions with alkenes. This has allowed us to examine the steric and electronic factors affecting the reaction at both the metal center and incoming carbon–carbon double bond.

Results

Thermal Exchange of Olefins in CpCo(dinitrosoalkane) Complexes. Heating compound **1** with norbornene (**2a**) or substituted norbornene[4] **2b** at temperatures between 45 and 85 °C in benzene-d_6 or toluene-d_8 converted it quantitatively into **3a,b** (eq 2) and 2,3-dimethyl-2-butene.



1

2a, R = H
b, R = CO$_2$Me

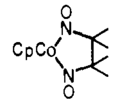
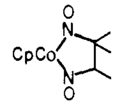
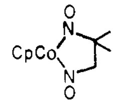
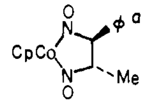
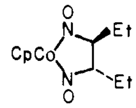
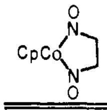
3a, R = H
b, R = CO$_2$Me

4

(2)

This olefin exchange was observed for other alkylnitroso complexes having sufficient stability to avoid decomposition by side reactions. For complexes that were too unstable to isolate, the following procedure was devised to test for olefin exchange. Typically, an excess of olefin was treated with [CpCoNO]$_2$ and NO gas at 0 °C in THF until all the dimer was consumed. The red solutions were then flash chromatographed on silica gel to separate the adducts from insoluble/polar materials. An excess of norbornene (**2a**) was then added under an argon purge, and the in situ formed alkylnitroso complex was converted into **3a**. Under these conditions, the yields of complex **3a** were based on the amount of [CpCoNO]$_2$ used.

Table I. Yields and Reaction Conditions for Olefin-Exchange Reaction between Dinitrosoalkane Complexes and 2a

Dinitrosoalkane Complex	Reaction Conditions	Isolated Yield of 3a
	C_6H_6, 80°C 2 hr	100%
	C_6H_6, 80°C 2 hr	83%
	C_6H_6, 80°C 2 hr	75%
 [a]	CH_2Cl_2, rt 48 hr	75% [b]
 [a]	C_6H_6, 80°C 22 hr	63% [b]
 [a]	THF, rt 6.5 hr	11% [b]

[a] Complex generated in situ. [b] Yield based on [CpCoNO]$_2$.

Table II. Observed Rate Constants for the Reaction between 1 (0.2-10^{-4} M) and 2b (0.4-10^{-3} M) at 75 °C in Toluene[a]

[1], M	[2b], M	[4], M	k_{obsd}, s^{-1}
2.0×10^{-2}	1.0×10^{-1}		4.28×10^{-4}
2.0×10^{-2}	4.0×10^{-1}		4.25×10^{-4}
1.0×10^{-3}	1.0×10^{-2}		4.27×10^{-4}
1.3×10^{-3}	2.2×10^{-1}		4.02×10^{-4}
5.0×10^{-4}	5.0×10^{-3}		4.63×10^{-4}
1.0×10^{-4}	1.0×10^{-3}		4.47×10^{-4}
1.0×10^{-4}	1.0×10^{-3}	0.20	1.6×10^{-4}
1.0×10^{-4}	1.0×10^{-3}	0.40	1.0×10^{-4}
1.0×10^{-4}	1.0×10^{-3}	0.60	7.3×10^{-5}
1.0×10^{-4}	1.0×10^{-3}	0.80	6.0×10^{-5}

[a] First two runs were monitored by ^{1}H NMR spectroscopy; rest were monitored by UV/vis spectrometry.

The isolated yields of **3a** for several exchange reactions are shown in Table I. They correlate roughly with the relative thermal stability of the alkylnitroso complexes. Those that are quite unstable, such as the ethylene-derived complex, give lower yields because they decompose to form insoluble materials in competition with the exchange reaction.

Kinetics of Olefin Exchange. A proposed mechanism for the exchange reaction is shown in Scheme I. Applying the steady-state approximation to the concentration of the reactive intermediate CpCo(NO)$_2$, one derives the rate expression given in eq 3. When $k_2[\mathbf{2}] \gg k_{-1}[\mathbf{4}]$, the equation simplifies to that shown

$$-\frac{d[\mathbf{1}]}{dt} = \frac{k_1k_2[\mathbf{2}][\mathbf{1}]}{k_{-1}[\mathbf{4}] + k_2[\mathbf{2}]} \tag{3}$$

$$-\frac{d[\mathbf{1}]}{dt} = k_1[\mathbf{1}] = k_{obsd}[\mathbf{1}] \tag{4}$$

in eq 4, which predicts that under these conditions the observed

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(3) (a) Brunner, H. *J. Organomet. Chem.* **1968**, *12*, 517. (b) Brunner, H.; Loskot, S. *Ibid.* **1973**, *61*, 401. (c) Becker, P. N.; White, M. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 5676. (d) Becker, P. N.; Bergman, R. G. *Organometallics*, in press.

(4) For kinetic runs, the diester derivative of norbornene was more convenient to use than norbornene itself because **2b** is a relatively nonvolatile solid that can be accurately weighed in milligram amounts.

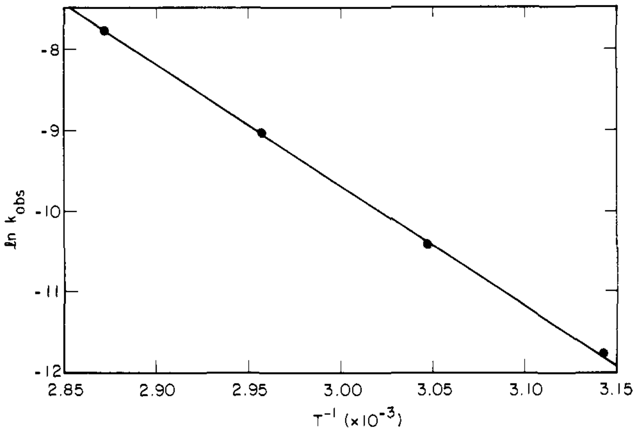


Figure 1. Arrhenius plot for the reaction of **1** (10^{-3} M) with **2b** (10^{-2} M) in toluene from 45 to 75 °C ($E_a = 29.4 \pm 0.4$ kcal/mol; $A = 1.3 \times 10^{15}$ s^{-1}).

rate should exhibit a first-order dependence on the concentration of **1** and no dependence on the norbornene concentration. Experimentally, this condition is satisifed[5] by employing a large excess of **2b**. The reaction rates at 75 °C in toluene were measured by both ^{1}H NMR and UV/vis spectroscopy. Data from both analytical methods gave good first-order plots with $k_{obsd} = (4.3 \pm 0.3) \times 10^{-4}$ s^{-1}. The rate remained constant upon varying the concentration of excess **2b** from 0.001 to 0.40 M (Table II).

Figure 1 shows the Arrhenius plot for this reaction determined over a temperature range of 45–75 °C. The activation energy (E_a) for this process is 29.4 ± 0.4 kcal/mol while the preexponential factor (A) is 1.3×10^{15} s^{-1}.

The large excess of norbornene employed in the above experiments was designed to trap the presumed $CpCo(NO)_2$ intermediate as it formed, thereby preventing any back reaction (k_{-1}) from occurring. To verify that the back reaction pathway was accessible, we next carried out a set of kinetic runs using added excess 2,3-dimethyl-2-butene. Under these conditions, $k_{-1}[4]$ is competitive with $k_2[2]$, and the full rate law in eq 3 holds. At high [2] and [4], these concentrations remain effectively constant during each run and allow determination of pseudo-first-order rate constants k_{obsd}. The reciprocal of k_{obsd} is given by eq 5. This

$$\frac{1}{k_{obsd}} = \frac{k_{-1}}{k_1 k_2}\frac{[4]}{[2]} + \frac{1}{k_1} \qquad (5)$$

predicts that a plot of $1/k_{obsd}$ vs. [4]/[2] should be linear having a slope equal to k_{-1}/k_1k_2 and an intercept value of $1/k_1$. Experimentally, the reaction required very large [4]/[2] ratios (greater than 200/1) in order to obtain a significant inhibition of the overall rate. At these high ratios, the absolute concentration of 2,3-dimethyl-2-butene (**4**) ranged from 0.2 to 0.8 M.

The data, plotted according to eq 5, are displayed in Figure 2. This demonstrates the predicted linear decrease in the reaction rate as the [4]/[2] ratio increases. From the slope in Figure 2, the ratio k_2/k_{-1}, which represents the selectivity of the intermediate for **4** or **2**, can be calculated. Its value is 115, meaning that substituted norbornene **2b** reacts 115 times faster than 2,3-dimethyl-2-butene (**4**) with $CpCo(NO)_2$ at 75 °C.

Stereochemistry of Olefin Exchange. We have presented evidence for the stereospecific formation of isomeric alkylnitroso complexes from (E)- and (Z)-3-methyl-2-pentene.[3c,d] We were now able to examine whether, under conditions for olefin exchange, these complexes would also stereospecifically release the olefin from which they were synthesized. Our mechanism proposes that the rate-determing step in the olefin-exchange reaction (Scheme I, line 1) is the microscopic reverse of the pathway for complex formation. Therefore, it should also occur stereospecifically. Indeed, when heated in separate benzene-d_6 solutions containing an excess of substituted norbornene **2b**, alkylnitroso complex **5** liberated only (E)-3-methyl-2-pentene (**6**) while complex **7** gave only (Z)-3-methyl-2-pentene (**8**) (eq 6 and 7).

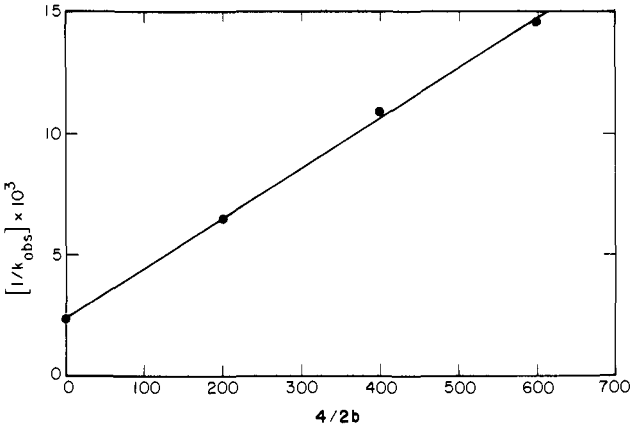
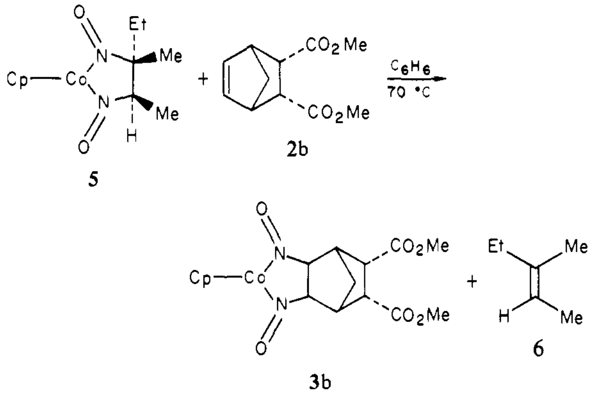
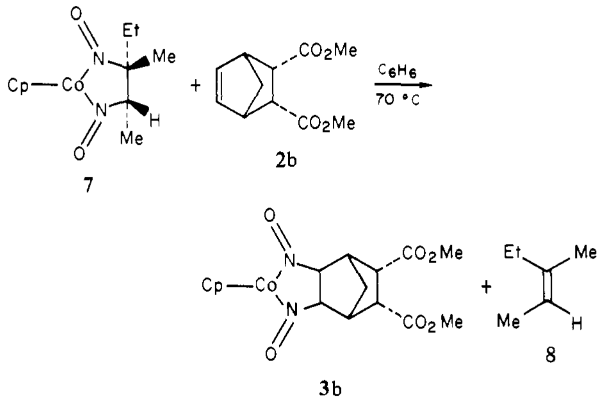


Figure 2. Plot of the ratio [4]/[2b] vs. $1/k_{obsd}$ for the reaction of **1** and **2b** with added **4** in toluene at 75 °C.



(6)



(7)

Photochemically Induced Olefin Exchange. Initial experiments were conducted in a Pyrex NMR tube containing a THF-d_8 solution of complex **1** (0.02 M) and substituted norbornene **2b** (0.02–0.2 M). Photolysis of these mixtures for 1 h at 0 °C using a high-pressure mercury lamp yielded the expected alkylnitroso complex **3b** and free 2,3-dimethyl-2-butene (**4**). Repetition of this experiment at −90 to 0 °C without any added norbornene showed the appearance of a signal in the ^{1}H NMR spectrum for free 2,3-dimethyl-2-butene at 1.6 (s) ppm but no new resonances in the cyclopentadienyl region (4–6 ppm). A small amount of green precipitate formed during the reaction. Thus, if $CpCo(NO)_2$ is generated at low temperature, either it is unstable upon warming to room temperature or it undergoes secondary photochemical reactions to form insoluble material.

To determine which absorption wavelength was causing the carbon-nitrogen bond cleavage, we recorded the electronic spectra of alkylnitroso complexes **1** and **3b** in cyclohexane. They were

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(5) In the temperature range 45–85 °C, reversion of **3** to $CpCo(NO)_2$ (Scheme I) does not occur. It becomes significant only at temperatures around 110 °C.

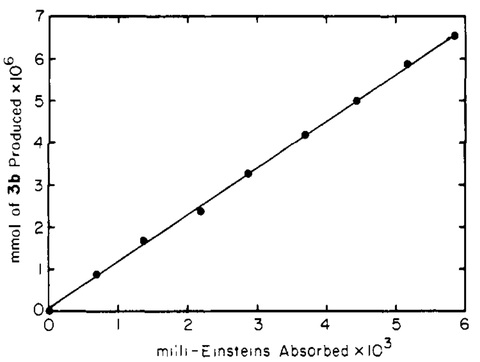
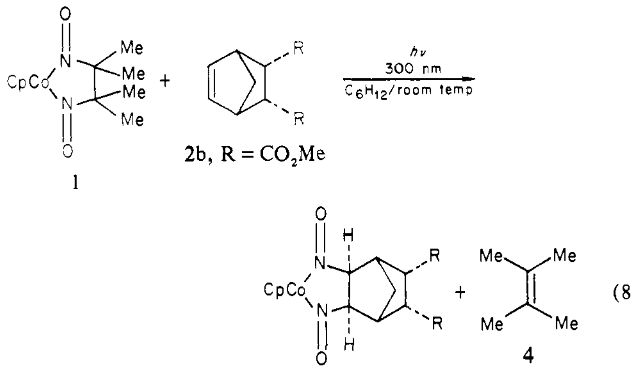


Figure 3. Plot of appearance of **3b** vs. photons absorbed at 300 nm for the reaction of **1** with **2b** in cyclohexane at 20 °C ($\Phi_{300} = 1.12 \times 10^{-3}$).

identical in line shape and differed only slightly in the values of their extinction coefficients. Both contained a near-UV maximum at 300 nm ($\epsilon \sim 28\,000$) and visible bands at 440 ($\epsilon \sim 4500$) and 520 nm ($\epsilon \sim 2500$). It was established that the absorption band at 300 nm was photoreactive by conducting an experiment where only light of wavelengths longer than 390 nm was permitted to pass through the reaction vessel. Under this constraint, the exchange reaction did not take place.

The quantum yield for the reaction in eq 8 was determined in cyclohexane at room temperature by using a CMX-4 flash-pumped dye laser as the source of 300-nm light and quantitative HPLC for analysis. The actinometry was performed by using an electronic integrator[6] calibrated against potassium ferrioxalate. The reaction was carried to only 7% conversion to prevent the product **3b** from absorbing large amounts of incident light. Figure 3 shows the linear relationship between the appearance of **3b** and the number of quanta absorbed. The quantum yield obtained from the slope of this line is 1.12×10^{-3}.



1

2b, R = CO$_2$Me

3b, R = CO$_2$Me

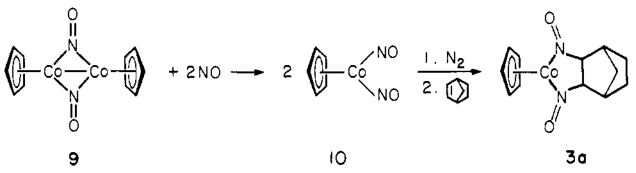
4

(8)

Generation and Direct Observation of CpCo(NO)$_2$. Having obtained evidence for the existence of CpCo(NO)$_2$ as a transient intermediate, we decided to attempt to generate the species under conditions where it might be directly observable.

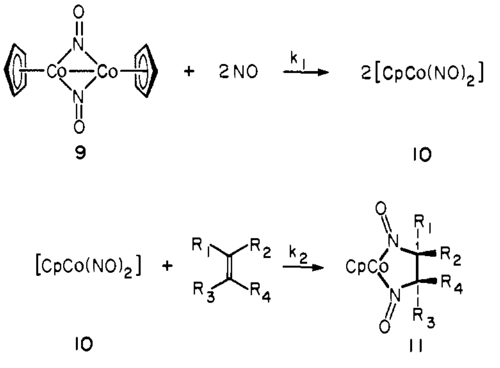
When [CpCoNO]$_2$ (**9**) is placed in a benzene or THF solution, it forms a dark green solution. If the solution is dilute enough (<0.05 M), one can observe that it changes color upon introduction of NO gas to give a lighter, brighter green solution. If this solution is allowed to stand, decomposition ensues. However, if it is transferred rapidly into an IR cell, one observes that the IR stretching frequencies of [CpCoNO]$_2$ at 1540 (s) and 1590 (s) cm^{-1} have diminished, while two new higher frequency absorptions have appeared at 1609 (s) and 1690 (m) cm^{-1}, consistent with the assignment of this species as CpCo(NO)$_2$. When excess NO is bubbled thrugh the system, decomposition to a brown insoluble precipitate occurs. Purging the solution with dry nitrogen to remove excess NO leaves the IR spectrum unchanged. Upon standing for extended time periods, the solution of CpCo(NO)$_2$ eventually deposits insoluble precipitate, the rate depending qualitatively upon the starting concentration of [CpCoNO]$_2$.

Scheme II



9 10 3a

Scheme III



NMR experiments confirm the existence and relative structural simplicity of the intermediate and demonstrate that it is diamagnetic. In a typical experiment, 2 equiv of NO gas was condensed into a frozen benzene-d_6 solution of [CpCoNO]$_2$ and the tube sealed under vacuum. On thawing, the room-temperature ^{1}H NMR spectrum showed 74% conversion (quantitative yield) of **9** (δ 4.53 (s)) to a substance exhibiting a single new Cp resonance at δ 4.22 (s). Similarly, monitoring the reaction between **9** and NO by UV in cyclohexane solution showed the replacement of the band due to **9** (λ_{max} 306 nm ($\epsilon \sim 36\,000$)) by a blue-shifted band at λ_{max} 255 nm ($\epsilon \sim 18\,000$ (estimated)).

Concentration of solutions exhibiting the spectroscopic absorptions characteristic of the intermediate again results in rapid decomposition to brown, intractable material, and this has so far prevented its isolation. However, treatment of a solution of the intermediate with norbornene (after purging with N$_2$ to remove NO) resulted in an immediate color change from green to red, the color of the norbornene/CpCo(NO)$_2$ adduct **3a** (Scheme II). This treatment also produced immediate disappearance of the IR bands of the intermediate and appearance of new bands at 1350 (s) and 1418 (m) cm^{-1} characteristic of **3a**. Evaporation of solvent followed by chromatography on silica gel provided the pure adduct **3a** in 72% isolated yield based on starting **9**.

To synthesize CpCo(NO)$_2$ by another route, we treated NaCpCoNO[7] with NOBF$_4$ in DME. Unfortunately, the only isolable product of this reaction was [CpCoNO]$_2$, formed in 46% yield. However, we were successful in making CpCo(NO)$_2$ from another dimeric starting material. When [Cp(NO)$_2$-μ-Cl]$_2$[8] was treated with either sodium or lithium cyclopentadienide in THF or dimethoxyethane (DME), the expected color change and the IR spectrum of CpCo(NO)$_2$ were observed (eq 9). This material also slowly decomposed upon standing.

$$[\mathrm{Co(NO)_2}\text{-}\mu\text{-}\mathrm{Cl}]_2 + 2\mathrm{MC_5H_5} \xrightarrow[\mathrm{DME}]{\mathrm{THF\ or}} \underset{\mathbf{10}}{\mathrm{CpCo(NO)_2}} + 2\mathrm{MCl} \quad (9)$$

$$\mathrm{M = Na, Li}$$

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[6] We used an electronc integrator on loan from Prof. W. G. Dauben at U.C. Berekely. It was a replica of that developed by Amrein, Gloor, and Schaffner (*Chimia* **1974**, *28*, 185–188).

[7] Weiner, W.; White, M. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3612.

[8] Prepared according to literature methods with recommended modifications. See: (a) Hieber, W.; Marin, R. *Z. Anorg. Allg. Chem.* **1939**, *240*, 241. (b) Sacco, A.; Rossi, M.; Nobile, C. *Ann. Chim.* (*Rome*) **1967**, *57*, 499.

Kinetics of Reaction between $CpCo(NO)_2$ and Olefins. Although $CpCo(NO)_2$ could not be isolated, we found that under dilute conditions (ca. 10^{-5}–10^{-4} M), air-free solutions exhibited remarkable stability. The UV/vis spectrum was unchanged over a 20-min period.

We decided to attempt direct kinetic studies on the reaction of this complex with olefins. The mechanism, depicted in Scheme III, proposes that a bimolecular reaction takes place between $CpCo(NO)_2$ and the olefin, producing alkylnitroso complex **11**. The rate law for this scheme is shown in eq 10. When a large excess of olefin is used, the equation simplifies to a rate law where $k_{obsd} = k_2[\text{olefin}]$ (eq 11). This predicts a pseudo-first-order dependence on metal concentration.

$$d[\mathbf{11}]/dt = k_2[\text{olefin}][\mathbf{10}] \tag{10}$$

$$d[\mathbf{11}]/dt = k_{obsd}[\mathbf{10}] \tag{11}$$

The availbility of a rapid-scan UV/vis spectrophotometer facilitated these kinetic studies. In a typical experiment, 2.0 mL of a dilute (ca. 3×10^{-5} M) solution of dimer **9** was reacted with NO gas for a few seconds in an air-protected quartz UV cell. This was sufficient to convert >95% (as evidenced by the change in the UV spectrum) of the material into the bright green $CpCo(NO)_2$ (**10**). The solution was purged of excess NO by dry nitrogen for a few seconds. A 2.0-mL aliquot containing an excess (>10 × [**10**]) of a known concentration (usually 10^{-3}–10^{-1} M) of the desired olefin was injected into the preformed solution of **10** and the reaction monitored spectrophotometrically from 200 to 800 nm. It was convenient to adjust the concentration of the reacting olefin so that the reaction took place with an observed half-life between 5 and 0.5 min.[9] In all experiments, conversion of $CpCo(NO)_2$ to the corresponding adducts **11** was observed. The spectral changes generated clear-cut isosbestic points as in the case of the reaction with 2,3-dimethyl-2-butene ($R_1 = R_2 = R_3 = R_4 = CH_3$) shown in Figure 4. These reactions were all followed to 3 half-lives and displayed excellent first-order kinetics in agreement with the predicted rate law. A typical plot is shown in the upper corner of Figure 4. Table III lists absolute and relative (to (*Z*)-3-hexene) bimolecular rate constants measured for a series of simple aliphatic olefins in cyclohexane solvent at 20 °C.

Having proven that this reaction was first order in [**10**], it remained to show that the reaction was also first order in olefin concentration and therefore second order overall. The derived rate law predicts that varying the concentration of excess olefin ought to linearly affect the observed first-order rate. A series of kinetic experiments were conducted in which the concentration of 2,3-dimethyl-2-butene was raised from 0.015 to 0.15 M. This produced the expected increase in reaction rate (Figure 5). The slope in Figure 5 is equal to k_2, the absolute bimolecular rate constant for the reaction.

If the transition state for forming these cobalt alkylnitroso complexes developed appreciable ionic character or polarity relative to the reactants, the rate ought to be accelerated by polar solvents. To test for this possibility, we measured the rates of reaction between 2,3-dimethyl-2-butene and $CpCo(NO)_2$ in a series of solvents of increasing polarity. The results are displayed in Table IV. As a measure of solvent polarity, we used the empirical scale, $E_T(30)$, determined by Dimroth and co-workers.[10] The rates are quite insensitive to solvent polarity. If there is any trend at all, it is that the reaction appears to be slightly decelerated in more polar media, meaning that the transition state must be of similar or slightly lower polarity than the reactants.

In order to probe the effect of electronic changes on the $CpCo(NO)_2$ fragment, two modified derivatives of $[CpCoNO]_2$

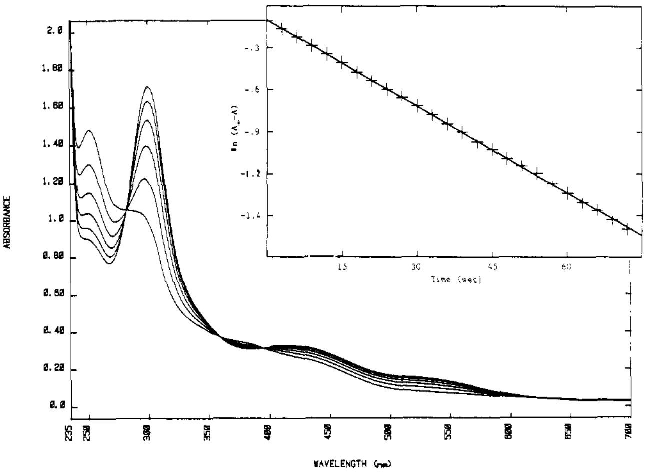


Figure 4. UV-visible spectra taken during reaction between **10** (3.95×10^{-5} M) and 2,3-dimethyl-2-butene (**4**) (6.7×10^{-2} M) in cyclohexane at 20 °C. Curves shown are at 20-s intervals. Inset shows pseudo-first-order plot using absorbance at 300 nm; points taken from full scans run every 3 s.

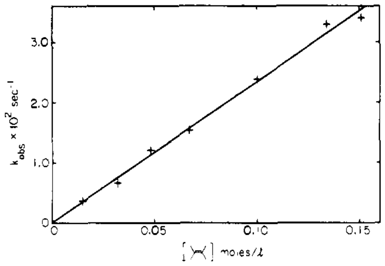


Figure 5. Plot of k_{obsd} vs. [**4**] for the reaction between **10** and **4** conducted in cyclohexane at 20 °C. The slope represents the value of the absolute bimolecular rate constant k_2 (0.23 M^{-1} s^{-1}) for the reaction.

Table III. Absolute and Relative Bimolecular Rate Constants for the Reaction of $CpCo(NO)_2$ with Olefins in Cyclohexane at 20 °C

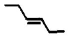
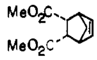
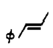
Olefin	k_2 (M^{-1} s^{-1})	k_{rel}	Olefin	k_2 (M^{-1} s^{-1})	k_{rel}
	1.3×10^2	4.8×10^3		9.0×10^{-2}	3.3
	51	1.9×10^3		7.8×10^{-2}	2.9
	3.9	1.4×10^2		2.7×10^{-2}	1.0
	6.6×10^{-2}	2.4		8.4×10^{-1}	31
	9.7×10^{-3}	3.6×10^{-1}			
	2.5×10^{-1}	9.3			
					
n-$C_4H_9CH{=}CH_2$	1.5×10^{-1}	5.6			

Table IV. Bimolecular Reaction Rates for $CpCo(NO)_2$ with 2,3-Dimethyl-2-butene at 20 °C

Solvent	k_2 ($M^{-1}s^{-1}$)	k_{rel}	$E_T(30)$[a] (kcal/mole)
Cyclohexane	0.24	1.0	30.9[b]
Toluene	0.19	0.8	33.9
THF	0.15	0.6	37.4
CH_2Cl_2	0.23	1.0	41.1
CH_3OH	0.19	0.8	55.5

[a] Cf. ref 10. [b] Value is that reported for n-hexane.

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[9] This was because some of the adducts formed (e.g., those from acyclic *Z*-disubstituted olefins) were not thermally stable and began to decompose after a few (~5) minutes in solution.

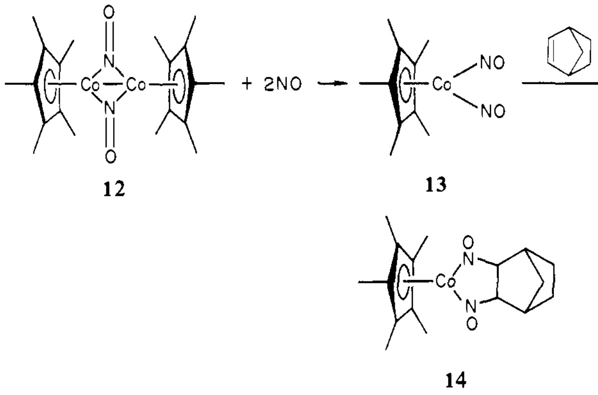
[10] Actual $E_T(30)$ values were taken directly from Kosower's book: Kosower, E. "An Introduction to Physical Organic Chemistry"; Wiley: New York, 1968, p 305.

Table V. Bimolecular Rate Constants (M^{-1} s^{-1}) for the Reaction between X-Co(NO)$_2$ and Olefins in Cyclohexane

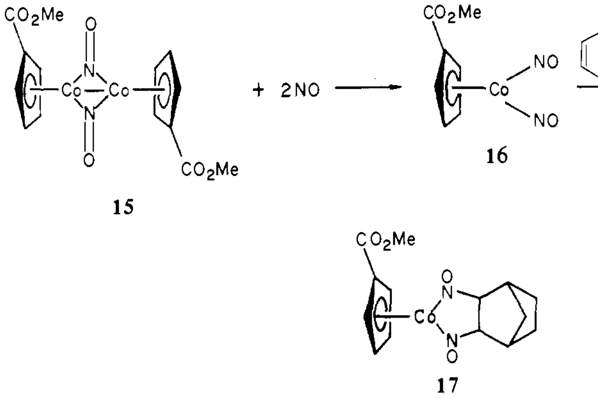
Olefin	X = $CO_2MeC_5H_4$–	X = C_5H_5–	X = Me_5C_5–
	116	129	59
	0.268	0.245	0.060
	0.048	0.066	0.024

were synthesized by nitrosylating the appropriate Cp-substituted derivative of CpCo(CO)$_2$. One contained the electron-donating pentamethylcyclopentadienyl ligand (**12**), and the other had an electron-withdrawing carbomethoxycyclopentadienyl ligand (**15**).

Both **12** and **15** react with NO gas to form the corresponding cobalt dinitrosyl intermediates. Their spectroscopic properties (IR, ^{1}H NMR, and UV/vis) resemble those of the parent CpCo(NO)$_2$ system (see Experimental Section), and both intermediates undergo cycloadditions with olefins to form the respective cobalt alkylnitroso complexes **14** and **17** (eq 12 and 13).



(12)



(13)

The dinitrosyl intermediate with the carbomethoxy group (**16**) had a half-life at 0.05 M that was approximately 5 times longer than that of $C_5H_5Co(NO)_2$. Under similar conditions, $Me_5C_5Co(NO)_2$ was much less stable than the C_5H_5 derivative.

To examine the effect of these electronically modified η^5-Cp ligands on the rates of reaction between the dinitrosyl intermediates and olefins, we employed the spectrophotometric procedure used previously in cyclohexane solvent and compared the rates for three olefins of widely differing reactivity. The results are shown in Table V. When the ligand is $C_5H_4CO_2Me$, the rates of addition are the same (within experimental error) as those for C_5H_5. For $Me_5C_5Co(NO)_2$, reaction rates are slightly lower, but only by a factor of 2–3. Thus, these modifications of the Cp ligand have virtually no effect on the reactivity of the dinitrosyl intermediates with olefins, despite their influence on the susceptibility of the mononuclear dinitrosyl to decomposition in the absence of alkene.

Discussion

Thermal Exchange. The olefin-exchange reaction (eq 2) observed for cobalt dinitrosoalkanes is an unusual process. It was initially perplexing to find that the cleavage of two carbon–nitrogen bonds was a lower energy process than dissociation of even one cobalt–nitroso bond. In retrospect, this is consistent with our finding[3] that the cobalt–alkylnitroso linkage cannot be replaced by dative ligands like phosphines. The metal–nitroso interaction is probably strengthened by a significant amount of back-bonding.

Most of the cobalt dinitrosoalkanes underwent the exchange reaction readily at refluxing benzene temperatures. There were two exceptions. The complex **3a** did not react at all with substituted norbornene **2b** until heated at 110 °C in toluene. Under these conditions, the exchange reaction was slow but observable. However, it could not be carried to completion because of competing decomposition. The nature of the exchange reaction equilibria demonstrates that the norbornene complexes are thermodynamically more stable than the other olefin adducts studied here. The reluctance of **3a** to lose norbornene is also consistent with the unusual robustness of this cobalt dinitrosoalkane.

The other exception is the adduct formed from *trans-β*-methylstyrene. This complex, which was stable enough to isolate and fully characterize,[3] was the only one that underwent the exchange reaction easily and cleanly at room temperature. This means that the carbon–nitrogen bonds of this complex are unusually weak. Perhaps the slight electron-withdrawing effect of the phenyl group lowers the energy barrier to reaction, making the olefin–dinitroso–alkane equilibrium shift more toward free olefin at a lower temperature.

The exchange reaction in eq 2 was found to be first order with respect to [**1**]. The observed rate constant for the disappearance of dinitrosoalkane **1** was invariant over a 200-fold range in the concentration of **2b** (0.001–0.2 M). Scheme I proposes a mechanism which agrees with these results. It consists of a rate-determining step involving the dissociation of 2,3-dimethyl-2-butene from the CpCo(NO)$_2$ fragment. This exists only in minute steady-state concentration because it is rapidly and irreversibly trapped by norbornene. This dissociation process is similar to an organic retrocycloaddition: our measured A factor of 1.3×10^{15} s^{-1} compares well with those found for retro-Diels–Alder reactions. For example, the fragmentation of 3-methylcyclohexene into butadiene and propene[11] has a log A = 15.1 s^{-1}.

The observation that added 2,3-dimethyl-2-butene (**4**) inhibits the reaction provides strong evidence that this olefin is binding to the intermediate. This is consistent with Scheme I if we assume that the first step is reversible. Under these conditions, a plot of $1/k_{obsd}$ vs. [**4**]/[**2**] (Figure 2) was linear in agreement with the predicted rate law in eq 5. Another possibility is that **1** could be reversibly forming an adduct with **4**. However, such an adduct must form in appreciable amounts to account for the observed rate inhibition. This pathway can be discounted since no other products were detectable by IR, UV, or ^{1}H NMR spectroscopy.

The slope of the line in Figure 2 corresponds numerically to the k_{-1}/k_1k_2 ratio. Since $k_1 = k_{obsd}$ when no excess olefin **4** is present, the k_2/k_{-1} ratio can easily be calculated. Its value represents the selectivity of the intermediate at 75 °C for **4** or **2**. We found that substituted norbornene **2b** was 115 times more reactive toward CpCo(NO)$_2$ than olefin **4** in this system. Such high reactivity is common in cycloadditions for bicyclo[2.2.1]hept-2-enes.[12]

From the kinetic data, we conclude that the olefin is released in the rate-determining step. Mechanistically, there are two

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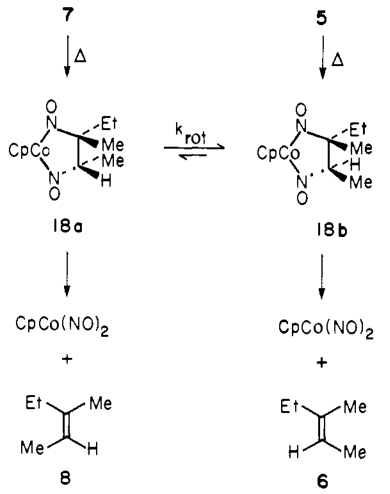
(11) Robinson, P. J.; Holbrook, K. A. "Unimolecular Reactions"; Wiley-Interscience: New York, 1972; p 212.

(12) For an explanation of this effect based on nonequivalent orbital extension see: (a) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4054. For recent counter arguments favoring other factors see: (b) Huisgen, R.; Ooms, P. H. J.; Mingin, M.; Allinger, N. L. *Ibid.* **1980**, *102*, 3951. (c) Rondam, N. G.; Paddon-Row, M. N.; Caramella, P.; Mareda, J.; Mueller, P. H.; Houk, K. N. *Ibid.* **1982**, *104*, 4974.

Scheme IV



distinct pathways for this to occur. At one extreme, the carbon–nitrogen bonds could cleave in a stepwise fashion. If this were the case, the stereospecifically prepared dinitrososalkane complexes **7** and **5** would generate acyclic intermediates **18a** and **18b** (Scheme IV). (We have chosen to represent **18a** and **18b** as diradicals, but zwitterionic structures are also possibilities.) If these species possess a significant lifetime, rotation about the carbon–carbon bond would be expected to rapidly interconvert them. Consequently, both **7** and **5** should yield a mixture of olefins **8** and **6** when subjected to the exchange reaction. At the other end of the mechanistic spectrum, both carbon–nitrogen bonds could break simultaneously in the transition state, much like a retro-Diels–Alder reaction. This predicts that the reaction should be stereospecific.

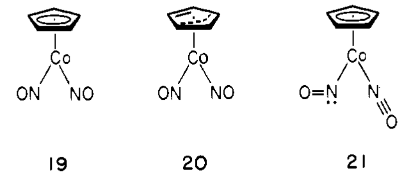
The experimental results support the concerted mechanism since **7** exclusively produces **8** while **5** gives only **6**. The stereospecificity found in both the olefin-exchange reaction and cobalt dinitrosoalkane synthesis suggests that they are related as microscopic reverse pathways sharing $CpCo(NO)_2$ as a common intermediate.

Photochemical Exchange. The olefin exchange appears to be a general reaction path available to these cobalt complexes. It was of interest to investigate whether, under photochemical conditions, the same reaction would occur or if some other reaction such as cobalt–nitroso bond cleavage could be observed.

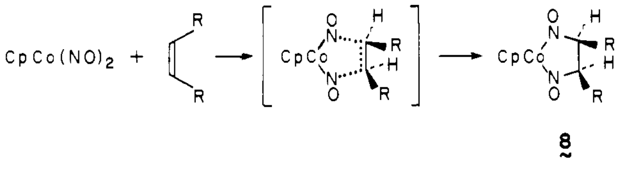
We found that photolysis of **1** in the presence of **2b** led to the same products as the thermally induced olefin-exchange reaction. By comparison, this reaction was much slower. This is a consequence of the reaction's low quantum yield which we found to be 1.12×10^{-3} at 300 nm. Quantum yields on this order of magnitude are unusual for ligand dissociation reactions in organometallic complexes.[13] The energy of an absorbed photon may be dissipated through radiationless decay. An alternative explanation is that the photochemical exchange occurs by a two-step mechanism, initially producing an intermediate like **18**. This can revert to starting material or go on to form products. Unfortunately, the photochemical reactions of **5** and **7** were too complex to use them to investigate this possibility.

Generation of $CpCo(NO)_2$. The kinetic studies discussed earlier presented evidence for existence of $CpCo(NO)_2$ at 75 °C. At lower temperatures, this compound is stable enough to observe directly. The reaction between $[CpCONO]_2$ and NO at room temperature resulted in a sensitive material that yielded cobalt dinitrosoalkanes upon addition of olefin (Scheme II). The observation of only two bands in the IR spectrum, one Cp signal in the NMR spectrum, and rapid formation of adduct **3a** strongly suggest that the reactive species is $CpCo(NO)_2$. The exact nature of the structure and bonding in $CpCo(NO)_2$ presents several interesting possibilities. One is the 20-electron species[14] **19** wherein each nitrosyl ligand contributes a maximum of three electrons to the η^5-C_5H_5Co framework (Scheme V). More energetically favorable structures that adhere to the 18-electron rule can be proposed: for example, η^3-C_5H_5(π-allyl) species **20**. If this is the structure, migration about the η^3-C_5H_5 ring must be fast on the NMR time scale since ^1H NMR spectroscopy shows a singlet Cp resonance down to −70 °C. Bending one of the nitrosyl ligands so that it becomes a one-electron donor produces isomer **21**. It is difficult to determine from spectral data alone which of these forms **19–21** makes the greatest contribution to the actual structure of $CpCo(NO)_2$. The two observed IR stretching frequencies occur too closely together to conclusively assign them to linear or bent NO groups. An X-ray diffraction study could provide a definitive answer. Unfortunately, our inability to isolate **10** thwarted this possibility. Perhaps a derivative of **10** stable enough for isolation and crystallization will be found in the future.

Scheme V



Scheme VI



$CpCo(NO)_2$/Olefin Kinetics. The reaction between $CpCo(NO)_2$ and 2,3-dimethyl-2-butene (**4**) yielding **1** was found to follow the predicted second-order rate law given in eq 10, consistent with the mechanism proposed in Scheme III. In the presence of a large (pseudo-first-order) excess of olefin, the reaction was first order in $[CpCo(NO)_2]$. An increase in the absolute concentration of added olefin produced the expected linear increase in the observed first-order rate constant (Figure 5). This proved that the reaction was bimolecular overall.

Table III lists the absolute and relative second-order rate constants for the reaction of a series of olefins with $CpCo(NO)_2$. There are a few trends worth noting. First, strain in the olefin increases its reactivity. Thus cyclopentene is preferred over cyclohexene by a factor of 60. The exceptionally high relative rates for norbornenes **2a** and **2b** are common in addition reactions involving these strained olefins.[12] The value of 204 calculated from these absolute rates for the relative rate of reaction of **10** with substituted norbornene **2b** and 2,3-dimethyl-2-butene (**4**) (i.e., k_2/k_{-1} in Scheme I) is in reasonable agreement, considering the difference in solvent and temperature, with the value of 115 calculated for this ratio from the slope of the line in Figure 2, as discussed earlier.

This reaction also has some slight steric requirements since 1-hexene reacts faster that any of the disubstituted hexenes. Although increased alkyl substitution results in a more sterically hindered double bond, it also makes the π-bond more electron rich.[15] This explains why 2,3-dimethyl-2-butene reacts fastest of all the isomeric hexenes studied. Presumably, the methyl groups are small enough (relative to CH_2CH_3) that electronic factors outweigh steric ones in this case. That this tetrasubstituted olefin reacted at all is strong evidence that this cyclization reaction is not taking place via initial olefin coordination to the cobalt atom. Transition-metal reactions involving olefin coordination usually

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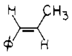
(13) Geoffroy, Gregory L.; Wrighton, Mark S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

(14) A classic example of a 20-electron complex is nickelocene: Wilkinson, G.; Pauson, P. L.; Birmingham, J. M.; Cotton, F. A. *J. Am. Chem. Soc.* **1953**, *75*, 1011.

(15) The acceleration of reaction rates for methyl-substituted olefins compared to ethyl or hydrogen-substituted olefins has been noted in the addition of bromine to olefins. See: (a) Grosjean, D.; Mouvier, G.; Dubois, J. E. *J. Org. Chem.* **1976**, *41*, 3869. (b) *Ibid.* **1976**, *41*, 3872.

Table VI. Relative Rates of Cycloaddition Reactions with Alkenes

Alkene	$CpCo(NO)_2$ C_6H_{12}/20 °C	ϕ-N=$\overset{\oplus}{N}$=$\overset{\ominus}{N}$ [a] CCl_4/25 °C	-Cl_6 [c] Dioxane/130 °C	OsO_4 [d] Pyridine/25 °C
	1960	5700	24	72
	59	56	20	22
	13	12[b]	0.9	—
n-$C_4H_9CH=CH_2$	2.3	7.3	—	—
	1	1	1	1

[a] Huisgen, Szeimes, and Möbius, 1967. [b] Alkene is styrene. [c] Sauer and Wiest, 1962. [d] Erickson and Clark, 1969.

follow the rate sequence $RCH{=}CH_2 \gg (Z)\text{-}RCH{=}CHR > (E)\text{-}RCH{=}CHR$ while tri- and tetrasubstituted olefins often show little tendency to react at all[16] Except for 1-hexene, the trend in olefin reactivity is completely opposite to this for $CpCo(NO)_2$. The mechanism cannot therefore be one involving classical olefin coordination. It suggests that the reaction takes place directly—probably in a concerted fashion—between the nitrogen atoms of the nitrosyl group and the π-bond of the olefin (Scheme VI).

We can rule out one other mechanistic possibility by looking at the data in Table III. It is doubtful that there is carbonium ion character developed in the transition state. This is because the gem-disubstituted olefin 2-ethyl-1-butene reacts at a rate similar to (*E*)-3-hexene. If there were any carbonium character, the former case would be expected to display enhanced reactivity since it can form a tertiary carbonium ion vs. a secondary one for 3-hexene. Furthermore, as Table IV shows, the rate constants for the reaction of $CpCo(NO)_2$ with **4** is insensitive to solvent polarity. A necessary consequence of forming a polar transition state or intermediate is that rate acceleration should be observed in more polar solvents.

Comparison to Model Reactions. Even with the knowledge that this cyclization reaction was occurring at the nitrosyl ligands, it was still difficult to explain why *Z* olefins reacted more slowly than their *E* isomers. Addition reactions to carbon–carbon double bonds in organic chemistry have traditionally shown a higher rate for *Z*-disubstituted olefins—an observation rationalized by noting that the approach of an incoming electrophile (e.g., Br^+) is more crowded and therefore slowed down by the *E* geometry.[17]

Another perplexing aspect of the reaction was the large rate acceleration induced by having a phenyl group attached to the olefin. In an attempt to find a model for the relative reactivities in our system, we examined the relative rates of some known cycloaddition reactions that employed simple aliphatic olefins as substrates. The data are presented in Table VI. We found a strikingly good correlation in relative reactivity between $CpCo(NO)_2$ and the 1,3-dipole phenyl azide. Although these are referred to as "1,3-dipolar" cycloadditions, good evidence is available that they proceed via concerted transition states, in which little change in polarity between ground and transition states occurs.[18] Huisgen observed that phenyl and other unsaturated groups like COOR activated olefins toward cycloaddition reaction with 1,3 dipoles.[18] He attributed this fact not to their electron-withdrawing effects but rather to the ability of these π-conjugated systems to delocalize electrons in the transition state, thereby lowering the barrier to the reaction. In support of this idea, olefins having nonconjugated electron-withdrawing groups, like halogens, react very slowly if al all.[18] Likewise, with $CpCo(NO)_2$ we have observed that a mixture of (*Z*)- and (*E*)-1-bromopropene reacts sluggishly compared to 1-hexene. For phenyl azide as well as for $CpCo(NO)_2$, the strained norbornene framework results in exceptionally high reaction rates while the mildly strained cyclopentene reacts only 15 times faster than cyclohexene.

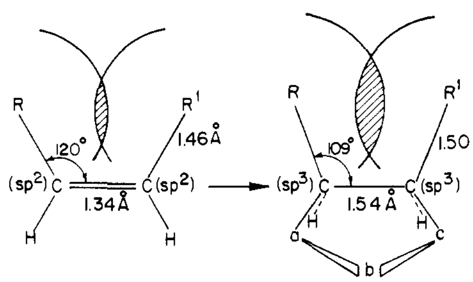


Figure 6. Steric changes occurring during the cycloaddition of a 1,3 dipole, *abc*, to a *Z*-disubstituted ethylene.

Data for two other possible model reactions—namely, Diels–Alder reaction with inverse electron demand and OsO_4 oxidation of olefins—follow the same general trend as the data for $CpCo(NO)_2$ and phenyl azide, but the differences in relative rates are not of the same magnitude. Solvent studies present further evidence in favor of a concerted reaction. When undergoing cycloadditions, 1,3 dipoles, in spite of their naively zwitterionic resonance structures, show no dependence of reaction rate on solvent polarity.[18] This behavior is similarly observed for $CpCo(NO)_2$.

A most important parallel between our system and 1,3-dipolar cycloadditions is that both react faster with *E*-disubstituted olefins than with *Z*. Figure 6 shows Huisgen's diagram for the transformation of a *Z*-disubstituted olefin into a five-membered ring during the cycloaddition of a 1,3 dipole designated *abc*.[19] The shaded areas represent the steric compression of the van der Waals radii of the *Z* substituents. For the alkene, the sp^2 hybridization places the *Z* R groups at an angle of 120° with respect to the C–C double bond. When a five-membered ring is formed, the distance between the carbons of the olefin increases to 1.54 Å but sp^3 hybridization lowers the bond angles to 109°. The overall result is that the two R groups experience greater steric compression in the five-membered ring than in the alkene. Since transition states for cycloadditions are considered to be "late", they resemble products more than starting materials. A significant part of this increased steric repulsion would be present in the transition state, increasing the barrier to reaction. When the two R groups are in an *E* configuration, this type of destabilization cannot occur.

What is the nature of the bonding of the nitrosyl ligands in $CpCo(NO)_2$ and why does it behave like a 1,3 dipole? One way for this complex to achieve an 18-electron configuration is to bend one of the nitrosyl ligands, converting it to a one-electron donor. If we consider[20] the bent NO group as formally NO^- and the other (linear) as three-electron donating NO^+, these valence formalisms bear a resemblance to those of organic 1,3 dipoles where the molecular structure is represented by a zwitterionic resonance hybrid. It would be interesting to know if other organometallic dinitrosyl complexes exist that undergo this type of cyclization reaction with olefins.

While this discussion has pointed out many parallels between the reaction we are studying and 1,3-dipolar cycloadditions, there is an important difference to be noted. The rate acceleration caused by conjugated electron-withdrawing substituents is cumulative for 1,3-dipolar cycloadditions. Thus, the two carbomethoxyl groups in dimethyl fumarate cause it to react faster than methyl acrylate. This is not observed for $CpCo(NO)_2$. While one phenyl or carbomethoxyl group may enhance reactivity, introduction of a second one deactivates the olefin. Presumably these results can be explained by balancing two competing effects: π

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[16] For a review see: Biellman, J.; Hemmer, H.; Levisalles, J. "The Chemistry of Alkenes"; Zabicky, J., Ed.; Interscience: New York, 1970: pp 215–265.

[17] Dubois, J. E.; Mouvier, G. *Bull. Soc. Chem. Chim. Fr.* **1968**, 1426.

[18] Huisgen, R.; Grashey, R.; Sauer, J. "The Chemistry of Alkenes"; Patai, S., Ed.; Interscience: New York, 1964; pp 806–878. For examples of other organotransition-metal reactions which have recently been suggested to resemble organic cycloadditions, see: (b) Coucouvanis, D.; Draganjac, M. *J. Am. Chem. Soc.* **1983**, *105*, 139. (b) Bolinger, M. C.; Rauchfuss, T. B. *Inorg. Chem.* **1982**, *21*, 3947.

[19] Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 633.

[20] For a review of structure and bonding in nitrosyl complexes see: Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339.

delocalization which increases reactivity and σ-electron withdrawal which lowers reactivity. Perhaps this is why CpCp$(NO)_2$ appears to react best with simple aliphatic olefins while organic 1,3 dipoles react with a wide variety of substituted double bonds.

Electronically Modified CpCo$(NO)_2$ Derivatives. One can affect the electronic situation in the CpCo$(NO)_2$ fragments by varying the substituents on the Cp ligand. We synthesized two analogues of the dimeric precursor to CpCo$(NO)_2$ (eq 12 and 13). Relative to C_5H_5, the permethylated ring in **12** should donate more electron density to the cobalt atom while the ester group in **15** should make that ligand more electron withdrawing.

There was a pronounced effect of these ligand substitutions on the stability of the CpCo$(NO)_2$ intermediate generated. The electron-withdrawing carbomethoxyl group makes **16** more robust than its C_5H_5 parent while the permethylated **13** is very unstable. This supports the theory that the instability of these dinitrosyl complexes results from an overabundance (>18) of electrons available to the metal center. Placing a ligand like Me_5C_5 on this intermediate shifts more electron density toward the cobalt atom and further destabilizes the molecule. Conversely, because they have the opposite effect, electron-withdrawing ligands should impart increased stability.

Despite the difference in the stability toward decomposition of **10**, **13**, and **16**, these dinitrosyl intermediates all react at similar rates with the series of olefins shown in Table V. Apparently whatever causes them to attack the olefin π bond is not affected by the electron density changes at the Cp ligand. This suggests that the driving force for the cyclization reaction is not the formation of a high-energy 20-electron intermediate that can be exothermically transformed into an 18-electron dinitrosoalkane complex upon reaction with an olefin. Perhaps it means that the "extra" electrons in these complexes are largely localized on the nitrosyl ligands.

Conclusion

We have discovered that dinitrosoalkane complexes exchange olefins thermally and have obtained kinetic evidence for formation of a discrete intermediate in these reactions. A reactive compound is formed by reaction of $[CpCoNO]_2$ with NO: this species has two IR nitrosyl stretching frequencies and a singlet C_5H_5 ^1H NMR resonance. It reacts cleanly in a bimolecular fashion with olefins to form cobalt dinitrosoalkanes. The most plausible formula consistent with all these observations is CpCo$(NO)_2$. The exact manner in which the nitrosyl groups and the cyclopentadienide ligand are bound to cobalt cannot be conclusively established from the spectroscopic data. Isolation of this dinitrosyl has been prevented by a decomposition reaction induced upon concentration of its solutions. The relative reactivity of CpCo$(NO)_2$ for olefins shows interesting parallels to the trends in the 1,3-dipolar cycloaddition reactions of phenyl azide. The carbomethoxyl derivative **16** displays enhanced stability relative to the C_5H_5 analogue **10**. Perhaps by adding more carbomethoxy substituents to the cyclopentadienide ligand, the barrier to decomposition can be raised enough to allow isolation—and perhaps crystallization—of the dinitrosyl intermediate. This might allow determination of the structure of the nitrosyl groups and provide insight into designing other organometallic systems that ought to react similarly.

Experimental Section

General information. All manipulations of oxygen- or water-sensitive materials were conducted under a prescrubbed recirculating atmosphere of nitrogen in a Vacuum Atmospheres HE-553 Dri-Lab with attached MO-40-1 Dri-Train or using standard Schlenk or vacuum line techniques. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian EM-390 90 MHz spectrometer or on 200- and 250-MHz high-field Fourier Transform instruments. The high-field systems consisted of Cryomagnetics Inc. Magnet, Nicolet Model 1180 data collection systems, and electronics assembled by Mr. Rudi Nunlist of U.C. Berkeley. Chemical shifts are reported relative to tetramethylsilane.

Infrared (IR) spectra were recorded on a Perkin-Elmer 283 grating spectrometer using either NaCl solution cells or KBr ground pellets. Ultraviolet (UV) and visible (vis) spectra were recorded on either a Carey 118 or an Hewlett-Packard 8450A UV/vis spectrophotometer with 1-cm quartz or fused silica cells. High-pressure liquid chromatography (HPLC) was performed on an Altex Model 324 gradient liquid chromatograph interfaced with a modified Hitachi Model 100-10 spectrophotometer and an Hewlett-Packard 3390A electronic integrator. Mass spectroscopic (MS) analyses were obtained on an AEI MS-1 spectrometer interfaced with a Finnigan 2300 data system. Elemental analyses were obtained at the U.C. Berkeley analytical facility. Melting points were recorded on a Thomas Hoover capillary melting point apparatus.

Tetrahydrofuran, diethyl ether, dimethoxyethane, benzene, and toluene were dried with sodium-benzophenone ketyl and distilled under nitrogen. Hexane was purified by 2 × 12 h of stirring over 98% sulfuric acid followed by 2 × 6 h of stirring over saturated $KMnO_4$ in 10% sulfuric acid. It was then sequentially washed with water, saturated Na_2CO_3, and water, dried over $MgSO_4$, filtered, and distilled under nitrogen from *n*-butyllithium. Methylene chloride was distilled from CaH_2 under nitrogen.

For UV/vis kinetics, spectral grade cyclohexane, toluene, tetrahydrofuran, and methylene chloride were dried by passing ~600 mL of each solvent down a 4 × 9 cm column of activated alumina under a dry-nitrogen atmosphere. Spectral grade methanol was predried by vacuum transferring from sodium metal followed by the above procedure. For all kinetic runs, freshly prepared solutions of $[CpCoNO]_2$, cobalt dinitrosoalkanes, and olefins were used. These olefins were purified and dried by passage through a column of activated alumina under a nitrogen atmosphere. Cyclohexene was refluxed for 30 min with maleic anhydride to remove traces of 1,3-cyclohexadiene (which interferes with UV spectra in the 250-nm region) before purification on alumina. Two olefins, dimethyl fumarate and *endo*-5,6-dicarbomethoxybicyclo[2.2.1]hept-2-ene (**2b**), were purified by recrystallization.

Unless otherwise stated, all reagents were used as purchased from suppliers without further purification. NO gas (Matheson) was used as purchased except for kinetic and NMR experiments where it was purified by passage through a U-tube containing silica gel (6–12 mesh) cooled to dry ice/acetone temperatures.[21]

Preparative Exchange Reactions of Isolable Dinitrosoalkane Complexes with Norbornene (2a). A weighed amount of dinitrosoalkane complex was dissolved in 2 mL of benzene in a 25-mL round-bottom flask. Ten equivalents of norbornene were added, and a reflux condenser was attached. The apparatus was flushed with argon and brought to reflux for 2 h whereupon the reaction was complete as judged by TLC on silica gel using 80% hexane/20% CH_2Cl_2/5% Et_2O as eluant. The mixture was placed on a 2 × 10 cm silica gel column and eluted with 75 mL of hexane (to remove excess norbornene) followed by 50 mL of 95% CH_2Cl_2/5% Et_2O which eluted **3a** as a red band. The solvent was removed to give a dark red solid, pure by NMR spectroscopy, whose identity[1,3c,d] was verified by ^1H NMR spectroscopy and TLC.

The actual amounts of dinitrosoalkane complex and norbornene used, and isolated **3a** obtained, in each experiment respectively were as follows: (1) CpCo$(C_6H_{12}N_2O_2)$ (**1**) (28 mg, 0.10 mmol), **2a** (110 mg, 1.17 mmol), and **3a** (30 mg, 0.10 mmol); (2) CpCo$(C_5H_{10}N_2O_2)$ (32 mg, 0.13 mmol), **2a** (110 mg, 1.17 mmol), and **3a** (29 mg, 0.10 mmol); (3) CpCo$(C_4H_8N_2O_2)$ (28 mg, 0.12 mmol), **2a** (115 mg, 1.22 mmol), and **3a** (19 mg, 0.07 mmol). Isolated yields are given in Table I.

Preparative Exchange Reaction of Unisolated Dinitrosoalkane Complexes with Norbornene (2a). In a drybox, a 25-mL three-neck pear-shaped flask equipped with magnetic stir bar, gas-tight stopcock, rubber septum, and an air-tight gas inlet tube was charged with a weighed amount of $[CpCoNO]_2$, 5 equiv of olefin, and 10 mL of CH_2Cl_2. The apparatus was transferred to a hood, placed under a positive pressure of argon, and cooled with an ice bath to 0 °C. NO gas was introduced through the inlet tube and slowly bubbled through the mixture for about 1 h at which time TLC showed no sign of the cobalt dimer starting material. Excess NO was removed by bubbling argon through the solution for 5 min. The reaction mixture was flash chromatographed on a 4 × 8 cm SiO_2 column with 95% CH_2Cl_2/5% Et_2O as eluant. The red dinitrosoalkane complexes moved with the solvent. The fraction containing the dinitrosoalkane complex was then concentrated to about 10 mL, and 10 equiv of norbornene were added with 40 mL of either C_6H_6 or CH_2Cl_2 depending on whether the reaction was carried out at 80 °C ((*E*)-3-hexene) or at room temperature (*trans*-β-methylstyrene and ethylene), respectively. The solution was flushed with argon and brought to the appropriate reaction temperature until the reaction was complete as judged by TLC on silica gel using 80% hexane/20% CH_2Cl_2/5% Et_2O as eluant. The solvent was removed in vacuo and the mixture chromatographed on a 4 × 8 cm SiO_2 column using hexane to elute excess norbornene and then 95% CH_2Cl_2/5% Et_2O to elute norbornene complex **3a**. Concentration under vacuum gave **3a** as a red solid whose yield (Table I) was based on the amount of $[CpCoNO]_2$ used.

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[21] Hughes, E. E. *J. Chem. Phys.* **1961**, *5*, 1531.

A varient of this procedure was utilized with ethylene as the entering olefin. The reaction was done in 10 mL of THF with a separate inlet tube for ethylene. The amount of ethylene was not quantified as it was bubbled through the solution continuously at a medium rate for the duration of the reaction. No column chromatography was done since the ethylene complex decomposed under these conditions. Instead, after the excess NO had been removed, solid **2a** was added directly to the reaction mixture.

^{1}H NMR Kinetic Study of the Reaction between 1 and 2b. A 5-mm NMR tube equipped with a standard taper 14/20 joint was charged with 5.2 mg (0.02 mmol) of **1**, 44.2 mg (0.21 mmol) of **2b**, and 2.0 mg (0.11 mmol) of ferrocene as an internal standard. The tube was taken to a vacuum line, and 1.0 mL of toluene-d_8 was condensed in at −196 °C. The tube was sealed under vacuum and then allowed to warm and dissolve the contents. An initial spectrum was recorded. The tube was then immersed in a constant temperature water bath set at 75.0 ± 0.1 °C. After a measured period of time, the tube was removed and plunged into an ice bath to quench the reaction and another spectrum was recorded. This procedure was repeated until >88% conversion had been achieved. The kinetic data were obtained from integration of the well-resolved C_5H_5 singlets of **1** at 4.72 ppm and **3b** at 4.66 ppm. Integration of these peaks against the internal standard at 3.98 ppm showed that the reaction was quantitative. A plot of ln $([\mathbf{1}]_t/[\mathbf{1}]_0)$ vs. time was linear for 3 half-lives with a slope $k_{obsd} = 4.28 \times 10^{-4}$ s^{-1}.

An identical experiment was carried out doubling the concentration of **2b** to 4.0 mg (0.40 mmol). The observed rate constant remained unchanged within the limits of experimental error ($k_{obsd} = 4.25 \times 10^{-4}$ s^{-1}).

UV/vis Kinetic Study of the Reaction between 1 and 2b. A 5.0-mL volumetric flask was charged with 0.0107 g (0.051 mmol) of **2b** and taken into the drybox. A 1.0-mL sample of a 5.0×10^{-3} M (0.0327 g in 25 mL) toluene solution of **1** was added, the volumetric flask was filled with dry spectral grade toluene to the 5.0-mL mark, and **2b** was allowed to dissolve. This solution containing **1** (1.0×10^{-3} M) and **2b** (1.0×10^{-2} M) was transferred to a 1.0-cm quartz cuvette and sealed with a greased ground glass stopper. The stopper was secured with a rubber band.

The curvette was placed in a Cary 118 spectrophotometer, and an initial reading at 560 nm was recorded. The curvette was then immersed up to its neck in a 75 ± 0.5 °C constant temperature bath, and the reaction was allowed to proceed. Every 10 min, the reaction was quenched by dipping the cuvette in an ice bath, and reequilibrated to room temperature and an absorbance measurement was recorded. This was repeated until >88% conversion (90 min) had been achieved. The A_∞ value was obtained by allowing the reaction to continue for a total of 240 min to verify that the absorbance measurement was no longer changing. Under these conditions, the total absorbance change at 560 nm was 0.6 unit. The observed rate constant was obtained from the slope of a first order ln $(A_t - A_\infty)$ vs. time plot carried out for more than 3 half-lives. This experiment was repeated by using a 20-fold increase in the concentration of **2b** (0.2268 g, 1.08 mmol, 2.2×10^{-1} M). The reaction was again repeated, this time decreasing the concentration of both **1** and **2b** tenfold to 1.0×10^{-4} and 1.0×10^{-3} M, respectively. Under these conditions, the total absorbance change for the reaction at 560 nm decreased to only 0.06 unit, making the error in the final A_∞ value greater. The measured rate constants are listed in Table II.

Determination of the Arrhenius Parameters for the Reaction between 1 and 2b. The reaction was carried out as described above in toluene solution using **1** (1×10^{-3} M) and **2b** (1×10^{-2} M) and measuring the absorbance change at 560 nm. Instead of using ground glass stoppered cells, the cuvettes had a 0.4-mm right-angle Kontes high vacuum Teflon stopcock . After >88% conversion had been achieved, the bath temperature was raised to 75 °C to accelerate determination of the A_∞ value. All k_{obsd} values were determined from slopes of first-order plots of ln $(A_\infty - A_t)$ vs. time. The rate constant at 45 °C (310 K) was determined by ^{1}H NMR in toluene-d_8 using the previously described techniques and plotted as shown in Figure 1.

Kinetics of the Reaction between 1 and 2b with Added 2,3-Dimethyl-2-butene (4). These experiments were performed in Teflon stopcock sealed 1-cm quartz cuvettes in toluene solution at 75 °C. Stock solutions containing a known concentration of **1**, **2b**, and **4** were combined in the appropriate amounts to yield the concentration listed in Table II. **4** (Aldrich) was purified by passage through a 2 × 9 cm activated alumina column under dry nitrogen. The reaction was carried out at 75 °C and monitored by the absorbance change at 560 nm; rate constants were plotted as shown in Figure 2.

Reaction of CpCo((*E*)-$C_6H_{12}N_2O_2$) (5) with 2b. A 5-mm NMR tube with attached 14/20 joint was charged with 3.0 mg (0.01 mmol) of **5** and 21.0 mg (0.1 mmol) of **2b**. A 1.0-mL sample of benzene-d_6 was condensed in under vacuum, the tube was sealed off, and its contents were allowed to warm and dissolve. The tube was heated at 70 °C for 140 min at which point ^{1}H NMR spectroscopy showed the mixture to contain 13% **5**, 87% **3b**, and (*E*)-3-methyl-2-pentene. The reaction was heated at 70 °C for an additonal 20 min, and the volatiles from the reaction were transferred under vacuum to a clean tube. An ^{1}H NMR spectrum showed resonances that corresponded exactly with those of a known sample of (*E*)-3-methyl-2-pentene (Albany Chemical): δ 5.25 (m, 1 H); 1.95 (q, $J_{H,H} = 7.4$ Hz, 2 H), 1.54 (d of m, 3 H), 1.53 (s, 3 H), 0.96 (t, $J_{H,H} = 7.4$ Hz, 3 H). No resonances were observed for the corresponding (*Z*)-3-methyl-2-pentene.

Reaction of CpCo((*Z*)-$C_6H_{12}N_2O_2$) (7) with 2b. A 5-mm NMR tube with attached 14/20 joint was charged with ~4 mg (0.01 mmol) of **7** and ~23 mg (0.10 mmol) of **2b**. A 1.0-mL sample of benzene-d_6 was condensed in under vacuum, and the tube was sealed off. The mixture was thawed and then brought to 70 °C for 150 min at which point an ^{1}H NMR spectrum showed that the mixture contained 94% **3b** and 6% **7**. Another ^{1}H NMR spectrum of the vacuum transferred volatiles clearly showed only resonances for (*Z*)-3-methyl-2-pentene identified by comparison with a known sample (Albany Chemicals): δ 5.19 (q, $J_{HH} = 6.7$ Hz, 1 H), 1.97 (q, $J_{H,H} = 7.6$ Hz, 2 H), 1.65 (sextet, $J_{H,H} = 1.4$ Hz, 3 H), 1.55 (d of m, 3 H), 0.90 (t, $J_{H,H} = 7.6$ Hz). No resonances due to (*E*)-3-methyl-2-pentene were observed.

Determination of the Quantum Yield for the Production of 3b in the Reaction between 1 and 2b. In a nitrogen-filled drybox, 2.0 mL of a standard solution containing **1** (5.02×10^{-5} M) and **2b** (5.00×10^{-3} M) in dry spectral-grade cyclohexane was pipetted into a 1-cm quartz cuvette with attached Teflon stopcock. A small magnetic stir bar was added, and the stopcock was closed. Seven more identical samples were prepared.

The magnetically stirred samples were irradiated with a CMX-4 flash-pumped dye laser using Rhodamine 590 tetrafluoroborate (Exciton) dye in conjunction with a frequency doubling prism to tune the laser to 300 nm. The number of photons absorbed by each sample was measured directly by using an electronic integrating actinometer[6] calibrated with potassium ferrioxalate.[22] The duration of irradiation ranged from 5 to 40 min, during which time the exchange reaction had proceeded from 0.5 up to 7% conversion. After a known quantity of photons was absorbed each sample was subjected to the analysis described below.

The solvent from a 1.0-mL aliquot was evaporated and the residue redissolved with 1.0 mL of a CH_3CN solution that contained **3a** (2.50×10^{-6} M) as an internal standard. A 10-mL sample of this mixture was injected on a 1 × 25 cm HPLC reverse-phase carbon-18 silica gel column with 5-μm particle size (Altex) using 80% CH_3CN/20% H_2O as solvent. With a UV detector set at 300 nm and a 2 mL/min flow rate, **3b**, **3a**, and **1** could be separated with retention times of 16.8, 21.6, and 24.0 min, respectively. Since the extinction coefficients for **3b** and **3a** at 300 nm were found to be identical and the concentration of **3a** was known, the exact amount of **3b** could be quantified by directly integrating its peak area against that for **3a**. Graphing these data (Figure 3) produced a straight line whose slope (1.12×10^{-3}) gave the measured quantum yield.

Generation of η^5-$C_5H_5Co(NO)_2$ (10) from $[CpCoNO]_2$ (9) and NO in THF and Its Reaction with Norbornene (2a). In a drybox, a 25-mL three-neck pear-shaped flask with attached air-tight gas inlet tube, Teflon stopcock, and rubber septum was charged with a stir bar and 30.4 mg (0.1 mmol) of **9** dissolved in 8 mL of THF. The apparatus was transferred to a hood and placed under a positive pressure of nitrogen. NO gas was bubbled slowly through the magnetically stirred solution for about 3 min during which time a color change to a brighter green had occurred. Nitrogen was bubbled through the solution for 3 min to remove excess NO. The IR spectrum of the resulting mixture showed absorptions for starting material (~10%) along with two new bands at 1609 (s) and 1692 (m) cm^{-1}. After the mixture was left standing for 10 min, 8 mL of a THF solution containing 35 mg (0.37 mmol) of norbornene (**2a**) was added rapidly via syringe. The solution immediately turned red, and IR showed that the absorption at 1609 and 1692 cm^{-1} had been replaced by those of **3a** at 1350 (s) and 1418 (m) cm^{-1}. Flash evaporation of solvent followed by chromatography on a 2.5 × 21 cm silica gel column using benzene to remove excess **2a** and **9**, followed by 95% CH_2Cl_2/5% Et_2O gave 40 mg (0.14 mmol) of **3a** (72% yield).

When addition of **3a** was omitted from this procedure, the CpCo$(NO)_2$ generated slowly formed an uncharacterizable precipitate over a 20-min period. Continued bubbling of NO gas through the solution accelerated this decomposition process. Attempts to isolate **10** by removing solvent resulted in rapid decomposition to a brown, intractable solid.

Generation of η^5-$C_5H_5Co(NO)_2$ (10) from $[CpCoNO]_2$ (9) and NO in Benzene-d_6. A 5-mm NMR tube was attached 14/20 joint was charged with 4.6 mg (0.015 mmol) of **9**. The tube was placed under vacuum, and in succession were condensed 0.55 mL of benzene-d_6, 0.015 mmol of

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[22] Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

Me_4Si, and 0.036 mmol of NO gas (purified) at −196 °C. When being thawed, the solution instantly turned bright green. The ^1H NMR spectrum showed an 83% conversion (98 ± 2% yield based on Me_4Si internal standard) of **9** (δ 4.53 (s, 5 H)) to a new singlet at δ 4.22 assigned to $CpCo(NO)_2$ (**10**). After 15 min at room temperature, precipitate begain to deposit in the tube concurrent with the disappearance of the new resonance at 4.22 ppm.

Generation of 10 from 9 and NO in THF-d_8. An NMR tube was charged with 4.4 mg (0.014 mmol) of **9**, 0.032 mmol of NO gas, and 0.6 mL of THF-d_8 according to the procedure described in the benzene-d_6 experiment. When the mixture was thawed, immediate reaction occurred, producing the bright green color of **10**. The ^1H NMR spectrum showed a 67% conversion of **9** (δ 4.82 (s, 5 H)) to **10** (δ 4.88 (s, 5 H)). Cooling this sample in the spectrometer probe to −60 °C failed to show any evidence for an η^3-$C_5H_5Co(NO)_2$ species. When the sample was rewarmed to ambient temperature, the resonance for $CpCo(NO)_2$ diminished as precipitate began to form.

Generation of 10 from $[Co(NO)_2$-μ-$Cl]_2$. In a drybox, a 100-mL round bottom flask equipped with magnetic stir bar was charged with 237 mg (0.77 mmol) of $[Co(NO)_2$-μ-$Cl]_2$[8] dissolved in 30 mL of dry THF. A 108-mg (1.5-mmol) sample of LiC_5H_5 dissolved in 20 mL of dry THF was added over a 30-s period through an addition funnel to the cobalt complex. After 3 min, the solution changed from brown to dark green. The IR spectrum showed the expected absorptions for $CpCo(NO)_2$ (**10**) at 1690 (m) and 1605 (s) cm^{-1} as well as a small amount of $[CpCoNO]_2$ (**9**) at 1540 (s) and 1590 (m) cm^{-1}. After a total of 15 min, the IR absorption for **10** began to decrease while those of **9** remained, and precipitate had begun to form.

Kinetics of the Reaction between 10 and Olefins. In a drybox, a 1-cm quartz cuvette with attached 14/20 joint was charged with 2.0 mL of a standard solution of **9** (~6 × 10^{-5} M) in spectral grade cyclohexane. Similarly, a 10-mL pear-shaped flask was charged with a known volume (usually 1.0 or 2.0 mL) of a standard solution of olefins in cyclohexane. Both solutions were sealed with a rubber septum and allowed to equilibrate for ~15 min in a constant temperature bath at 20 °C. NO gas (purified) was then bubbled through a needle into the cobalt solution for ~3–5 s—just enough to produce the color change to a bright green solution (too much NO gas causes decomposition of $CpCo(NO)_2$; having some **9** still present did not interfere with the kinetic measurements). After **10** had been generated, excess NO was purged from the solution by bubbling a stream of dry nitrogen through it for between 3 and 5 s. The olefin solution was added rapidly to **10** via cannula under nitrogen. The cuvette was shaken briefly to ensure mixing of the contents and was immediately placed in the cavity of an HP 8450A spectrophotometer. Full scan spectra from 200 to 800 nm (scanning time, 1.0 s) were recorded repeatedly (from every 2 to 50 s depending on the reaction rate) until the reaction was complete (~6–7 half-lives). All reactions showed well-defined isosbestic points (cf. Figure 4).

Because the reactions were completed so quickly (<5 min), we estimate our temperature control to be ±2 °C at 20 °C. Repeated runs gave measured rate constants that varied by ±6%. Rate constants were obtained as the slope from a plot of ln $(A_t - A_\infty)$ vs. time where the absorption change was measured at 300 nm. Each reported rate constant (Tables III and IV) is the average value of at least two separate experiments.

Preparation of $[\eta^5$-$(CH_3)_5C_5CoNO]_2$ (12). In a drybox, a 250-mL three-neck pear-shaped flask with attached air-tight gas inlet, Teflon stopcock, and rubber septum was charged with 3.4 g (15 mmol) of $Me_5C_5Co(CO)_2$[23] dissolved in 80 mL of CH_2Cl_2. The sealed apparatus was placed under positive pressure of argon in a hood, and NO gas was slowly bubbled through the magnetically stirred solution for 90 min. After this time, TLC on silica gel (20% CH_2Cl_2/80% hexane) showed no starting material. Excess NO was removed by bubbling with Argon. The reaction mixture was taken into a drybox, filtered through a medium porosity frit, and concentrated to 8 mL. This residue was dissolved in 30 mL of warm hexane and upon cooling gave analytically pure **12** as black needles. Two crops were collected totaling 3.2 g (7.1 mmol, 95% yield): mp (N_2) 212 °C; IR (hexane) 1560 (m), 1510 (s) cm^{-1}; ^1H NMR (C_6D_6) δ 1.65 (s, 30 H); MS (70 EV), *m/e* 448 (M^+). Anal. Calcd for $C_{20}H_{30}N_2O_2Co_2$: C, 53.58; H, 6.74; N, 6.25; Co, 26.3. Found: C, 53.69; H, 6.83; N, 6.24; Co, 27.2.

Preparation of $[\eta^5$-$(CO_2CH_3)C_5H_4CoNO]_2$ (15). In a procedure analogous to that for **12**, 322 mg (1.3 mmol) of $(CO_2CH_3)C_5H_4Co(CO)_2$[24] was dissolved in 9 mL of CH_2Cl_2 in a 25-mL flask. The magnetically stirred solution was reacted with NO gas for 35 min after which time it was returned to a drybox and chromatographed on a 2.5 × 21 cm silica gel column using 33% Et_2O/67% hexane as eluent. Starting material eluted first as a red band. A more polar solvent mixture (70% Et_2O/30% hexane) was then used to more rapidly elute **15** as a dark green band. Recrystallization from 10 mL of Et_2O at −40 °C gave 160 mg (0.4 mmol, 56% yield) of analytically pure **15** as black crystals: mp (N_2) 73–74.5 °C; IR (CH_2Cl_2) 1715 (s), 1608 (m), 1555 (s) cm^{-1}; ^1H NMR (C_6D_6) δ 5.25 (t, $J_{H,H}$ = 2.3 Hz, 4 H), 4.41 (t, $J_{H,H}$ = 2.3 Hz, 4 H), 3.54 (s, 6 H); MS (70 eV), *m/e* 424 (M^+). Anal. Calcd for $C_{14}H_{14}N_2O_6Co_2$: C, 39.65; H, 3.33; N, 6.60; Co, 27.8. Found: C, 39.83; H, 3.39; N, 6.57; Co, 26.3.

Generation of $(CO_2CH_3)C_5H_4Co(NO)_2$ (16) from 15 and NO in THF and Its Reaction with Norbornene (2a). In a drybox, a 25-mL pear-shaped flask with attached air-tight gas inlet, Teflon stopcock, and rubber septum was charged with 20 mg (0.05 mmol) of **15** dissolved in 10 mL of THF. The vessel was placed in a hood under a positive pressure of nitrogen, and NO gas was slowly bubbled through the reaction with stirring for 2 min. The solution turned a brighter green. After the excess NO was removed with nitrogen, an IR spectrum showed two new stretches at 1710 (br, s) and 1620 (s) cm^{-1} consistent with formation of dinitrosyl **16**. A 5-mL THF solution containing 30 mg (0.32 mmol) of **2a** was added rapidly to the reaction via syringe. The mixture immediately became red, and its IR spectrum contained new absorptions at 1428 (m) and 1360 (s) cm^{-1} consistent with transformation of **16** to the norbornene adduct **17**. Attempted concentration of solutions of **16** led to decomposition.

Reaction between Dinitrosyls 13 and 16 and Olefins. A. Generation of 16 from 15 and NO in Benzene-d_6. A 5-mm NMR tube with attached 14/20 joint was charged with 5.0 mg (0.012 mmol) of **15**. While under vacuum, 0.6 mL of benzene-d_6, 0.014 mmol of Me_4Si, and 0.029 mmol of NO (purified) were condensed into the tube in succession. After the tube was sealed, the solution turned bright green upon thawing. The ^1H NMR spectrum revealed a clean, 60% conversion (100% yield based on Me_4Si internal standard) of **15** to a new product with resonances at δ 5.56 (t, $J_{H,H}$ = 2.4 Hz, 2 H), 4.39 (t, $J_{H,H}$ = 2.4 Hz, 2 H), and 3.43 (s, 3 H) that are consistent with $(CO_2CH_3)C_5H_4Co(NO)_2$ (**16**). When the mixture was left standing for 20 more minutes, the conversion increased to 75%. After 60 min, the solution began to show signs of decomposition of **16** to an insoluble precipitate.

B. Generation of $Me_5C_5Co(NO)_2$ (13) from 12 and NO. $Me_5C_5Co(NO)_2$ (**13**) is unstable when generated at concentrations greater than 4 × 10^{-3} M. When generated at lower concentrations (ca. 10^{-5} M), UV/vis absorptions consistent with the formation of this material can be observed.

C. Kinetics. In a procedure exactly analogous to that for measuring kinetics between **10** and olefins, standard solutions of the preformed dinitrosyls **13** and **16** were reacted with a known concentration of a series of three olefins at 20 °C in spectral-grade cyclohexane. Well-defined isosbestic points were observed. Absorbance changes were measured at 304 nm, and the rate constants reported in Table V are average values from two separate experiments.

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Registry No. **1**, 82640-85-5; **2a**, 498-66-8; **2b**, 39589-98-5; **3a**, 51262-48-7; **3b**, 51213-30-0; **4**, 563-79-1; **5**, 84849-65-0; **7**, 84849-00-8; **9**, 51862-20-5; **12**, 85202-43-3; **15**, 85202-44-4; NO, 10102-43-9; $[Co(NO)_2$-μ-$Cl]_2$, 13931-93-6; LiC_5H_5, 16733-97-4; $Me_5Cr_5Co(CO)_2$, 12129-77-0; $(CO_2CH_3)C_5H_4Co(CO)_2$, 36655-66-0; norbornene, 498-66-8; cyclohexene, 110-83-8; cyclopentene, 142-29-0; 1-propenylbenzene, 873-66-5; 1-hexene, 592-41-6.

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