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Observations Regarding the Mechanisms of O Atom Transfer from Metal Nitro Ligands to Oxidizable Substrates

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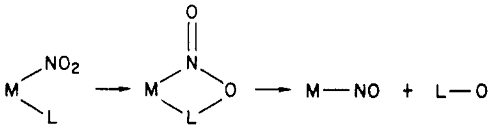
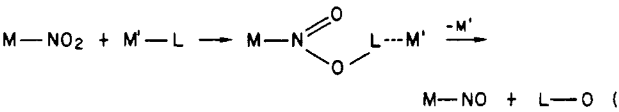
New experimental evidence is presented related to the mechanism of O atom transfer from metal nitro complexes to alkenes and carbon monoxide. Oxidation of alkenes by the nitro complex (py)CoTPPNO$_2$ in the presence of Pd(CH$_3$CN)$_2$Cl$_2$ as a cocatalyst is found to give product distributions that do not exactly match those expected for the simple intermolecular bimetallic O atom transfer originally proposed. Pyridine, nitro, and nitrosyl ligand exchange between the cobalt and palladium are found to be facile. In one plausible revised mechanism, the bimetallic alkene oxidation could therefore proceed via nitro group transfer to palladium, oxidation via the same metallacycles as for the monometallic Pd(CH$_3$CN)$_2$ClNO$_2$ catalyst, and transfer of the resulting nitrosyl ligand back to cobalt. Several other complex mechanisms cannot be ruled out. Other systems were also investigated, but no evidence could be found for a bimetallic open-chain intermediate formed by intermolecular addition of a metal nitro complex to a coordinated alkene. A literature claim for intermolecular O atom transfer from metal nitro groups to carbon monoxide based on isotopic double-labeling experiments is incomplete due to the absence of suitable control experiments. Attempts to carry out the requisite controls were hampered by experimental limitations, but the results obtained again show that there is no compelling evidence for intermolecular O atom transfer from a metal nitro group.

Transition-metal nitro complexes are known to undergo a wide variety of stoichiometric and catalytic O atom transfer reactions that result in the oxidation of alkenes,[1-4] carbon monoxide,[5-14] nitrite ion,[15,16] phosphines,[6,11b,16c,17,18] carbon sulfide,[10] nitric oxide,[19] isonitriles,[20] and alcohols.[21] The nature of the O atom transfer step has been the subject of much speculation. The coordinated nitro group is ambiphilic.[2a,21] It apparently acts as a weak nitrogen-centered electrophile toward alcohols (and possibly an oxygen-centered electrophile toward phosphines and coordinated nitrite) but as a mild nucleophile toward coordinated CO, CS, NO, and alkenes. Two general mechanisms have been proposed for the latter class of reactions: (1) intramolecular nucleophilic O atom transfer via a metallacyclic intermediate (eq 1)[2c,3,8a-c,10,11a,12,13,19,20] and (2)



(1)

intermolecular nucleophilic O atom transfer via a bimetallic open-chain intermediate (eq 2).[2a-c,11b,c] Until



(2)

recently, no examples of either of the key intermediates in eq 1 and 2 had been conclusively reported. Heterometallacyclopentanes (eq 1, L = alkene) have now been well characterized in the oxidation of alkenes by Pd(CH$_3$CN)$_2$ClNO$_2$.[3] In the process of attempting to verify whether these metallacycles are actually involved in the O atom transfer step, we have been led to reinvestigate two

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Table I. Alkene Oxidation Reactions[a]

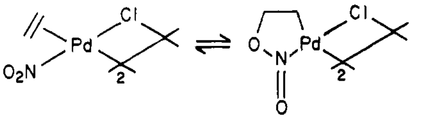
catalyst[b]	alkene	T, °C	time, h	[MNO_2], mM	products (% yield)[c]: ketone	epoxide	2-en-1-ol	2-en-1-one
$PdNO_2$[d,e]	1-decene	25	48	8	95	-	-	-
$CoNO_2$/Pd	1-decene	60	19	10	3	-	-	-
$PdNO_2$	cycloheptene	60	2	10	9	55	12	26
$PdNO_2$	cycloheptene	60	2	40	3	43	2	23
$CoNO_2$/Pd	cycloheptene	60	2	10	4	18	-	-
$CoNO_2$/Pd	cycloheptene	60	2	20	8	18	-	-
$CoNO_2$/Pd	cycloheptene	60	2	40	14	8	-	-
$PdNO_2$[e]	*cis*-cyclooctene	60	3	29	6	12	7	-
$CoNO_2$/Pd	*cis*-cyclooctene	60	1.5	10	8	3	-	-
$PdNO_2$	*trans*-cyclooctene	60	0.5	29	57	4, 5[f]	-	-
$CoNO_2$/Pd	*trans*-cyclooctene	60	2.5	10	13	-	-	-
$PdNO_2$[e]	norbornene	25	72	19	-	90	-	-
$CoNO_2$/Pd[g]	norbornene	25	1.5	11	-	21	-	-
$CoNO_2$/Pd[g,h]	norbornene	25	0.2	10	-	75	-	-
$CoNO_2$[g]	norbornene	25	1.5	10	-	-	-	-
$PdNO_2$[e]	bicyclo[2.2.2]octene	60	2	20	-	70	-	-
$CoNO_2$/Pd	bicyclo[2.2.2]octene	25	2	10	-	14	-	-

[a] Reactions run in 1,2-dichloroethane with an alkene/nitro complex ratio of 1:1, Pd/Co = 2.5:1, unless otherwise noted. [b] $PdNO_2 = Pd(CH_3CN)_2ClNO_2$, $CoNO_2$ = (py)CoTPPNO$_2$, Pd = $Pd(CH_3CN)_2Cl_2$. [c] GC yields based on nitro complex (– = <2%). [d] Toluene solution. [e] Reference 3d. [f] *cis*-Epoxide. [g] Alkene/$CoNO_2$ = 10:1. [h] Reference 2c.

nitro group O atom transfer reactions that were proposed to proceed via the bimolecular mechanism given in eq 2. Our observations on these systems are reported here.

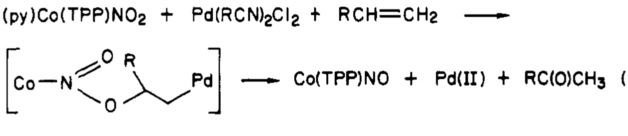
Results and Discussion

The observation of heterometallacycles in the reaction of $Pd(CH_3CN)_2ClNO_2$ with alkenes only provided circumstantial evidence for O atom transfer by mechanism 1, since these metallacycles and their alkene nitro precursors are in rapid equilibrium under the reaction conditions (eq 3).[3] Under these circumstances, the O atom transfer step could easily occur by either eq 1 or 2. The high substitutional lability of Pd(II) precluded the use of classical isotopic double-labeling techniques to distinguish between these alternatives. Differentiation by kinetic methods also seemed impossible due to the complex set of preequilibria present. An indirect test based on the product distributions observed was therefore employed.[3d] It can be argued that oxidation of *cis*- and *trans*-cyclooctene via eq 1 should be stereospecific (the two isomers yielding different product distributions), while oxidation of the same alkenes via eq 2 should at best be stereoselective (the two isomers yielding the same product distributions). The marked stereospecificity actually observed and the specific products formed (primarily epoxide for the cis alkene and exclusively ketone for the trans alkene) provided strong evidence that O atom transfer in that system actually occurs via eq 1 and the observed metallacycles.



(3)

In order to strengthen the indirect arguments used, it seemed desirable to experimentally test the hypothesis that bimolecular O atom transfer via eq 2 should only by stereoselective and that the primary product formed from both *cis*- and *trans*-cyclooctene should be cyclooctanone. A bimetallic Co/Pd system that has been suggested to proceed by such an intermolecular mechanism (eq 4)[2a,22] was selected for the test. In general, the yields of oxidized products observed (Table I) are lower and the reaction rates higher for the bimetallic Co/Pd system than the monometallic Pd system.[23,24] Surprisingly, the bimetallic product distributions are not obviously consistent with either mechanism 1 or 2! In particular, while both *cis*- and *trans*-cyclooctene give ketone as the primary product as expected for bimolecular oxidation via eq 2, the product distributions are not quite identical as they should be for a stereoselective reàction. Furthermore, the product distribution in the oxidation of *cis*-cycloheptene is strongly concentration dependent. At low concentrations, the major product is that predicted by eq 1, epoxide; while at high concentrations, the major product is that predicted by eq 2, ketone. This concentration dependence is not seen in oxidations employing $Pd(CH_3CN)_2ClNO_2$.



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The unexpected results of the above stereochemical studies led us to carry out a more thorough investigation of the mixed Co/Pd system. First, an alternative one step synthesis of (py)CoTPPNO$_2$ was found that employs silver nitrite as both the oxidant and nitrating reagent for CoTPP (eq 5). The product obtained was shown spectroscopically to be the same as that obtained by the two-step literature preparation[21] based on nitrosylation of CoTPP with nitric oxide followed by air oxidation in the presence of pyridine. The material prepared by both

$$\mathrm{CoTPP + AgNO_2 + py \xrightarrow{MeCN} (py)CoTPPNO_2 + Ag} \qquad (5)$$

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(22) py = pyridine, TPP = *meso*-tetraphenylphorphyrin.

(23) Control experiments show that epoxides are not isomerized to ketones under either of the reaction conditions, although all epoxides investigated do decompose to products other than ketones in the mixed Co/Pd systems at longer reaction times.

(24) A notable exception is ethylene for which yields of acetaldehyde are higher in the bimetallic system.[2a,3d] The lower yields of ketones obtained with higher terminal alkenes in the Co/Pd system has also been confirmed by the original workers (Mares, F., personal communication). A reaction of 1-decene with (py)CoTPPNO$_2$ and $Pd(CH_3CN)_2Cl_2$ conducted in tetrahydrofuran gave a 25% yield of 2-decanone, a substantial improvement over the same reaction in 1,2-dichloroethane (Table I). Whether this is due to trace amounts of water in the THF leading to Pd(II) Wacher chemistry or whether this is a true solvent effect is not known at the present. Reactions of the cyclic alkenes in the Co/Pd system in THF did not show such a dramatic effect, instead unidentified byproducts were observed.

routes also behaved identically in the alkene oxidation reactions.

The vibrational assignments associated with the nitro group were confirmed by ^{15}N labeling studies (See Experimental Section). The previously unreported ^1H NMR spectrum of $(py)CoTPPNO_2$ shows that the pyridine protons are shifted upfield by as much as 6 ppm on coordination due to the porphyrin ring current. This is a characteristic spectral feature of axial ligands in metal porphyrin systems.[25] The signals due to the pyridine protons were not always well resolved, however, apparently due to exchange on the NMR time scale with traces of free pyridine.[26] The large chemical shift difference between free and coordinated pyridine in this system means that very small amounts of excess pyridine can lead to substantial line broadening. This rapid NMR exchange is easily verified by the purposeful addition of free pyridine.[27] Infrared and NMR spectra furthermore show that when $(py)CoTPPNO_2$ is mixed with $Pd(CH_3CN)_2Cl_2$, the pyridine ligand is rapidly transfered to the palladium, while a liberated acetonitrile appears to become weakly associated with some of the cobalt (eq 6; see Experimental Section).

$$\text{(py)CoTPPNO}_2 + \text{Pd(MeCN)}_2\text{Cl}_2 \xrightarrow[<5\text{ min}]{\text{CDCl}_3} \text{MeCN} + \text{(MeCN)CoTPPNO}_2 + \text{CoTPPNO}_2 + [\text{Pd(py)Cl}_2]_2 \quad (6)$$

Infrared studies show that nitro group transfer from $(py)CoTPPNO_2$ to Pd(II) is also fast but that the equilibrium favors bonding of the nitro group to the cobalt in preference to the palladium (eq 7 and 8). Nitrosyl transfer between palladium and cobalt is similarly facile with the equilibrium again favoring the cobalt nitrosyl (eq 9 and 10). Similar nitrosyl exchange reactions have been reported previously.[28]

$$\text{(py)CoTPPCl} + \text{Pd(MeCN)}_2\text{ClNO}_2 \xrightarrow[<15\text{ min}]{\text{CDCl}_3} \text{MeCN} + \text{(MeCN)CoTPPNO}_2 + \text{CoTPPNO}_2 + [\text{Pd(py)Cl}_2]_2 \quad (7)$$

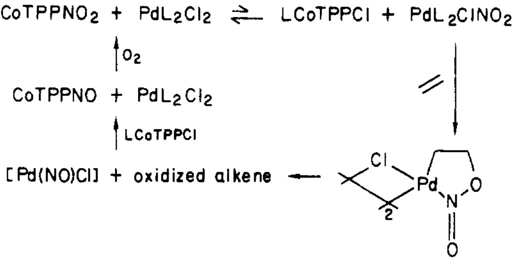
$$\text{(py)CoTPP}^{14}\text{NO}_2 + \text{Pd(MeCN)}_2\text{Cl}^{15}\text{NO}_2 \xrightarrow[<1\text{ h}]{\text{DCE}} \text{MeCN} + \text{(MeCN)CoTPP*NO}_2 + \text{CoTPP*NO}_2 + [\text{Pd(py)Cl*NO}_2]_2 \quad (8)$$

$$* = {}^{14}\text{N}/{}^{15}\text{N mixture}$$

$$\text{(py)CoTPPCl} + [\text{PdCl(NO)}]_n \xrightarrow[<2\text{ h}]{\text{DCE}} \text{CoTPPNO} + [\text{Pd(py)Cl}_2]_2 \quad (9)$$

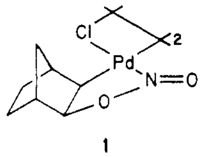
$$\text{CoTPP}^{15}\text{NO} + [\text{PdCl(}^{14}\text{NO)}]_n \xrightleftharpoons[<20\text{ min}]{\text{CH}_2\text{Cl}_2} \text{CoTPP}^{14}\text{NO} + [\text{PdCl(}^{15}\text{NO)}]_n \quad (10)$$

Scheme I. Alternate Mechanism for Bimetallic Oxidation



L = CH_3CN, pyridine

These results suggest that it might be possible for the Co/Pd mediated alkene oxidation to proceed via a nitro group transfer mechanism (Scheme I). Transfer of the nitro group from Co to Pd would generate small concentrations of the same $Pd(CH_3CN)_2ClNO_2$ catalyst as is present in our recently reported monometallic system.[3] Subsequent metallacyclic oxidation of the alkene would give a Pd nitrosyl that would rapidly transfer the nitrosyl ligand back to cobalt to give the observed intermediate cobalt nitrosyl. This species would then be reoxidized by known chemistry back to the cobalt nitro complex.[2] Further evidence for this hypothesis is the observation in both IR and ^1H NMR spectra of trace amounts of the appropriate metallacycle 1 in the reaction of $(py)CoTPPNO_2$ with norbornene in the presence of $Pd(CH_3CN)_2Cl_2$. This metallacyclic intermediate was present to a slightly larger extent with $PPh_3CoTPPNO_2$ was employed in place of $(py)CoTPPNO_2$.



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There are several important observations that need further explanation if the proposal that the Co/Pd system is a variation on the straight Pd system is to be considered plausible. First, the rates of alkene oxidation in the Co/Pd system are significantly *faster* than in the monometallic system (cf. especially norbornene in Table I[29]). Secondly, the product distributions observed as a function of alkene and concentration are not identical for the two systems. Both of these inconsistencies may be due to interactions of the palladium metallacyclic intermediates with one or more of the cobalt species present.[30] Thus, proton NMR spectra show that both $(H_2O)CoTPPCl$ and $(CH_3CN)CoTPPNO_2$ enhance the rate of decomposition of norbornene metallacycle 1 to epoxynorbornane by about a factor of 50. Rate enhancements of this type (which could be somewhat different under the actual reaction conditions) might compensate for the lower rates predicted by the unfavorable nitro transfer equilibrium in Scheme I, leading to the faster observed overall rates. Stronger rate enhancements are seen with the powerful Lewis acid $BF_3{\cdot}Et_2O$ that reacts with the norbornene metallacycle instantaneously to give $[PdCl(NO)]_n$. (Epoxynorbornane could not be detected, presumably due to decomposition by the BF_3). The cobalt complexes present could also increase the selectivies for ketones as observed by coordinating to the nitrite functionality present in the metallacycle and thereby affecting the ring opening equilibrium.[3d]

Other possible explanations for the anomalous product distributions observed in the bimetallic Co/Pd system are that (a) intra- and intermolecular pathways are competitive

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(27) Although Co(III) complexes are usually substitutionally inert, the axial ligands in Co(III) porphyrin and related complexes are known to be quite labile. See, for example: Pasternack, R. F.; Cobb, M. A.; Sutin, N. *Inorg. Chem.* **1975**, *14*, 866–873.

(28) Ungermann, C. B.; Caulton, K. G. *J. Am. Chem. Soc.* **1976**, *98*, 3862–3868.

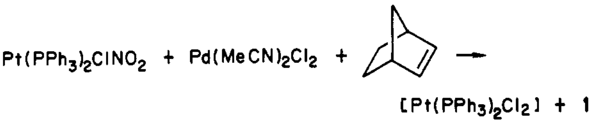
(29) The cause of the marked rate and yield discrepancies between the two sets of workers in the bimetallic oxidation of norbornene (Table I) could not be determined. The exact literature conditions for the bimetallic oxidation of norbornene are unknown, however, since the solvent and dissolved norbornene were measured *prior* to purging with argon for 45 min.[2c]

(30) NMR spectra show that alcohols, ethers, and epoxides bond quite well to CoTPPX species, but no interaction can be observed with *n*-BuONO.

with some product being formed by both paths or (b) that the O atom transfer takes place from a cobalt nitro group to a palladium-bound alkene but that the palladium is held in close proximity to the cobalt, perhaps by coordination to the porphyrin pyrole double bonds. A rigorous experimental distinction between these numerous possibilities does not appear possible.[31] It does seem clear, however, that the mechanism of the bimetallic Co/Pd mediated alkene oxidation reaction is considerably more complicated than the simple intermolecular O atom transfer originally suggested.

In an attempt to find a simpler bimetallic system, Pt(II) and Ru(II) nitro complexes were investigated as oxygen atom sources in conjunction with a Pd(II) cocatalyst. While Pt(diphos)ClNO$_2$ does not oxidize 1-decene by itself, in the presence of Pd(CH$_3$CN)$_2$Cl$_2$, 2-decanone is formed in 25% yield in 1 h at room temperature. This rate is very comparable to that observed with Pd(CH$_3$CN)$_2$ClNO$_3$.[3a] As is the case for cobalt, nitro group transfer from palladium to platinum can be shown to occur in less than 20 min at room temperature (eq 11). Although the equilibrium appears to completely favor bonding of the nitro group to Pt(II) in the absence of norbornene, the addition of norbornene causes complete transfer of NO$_2^-$ to the palladium driven by the formation of metallacycle 1 (eq 12). Similar results are obtained when Ru(CO)$_2$(NO$_2$)$_2$(PPh$_3$)$_2$ (2) is employed as the nitro complex,[32] except that now the nitro group prefers to be bonded to the palladium even in the absence of alkene (eq 13).

$$\mathrm{Pt(PPh_3)_2Cl_2 + Pd(MeCN)_2ClNO_2 \rightarrow Pt(PPh_3)_2ClNO_2 + [Pd(MeCN)_2Cl_2]} \quad (11)$$



(12)

$$\mathrm{Ru(PPh_3)_2(CO)_2(NO_2)_2 + Pd(CH_3CN)_2Cl_2 \rightarrow Ru(PPh_3)_2(CO)_2Cl_2 + L_{\mathit{n}}PdNO_2} \quad (13)$$

Several attempts were then made to spectroscopically detect a bimolecular species resulting from an intermolecular addition reaction. The cobalt–palladium complex in eq 4 would not be expected to be easily observed since palladium alkyl complexes are generally unstable.[33] The much greater stability of Fp–alkyl (Fp = η^5-C$_5$H$_5$Fe(CO)$_2$) and platinum–alkyl complexes led us to examine the reaction of Fp and platinum alkene complexes with metal nitro complexes (eq 14–18). In no case was infrared or NMR evidence obtained for a bimetallic intermediate, even in the case of the highly activated Fp–vinyl ether complex.[34]

$$\mathrm{(py)CoTPPNO_2 + PtCl_3(C_2H_4)^- \rightarrow CoTPPNO_2 + Pt(py)(C_2H_4)Cl_2} \quad (14)$$

$$\mathrm{(py)CoTPPNO_2 + CpFe(CO)_2(1\text{-}decene)^+ \rightarrow NR} \quad (15)$$

$$\mathrm{(py)CoTPPNO_2 + CpFe(CO)_2(H_2C{=}CHOC_2H_5)^+ \rightarrow NR} \quad (16)$$

$$\mathrm{(py)CoTPPNO_2 + Pt(Me_2NC_2H_4NMe_2)(C_2H_4)Cl^+ \rightarrow NR} \quad (17)$$

$$\mathrm{Pt(Ph_2PC_2H_4PPh_2)ClNO_2 + CpFe(CO)_2(1\text{-}decene)^+ \rightarrow NR} \quad (18)$$

The only explicit literature claim for intermolecular nucleophilic[35] metal nitro group O atom transfer is based on the observation of ^{13}C^{18}O^{16}O in the isotopic double labeling experiment summarized in eq 19.[11b,c] This is a very complicated system.[11b,c,32,36] As suggested by the multiple products in eq 19, there are actually two O atom transfer reactions that occur. The first is primarily O atom transfer to CO (45 min at 110 °C) to give Ru(PPh$_3$)$_2$(CO)(NO)(NO$_2$), while the second is primarily O atom transfer to triphenylphosphine (4 h at 110 °C). Single label isotopic studies showed that reversible O atom exchange between NO$_2$ and CO apparently also occurs (eq 20). The published evidence[11b] for this reversible exchange may not be definitive since in a related nickel system,[11a] no scrambling of the labels was seen in the product nitrosyl,[12d] only in the CO$_2$. Furthermore, the conclusions drawn from the double label experiment given in eq 19 are potentially invalid since no control reactions were conducted to prove that the isotopic labels do not scramble by ligand exchange prior to O atom transfer. We have therefore reexamined both of these questions.

$$\mathrm{Ru(PPh_3)_2(^{13}CO)_2(N^{16}O_2)_2 + Ru(PPh_3)_2(^{12}CO)_2(N^{18}O_2)_2 \xrightarrow[PPh_3,\ 110\,^\circ C]{PhMe} Ru(PPh_3)_2(N^{*}O)_2 + C'^{*}O_2 + {}^{*}OPPh_3} \quad (19)$$

$$* = {}^{16}\mathrm{O}/{}^{18}\mathrm{O}\ \text{mixture};\ ' = {}^{12}\mathrm{C}/{}^{13}\mathrm{C}\ \text{mixture}$$

$$\mathrm{Ru(PPh_3)_2(C^{16}O)_2(N^{18}O_2)_2 \xrightarrow[110\,^\circ C]{PhMe} C^{18}O_2 + C^{16}O_2 + C^{16}O^{18}O + Ru(PPh_3)_2(N^{?}O)_2 + \ldots} \quad (20)$$

The reaction of [Ru(PPh$_3$)$_2$(CH$_3$CN)$_2$(C^{16}O)$_2$]$^{2+}$ with KN^{18}O$_2$ in methanol at 65 °C for 4 h leads to the formation of ^{18}O labeled Ru(PPh$_3$)$_2$(CO)$_2$(NO$_2$)$_2$ (2), which is found by infrared spectra to contain significant though not statistical incorporation of ^{18}O into the carbonyl ligands. Similar results have been seen in the synthesis of labeled 2 starting from Ru(PPh$_3$)$_2$(CH$_3$CN)$_2$(C^{18}O)$_2$ and NaN^{16}O$_2$.[11c] These results indicate that reversible isotope exchange must occur under the synthesis conditions. When isolated 2 containing a partially equilibrated ^{18}O label is heated in toluene at 57 °C for 24 h, however, no dramatic increase in the amount of scrambling could be detected. (The variable isomer ratios present[36] precluded an accurate determination of the change in isotopic composition of the carbonyl ligands.) The more rapid exchange seen under the synthesis conditions may be due to attack of the more

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[31] The marked concentration dependence of the product distributions observed in the oxidation of cycloheptene with the bimetallic CoNO$_2$/Pd system could be taken as evidence for a competition between intra- and intermolecular pathways, since the latter should become more important at higher concentrations. The cobalt-induced decomposition of the intermediate metallacycle in the nitro group transfer mechanism of Scheme I would also be expected to display a concentration dependence, however.

[32] As in the original paper,[11b] Ru(PPh$_3$)$_2$(CO)$_2$(NO$_2$)$_2$ is used to denote the apparently equilibrium mixture of Ru(PPh$_3$)$_2$(CO)$_2$(ONO)$_2$ and Ru(PPh$_3$)$_2$(CO)$_2$(ONO)(NO$_2$).

[33] Weinberg, E. L.; Hunter, B. K.; Baird, M. C. *J. Organomet. Chem.* **1982**, *240*, 95–102.

[34] Change, T. C.-T.; Foxman, B. M.; Rosenblum, M.; Stockman, C. *J. Am. Chem. Soc.* **1981**, *103*, 7361–7362.

[35] Meyer has reported evidence for what is presumeably an electrophilic intermolecular nitro group O atom transfer to coordinated nitrite ion.[18]

[36] The ratio of isomers present is dependent on the previous solvent treatment (see Experimental Section), an observation not noted in the literature concerning 2. It is not clear that the two isomers observed in the solid state (isomers A and B of Table II) are the same as those observed in solution by NMR (Ru(PPh$_3$)$_2$(CO)$_2$(ONO)$_2$ and Ru(PPh$_3$)$_2$(CO)$_2$(NO$_2$)(ONO)),[11b,c] since the IR absorbances attributable to the N-bonded NO$_2$ groups are of equal intensity vs. phosphine bands in both isomers A and B (see Table II). Solution IR spectra are uninformative due to the appearance of single broad bands for the CO stretches.[11b,c]

nucleophilic free nitrite ion on the more electrophilic carbonyl ligands present in the cationic nitrile complex.

The double label crossover study (eq 19) was then reexamined, again using highly isotopically enriched species and infrared analysis in place of the low level labeling and isotope ratio mass spectrometric analysis employed by the previous workers.[11b,c] The most important result is given by eq 21. Regardless of the detailed

$$\mathrm{Ru(PPh_3)_2(^{13}CO)_2(N^{16}O_2)_2} + \mathrm{Ru(PPh_3)_2(^{12}CO)_2(N^{18}O_2)_2} \xrightarrow[\mathrm{PPh_3,\ 55\ ^\circ C}]{\mathrm{PhMe}} \mathrm{Ru(PPh_3)_2(C'{*}O)_2(N{*}O_2)_2} \qquad (21)$$

$$* = {}^{16}\mathrm{O}/{}^{18}\mathrm{O}\ \text{mixture};\ ' = {}^{12}\mathrm{C}/{}^{13}\mathrm{C}\ \text{mixture}$$

mechanism(s) involved, the observation of species containing $^{13}C^{18}O$ ligands shows that (1) an intermolecular exchange of ligands or oxygen atoms or both occurs and that (2) reversible exchange of oxygen atoms between carbonyl and nitro groups does in fact occur at 55 °C. The mixed label CO_2 formed in eq 19 therefore provides no information concerning the intra- vs. intermolecular nature of the 110 °C irreversible O atom transfer.

Control experiments were then performed in an attempt to determine the type of the intermolecular process present and the molecularity of the reversible exchange that occurs at 55 °C. Carbon monoxide ligand exchange does not appear to be significant under the reaction conditions since infrared spectra show that reaction 22 is negligible.

$$\mathrm{Ru(PPh_3)_2(^{13}CO)_2(NO_2)_2} + \mathrm{Ru(PPh_3)_2(^{12}CO)_2(NO_2)_2} \overset{57\ ^\circ\mathrm{C}}{\underset{24\ \mathrm{h}}{\nrightarrow}} \mathrm{Ru(PPh_3)_2(^{13}CO)(^{12}CO)(NO_2)_2} \qquad (22)$$

Definitive evidence could not be obtained regarding NO_2 ligand exchange since no technique could be found to monitor the exchange.[37] The observation of facile NO_2/Cl ligand exchange observed between $Ru(PPh_3)_2(CO)_2(NO_2)_2$ and $Pd(CH_3CN)_2Cl_2$ (eq 13) suggests, however, that NO_2 group exchange between two Ru complexes might also be kinetically facile. Therefore, since ligand exchange cannot be ruled out, it is not possible to determine whether either the reversible or irreversible O atom exchange is intra- or intermolecular.

In summary, while we certainly do not rule out the possibility that intermolecular nucleophilic nitro group O atom transfer can occur, the results presented here indicate that definitive examples of such a reaction have yet to be clearly demonstrated. It seems likely that the oxygen atom of a metal nitro group is only a weak nucleophile because of the formal positive charge on the adjacent nitrogen. As such, attack on a weakly electrophilic coordinated substrate ligand such as CO or alkene should be much more likely to occur via a metallacyclic intermediate where nucleophilic addition is enhanced by the favorable entropy term (chelate effect) associated with an intrametallic mechanism.[38]

Experimental Section

General Data. General procedures employed have been described elsewhere.[3d] CoTPP was purchased from Strem. $AgN^{18}O_2$ was prepared as previously described;[3c] $Ag^{15}NO_2$ was prepared by a similar procedure using $Na^{15}NO_2$ (Stohler 99% ^{15}N).

Preparation and Spectra of CoTPPNO. CoTPPNO was prepared as described in the literature from the interaction of CoTPP and nitric oxide in dichloromethane solution under nitrogen.[39] Evaporation of solvent gave a brown solid that was washed with hexane and dried under vacuum: IR (Nujol) 1700 (vs, ν (NO)), 1598 (m), 1353 (s), 1175 (s), 1074 (s), 1002 (vs), 997 (s), 802 (s), 753 (s), 717 (m), 704 (m), 666 (w), 531 (w), 521 (vw), 510 (vw, δ (CoNO)), 461 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.90 (s, 8 H), 8.15 (br t, 8 H), 7.76 (br s, 12 H).

$CoTPP^{15}NO$ was prepared from the reaction of $(CH_3CN)CoTPP^{15}NO_2$ with norbornene in the presence of $Pd(CH_3CN)_2Cl_2$ in $CDCl_3$ for 3 h: IR (KBr disk) 1669 (vs. ν (^{15}NO)), 499 cm^{-1} (w, δ ($Co^{15}NO$)).

Preparation and Spectra of (py)CoTPPNO$_2$. A. (py)CoTPPNO$_2$ was prepared as described in the literature by the air oxidation of CoTPPNO in the presence of pyridine:[21] IR (KBr disk) 1598 (m), 1443 (m), 1424 (m, ν (NO_2)), 1350 (m), 1308 (vs. ν (NO_2)), 1216 (w), 1205 (w), 1175 (w), 1068 (m), 1006 (vs), 997 (s), 815 (s, δ (ONO)), 796 (s), 752 (s), 701 (vs), 665 (w), 634 (vw) cm^{-1} (lit.[21] (Nujol) 1320, 1220, 820 cm^{-1}); ^1H NMR ($CDCl_3$) δ 9.08 (impurity, ~1.5 H), 8.98 (s, 8 H), 8.08 (t, $J = 3.5$ Hz, 8 H), 7.73 (m, 12 H), 5.98 (t, $J = 6$ Hz, 1 H), 4.94 (t, $J = 6$ Hz, 2 H), 1.01 (d, $J = 6$ Hz, 2 H).

B. (py)CoTPPNO$_2$ was prepared in one step by treating a suspension of CoTPP (358 mg, 0.533 mmol) in acetonitrile (45 mL) with pyridine (48 μL, 0.593 mmol) and silver nitrite (89.5 mg, 0.582 mmol, dissolved in 5 mL of MeCN) under nitrogen. The reaction mixture was refluxed for 7 h and then filtered in air. The purple precipitate containing the desired product and silver metal was washed with acetonitrile (2 × 10 mL) and then extracted with dichloromethane. The dichloromethane extracts were evaporated to give brilliant purple microcrystalline (py)CoTPPNO$_2$ (280 mg, 69%) identified by comparison of IR and ^1H NMR spectra with an authentic sample. The material contained a trace of dichloromethane but did not show the NMR impurity at δ 9.08. Similar preparations were carried out more quickly at room temperature for 2–4 h, giving yields of 60–80%.

C. (py)CoTPPNO$_2$ was also prepared from the reaction of (py)CoTPPCl[40] (50 mg, 0.066 mmol) and silver nitrite (11 mg, 0.071 mmol) in acetonitrile (5 mL) for 20 min at room temperature. The reaction was worked up as in **B** and the product identified by IR and ^1H NMR spectra.

(py)$CoTPP^{15}NO_2$ was prepared as in C by using $Ag^{15}NO_2$: IR (KBr disk) 1399 (s, ν ($^{15}NO_2$)), 1290 (vs, ν ($^{15}NO_2$)), 807 (vs, δ ($O^{15}NO$)).

Synthesis of "(CH$_3$CN)CoTPPNO$_2$". (H_2O)CoTPPCl[41] (84.8 mg, 0.126 mmol) and silver nitrite (19.3 mg, 0.126 mmol) in 10 mL of acetonitrile were stirred at room temperature for 4 h. The solvent was removed and the residue extracted with dichloromethane (2 × 20 mL). Removal of the dichloromethane gave 84 mg (95%) of a purple crystalline product for which spectral data

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[37] Although it has been shown that no exchange occurs between 2 and KNO_2,[11b,c] this is not surprising due to the exceedingly low solubility of ionic nitrite in toluene. In contrast to carbonyl exchange, nitro group exchange between $Ru(PPh_3)_2(CO)_2(^{14}NO_2)_2$ and $Ru(PPh_3)_2(CO)_2(^{15}NO_2)_2$ cannot be monitored by infrared spectroscopy, since the infrared spectrum of the authentic mixed label species $Ru(PPh_3)_2(CO)_2(^{14}NO_2)(^{15}NO_2)$ is unresolvable from the two singly labeled species also present. This is due to the much smaller coupling between the N–O stretching modes of the two nitro groups on the Ru vs. the strongly coupled CO stretching modes. In theory, mass spectrometry could be used but substantial thermal decompostion would undoubtedly occur in the process and spectral analysis would be difficult due to the complex Ru isotope pattern. The only other technique that would appear to be able to detect the mixed label species in the presence of the two singly labeled species would be NMR via an analysis of ^{31}P–^{15}N coupling patterns. The mixture of isomers present (dominated by O-bonded linkage isomers) would make this experiment difficult also.

[38] A particularly good candidate for intermolecular nitro group O atom transfer would appear to be the Allied Co/Tl system.[2b] Tl(III) is a strong electrophile, and therefore a Tl(III) alkene complex is probably best written as an alkyl complex with a β-carbonium ion that could be readily trapped by even a weakly nucleophilic coordinated nitro group. (In our hands, brief attempts to prepare Tl(III) nitro complexes that might effect intramolecular nitro group O atom transfer were unsuccessful as judged from infrared spectra and reactions with alkenes).

[39] Wayland, B. B.; Minkiewicz, J. V.; Abd-Elmageed, M. E. *J. Am. Chem. Soc.* **1974**, *96*, 2795–2801.

[40] Yamamoto, K.; Tonomura, S. *Sci. Papers Inst. Phys. Chem. Res.* **1964**, *58*, 122.

[41] Sakurai, T.; Yamamoto, K.; Naito, H.; Nakamoto, N. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3042–3046. We obtained the aquo complex from this preparation prior to recrystallization (^1H NMR ($CDCl_3$) δ 2.37 (s, 2 H), shifting to δ 3.44 on reaction with pyridine).

are consistent with a mixture of $(CH_3CN)CoTPPNO_2$ and $CoTPPNO_2$: IR (KBr disk) 1597 (m), 1453 (m, ν (NO_2)), 1439 (m), 1350 (s), 1306 (vs, ν (NO_2)), 1283 (vs, ν (NO_2)), 1176 (m), 1073 (m), 1006 (vs), 997 (s), 813 (m, δ (ONO)), 806 (m, δ (ONO)), 798 (m), 751 (vs), 703 (vs), 665 (m), 530 (w), 463 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.98 (s, 8 H), 8.18 (m, 8 H), 7.76 (m, 12 H), 1.91 (chemical shift variable and temperature dependent) (s, ~2–3 H).

$(CH_3CN)CoTPP^{15}NO_2$ was prepared similarly by using $Ag^{15}NO_2$: IR (KBr disk) 1421 (m, ν ($^{15}NO_2$)), 1288 (s, ν ($^{15}NO_2$)), 1263 (vs, ν ($^{15}NO_2$)), ~803 (s, δ ($O^{15}NO$)).

Reaction of (py)CoTPPNO$_2$ with Alkenes in the Presence of Pd(II). $(py)CoTPPNO_2$ (~10 mM), $Pd(CH_3CN)_2Cl_2$ (~2.5 equiv) or $Pd(PhCN)_2Cl_2$, and alkene (1–10 equiv) were mixed in the appropriate solvent under nitrogen, and the reaction was monitored by GC as a function of time. The results were independent of whether the cobalt nitro complex was prepared by method **A** or **B**. Quenching the reaction with bis(diphenylphosphino)ethane prior to injection into the GC also had no effect on the product yields obtained. Products were identified on the basis of coinjection with authentic samples. Epoxycycloheptane was further confirmed by coinjection on three different GC columns and by NMR spectra taken after quenching the reaction with excess pyridine. (Unquenched aliquots showed that the epoxide was coordinated to the cobalt as evidenced by upfield shifts of the epoxide protons). *exo*-Epoxynorbornane was also identified by its proton NMR.

Cobalt–Palladium Ligand Scrambling Reactions. A. Pyridine Exchange. A 1:1 mixture of $(py)CoTPPNO_2$ and $Pd(CH_3CN)_2Cl_2$ was dissolved in $CDCl_3$ and monitored by ^1H NMR. Transfer of the pyridine from Co to Pd is complete in less than 4 min at ambient probe temperature as indicated by the disappearance of the high-field resonances due to pyridine coordinated to cobalt and the appearance of multiplets at δ 8.56 and 7.38 due to pyridine coordinated to palladium (confirmed by independent reaction of $Pd(CH_3CN)_2Cl_2$ with pyridine). IR spectra taken after removal of solvent showed that the only nitro group absorptions present (1451, 1308, 1283, and 806 cm^{-1}) were those attributable to $(CH_3CN)CoTPPNO_2$ and $CoTPPNO_2$.

B. Nitro Group Exchange. One equivalent of $Pd(CH_3CN)_2ClNO_2$ was added to (py)CoTPPCl in $CDCl_3$ in an NMR tube. As in **A** above, immediate transfer of pyridine from cobalt to palladium was observed. An IR spectrum of the $CDCl_3$ solution showed that the only nitro ligands present were those bonded to cobalt. An IR spectrum taken after removal of solvent was essentially identical with that in **A**, again indicating complete transfer of the nitro group to cobalt. Nitro group transfer to Co was also observed in solution IR spectra.

A solution of $(py)CoTPP^{14}NO_2$ (6 mg) and $Pd(CH_3CN)_2Cl^{15}NO_2$ (2.1 mg) in 1,2-dichloroethane was stirred at room temperature for 1 h. After removal of solvent an IR spectrum showed absorptions attributable to $CoTPP^{15}NO_2$ (1264 cm^{-1}) and $[PdPyCl^{14}NO_2]_2$ (1320 cm^{-1}).

C. Nitrosyl Exchange. A 1:1.2 mixture of (py)CoTPPCl (6.6 mg) and $[PdCl(NO)]_n$[1] (1.8 mg) in 1,2-dichloroethane (3 mL) was stirred for 2 h under nitrogen. An IR spectrum taken after removal of solvent showed that CoTTPNO (1697 cm^{-1}) was the only nitrosyl complex present. ^1H NMR spectra confirmed the presence of CoTPPNO and also showed resonances attributable to palladium bound pyridine.

A mixture of $CoTPP^{15}NO$ (2 mg) and $[PdCl(^{14}NO)]_n$ (1 mg) in dichloromethane (1 mL) was stirred under nitrogen for 20 min at room temperature. After removal of solvent, an IR spectrum showed that $CoTPP^{14}NO$ (1698 cm^{-1}) was present.

Spectral Studies of the Reaction of Norbornene with Cobalt–Palladium Systems. A. (py)CoTPPNO$_2$ + Pd(CH$_3$CN)$_2$Cl$_2$. To a 1:2.1 mixture of $(py)CoTPPNO_2$ (7 mg) and $Pd(CH_3CN)_2Cl_2$ (5 mg) in $CDCl_3$ (0.5 mL) in an NMR tube was added 1 equiv of norbornene (11.5 μL of a 0.8 M $CDCl_3$ solution). An ^1H NMR spectrum taken after 6 min showed a weak broad peak at 4.35 ppm, similar to that observed for metallacycle 1 in the presence of acetonitrile. The formation of epoxynorbornane and CoTPPNO (~25 % in 1 h) was then observed. After 1 h an infrared spectrum taken of the same sample in $CDCl_3$ solution showed a strong peak at 1690 cm^{-1} due to CoTPPNO, a peak at 1286 cm^{-1} due to $CoTPPNO_2$, and a weak peak at 1617 cm^{-}1 attributable to metallacycle 1.

B. PPh$_3$CoTPPNO$_2$ + Pd(CH$_3$CN)$_2$Cl$_2$. To a 1:2.5 mixture of $PPh_3CoTPPNO_2$ (7 mg) and $Pd(CH_3CN)_2Cl_2$ (5 mg) in $CDCl_3$ (0.5 mL) was added ~1 equiv of norbornene. After 1 h at room temperature, an NMR spectrum showed a weak second-order AB quartet centered at 4.33 ppm characteristic of metallacycle 1, together with resonances attributable to both CoTPPNO and $CoTPPNO_2$. The presence of these three species was also confirmed by the observation of characteristic peaks in the infrared.

C. Cobalt-Induced Decomposition of Metallacycle 1. To a solution of norbornene metallacycle 1[3c] (3.1 mg) in $CDCl_3$ (0.5 mL) was added 1 equiv of $(H_2O)CoTPPCl$[41] (7.4 mg), and the reaction was monitored by ^1H NMR spectroscopy. The metallacycle was completely decomposed to epoxynorbornane after 1.5 h at ambient probe temperature, accompanied by the formation of CoTPPNO. Infrared spectra taken of the completed reaction mixture after removal of solvent showed that the only nitrosyl species present was CoTPPNO, together with a trace of $CoTPPNO_2$. Similar results were obtained when $(CH_3CN)CoTPPNO_2$ was employed.

BF$_3$-Induced Decomposition of Metallacycle 1. To a solution of norbornene metallacycle 1 (5.4 mg) in $CDCl_3$ (0.5 mL) was added 1 equiv of $BF_3{\cdot}Et_2O$ (2.35 μL). The color of the solution immediately turned to a dark green, and a black precipitate formed. No norbornene or epoxynorbornane could be observed in the NMR. The black solid was shown to contain $[PdCl(NO)]_n$ identified by comparison of its infrared spectrum with that of an authentic sample.

Alkene Oxidation by Platinum–Palladium Systems. A. 1-Decene. 1-Decene (0.25 mL, 1.32 mmo.) and dodecane (15.1 mg) were added to a 1:1 mixture of $Pt(diphos)ClNO_2$[42] (36.6 mg) and $Pd(CH_3CN)_2Cl_2$ (14 mg) in 1,2-dichloroethane solution (10 mL) under nitrogen. After 20 min at room temperature GC analysis showed that 2-decenone had formed in 20% yield, increasing to 25% after 1 h. The mixture was then refluxed for 2.5 h at which time GC analysis showed that tne 2-decanone production had leveled out at 68%. No reaction was observed in the absence of $Pd(CH_3CN)_2Cl_2$.

B. Norbornene. A 1:1 mixture of $Pt(PPh_3)_2ClNO_2$ (10.7 mg) and $Pd(CH_3CN)_2Cl_2$ (3.5 mg) was dissolved in 1,2-dichloroethane (2 mL). Infrared spectra taken after 1 h showed that the nitro group was still bound to the platinum. A reverse reaction of $Pt(PPh3)_2Cl_2$ with $Pd(CH_3CN)_2ClNO_2$ was found by IR spectroscopy to result in essentially complete transfer of the nitro group from palladium to platinum. NMR spectra showed that addition of 1 equiv of norbornene to either of the above reaction mixtures led to the quantitative formation of metallacycle 1.

Norbornene Oxidation by Ruthenium–Palladium Systems. A 1:2 mixture of $Ru(PPh_3)_2(CO)_2(NO_2)_2$[11b] (7 mg) and $Pd(CH_3CN)_2Cl_2$ (5 mg) was dissolved in dichloromethane (2 mL). Solvent was removed after the solution was stirred for 20 min at room temperature. An IR spectrum (KBr) showed that complete transfer of the nitro group from Ru to Pd had occurred with the formation of $Ru(PPh_3)_2(CO)_2Cl_2$ (ν (CO) 2061, 2002; δ (RuCO) 618, 579 cm^{-1}) and a palladium nitro complex (ν (NO_2) 1452, 1317; δ (ONO) 822 cm^{-1}). This mixture was dissolved in $CDCl_3$ and 1 equiv of norbornene added. Metallacycle 1, the only norbornene derived material initially observed in the NMR, was observed to decompose at the usual rate of ~3%/h to epoxynorbornane.

Preparation of Ru(PPh$_3$)$_2$(CO)$_2$(NO$_2$)$_2$ (2) and Isotopic Derivatives. Unlabeled **2** was prepared as described in the literature by the reaction of $[Ru(CO)_2(PPh_3)_2(CH_3CN)_2]^{2+}$ with KNO_2 in refluxing methanol followed by recrystallization from dichloromethane–methanol.[11b,c] Infrared spectra of the material thus obtained are in good agreement with the literature values.[11b,c] When **2** was recovered from solutions in polar solvents (CH_2Cl_2, MeOH, CH_3CN), the isomer ratio was also similar to that observed in the literature, consisting primarily of isomer A (Table II). When **2** was recovered from solutions in nonpolar solvents (toluene), however, the isomer ratio was usually dramatically altered, favoring isomer B (Table II). The interconversion is reversible, is quite facile (occurring at room temperature), and is not entirely reproducible (perhaps due to preferential crystallization of one

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[42] (a) Cherwinski, W. J.; Clark, H. C. *Inorg. Chem.* **1971**, *10*, 2263–2267. (b) Dixon, K. R.; Moss, K. C.; Smith, M. A. R. *Can. J. Chem.* **1974**, *52*, 692–695.

Table II. Infrared Spectral Data for Isotopically Labeled $Ru(PPh_3)_2(CO)_2(NO_2)_2$[a]

isotopic species	isomer A	isomer B
	ν_{CO},[b] cm^{-1}	
$(^{12}C^{16}O)_2$	2043, 1983	2052, 1995
$(^{12}C^{16}O)(^{12}C^{18}O)$	2024, 1959	2033, 1969
$(^{12}C^{16}O)(^{13}C^{16}O)$	2023, 1959	2033, 1969
$(^{12}C^{18}O)_2$	1999, 1940	2008, 1950
$(^{12}C^{18}O)(^{13}C^{16}O)$	(1997, 1939)[c]	(2006, 1949)[c]
$(^{13}C^{16}O)_2$	1996, 1939	2005, 1949
$(^{12}C^{18}O)(^{13}C^{18}O)$	1977, 1913	1987, ~1923
$(^{13}C^{16}O)(^{13}C^{18}O)$		
$(^{13}C^{18}O)_2$	~1950, 1893	~1958, 1904
	ν_{NO}, cm^{-1}	
$(^{14}N^{16}O_2)_2$: M-NO_2[d]	1406 (51),[e] 1314 (16) 816 (vw)	1409 (59), 1314 (16) 816 (vw)
M-ONO[d]	1389 (36), 1070 (sh) 1060 (41)	1399 (78), 1085 (70) 1070 (sh)
$(^{15}N^{16}O_2)_2$: M-NO_2[d]	1383 (s), 1290 (w) 810 (vw)	1385 (s), 1290 (w) 810 (vw)
M-ONO[d]	1360 (m), 1035 (m, br)	1373 (s), 1061 (s, br)

[a] Spectra recorded as KBr disks. [b] All bands are strong. [c] Inferred positions. [d] Ligand types attributed to observed bands. [e] Values in parentheses are relative absorbances vs. phosphine band of absorbance 100 at 1436 cm^{-1}.

isomer depending on the exact evaporation conditions).

The ^{13}CO labeled species was prepared similarly according to the literature procedure[11b,c] and the IR spectra recorded (Table II). The $N^{18}O_2$ labeled complex was prepared as described in the literature except that the KNO_2 (prepared from $AgN^{18}O_2$ and KCl) was enriched to approximately 69% ^{18}O. Under the synthesis conditions, some of the ^{18}O label is incorporated into the CO ligands (and conversely ^{16}O into the nitro ligands) by reversible O atom exchange.[11c] Table II lists the CO stretching frequencies observed for the various isotopic species present. The $(C^{16}O)_2$ species was observed to be the major species present, indicating that the exchange had not yet reached the expected statistical 29% $(C^{16}O)_2$, 50% $(C^{16}O)(C^{18}O)$, and 21% $(C^{18}O)_2$ equilibrium mixture. Heating the isolated ^{18}O labeled species in toluene at 57 °C for 23 h led to no clearly marked change in the oxygen isotopic distribution in the CO ligands, but quantitative analysis was complicated by the variable isomer ratios obtained. Species containing both ^{13}C and ^{18}O isotope labels were obtained by reacting $[Ru(CH_3CN)_2(^{13}CO)_2(PPh_3)_2]^+$ with $KN^{18}O_2$. The infrared spectral assignments in the CO region are included in Table II. $^{15}NO_2$-labeled 2 was prepared by the standard procedure[11b,c] except that $K^{15}NO_2$ was employed. The infrared spectra in the NO stretching regions given in Table II confirm the literature assignments for the NO stretches.

Isotopic Scrambling between $Ru(PPh_3)_2(CO)_2(N^{18}O_2)_2$ and $Ru(PPh_3)_2(^{13}CO)_2(NO_2)_2$. A mixture of $Ru(PPh_3)_2(CO)_2(N^{18}O_2)_2$[19] (5 mg), and $Ru(PPh_3)_2(^{13}CO)_2(NO_2)_2$[19] (5 mg) was dissolved in toluene (2 mL) and stirred at 57 °C for 24 h. The solvent was evaporated under vacuum, and infrared spectra showed the presence of isomer B with infrared bands at 1987, 1961, 1924, and 1903 cm^{-1} corresponding to species containing both a ^{13}C and a ^{18}O label (Table II). Bands at these frequencies were not observed when either the $(^{13}CO)_2$ or $(N^{18}O_2)_2$ complexes were heated separately at 57 °C for 24 h. Similar results were obtained when the reaction was conducted in the presence of 4 equiv of triphenylphosphine.

Test for CO Exchange. Complex **2** (15 mg) and $[(^{13}CO)_2]$-**2** (15.7 mg) were dissolved in toluene (8 mL) and heated at 57 °C for 24 h. No significant increase in the small amount of the mixed label complex $[(^{12}CO)(^{13}CO)]$-**2** present could be detected. Similar results were obtained in the presence of triphenylphosphine.

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Registry No. **1**, 82135-64-6; **2** (isomer 1), 92937-68-3; **2** (isomer 2), 77906-76-4; **2** $N^{18}O_2$ labeled (isomer 1), 77906-80-0; **2** ^{13}CO labeled (isomer 1), 78222-99-8; **2** $N^{18}O_2$ labeled (isomer 2), 92937-69-4; **2** ^{13}CO labeled (isomer 2), 92937-70-7; $Pd(CH_3CN)_2ClNO_2$, 77933-52-9; (py)$CoTPPNO_2$, 75778-52-8; $Pd(CH_3CN)_2Cl_2$, 14592-56-4; $CoTPP^{15}NO$, 92937-72-9; $(CH_3CN)CoTPPNO_2$, 92937-73-0; $CoTPPNO_2$, 92937-74-1; $(CH_3CN)CoTPP^{15}NO_2$, 92937-75-2; $CoTPP^{15}NO_2$, 92937-76-3; $Ru(PPh_3)_2(CO)_2Cl_2$, 14564-35-3; CoTPPNO, 42034-08-2; CoTPP, 14172-90-8; (py)CoTPPCl, 57384-22-2; (py)$CoTPP^{15}NO_2$, 92937-71-8; $(H_2O)CoTPPCl$, 80420-32-2; $Pd(CH_3CN)_2Cl^{15}NO_2$, 92999-46-7; $[PdCl(NO)]_n$, 92937-67-2; $PPh_3CoTPPNO_2$, 92937-77-4; Pt(diphos)$ClNO_2$, 92937-78-5; $Pt(PPh_3)_2ClNO_2$, 33915-19-4; $Pt(PPh_3)_2Cl_2$, 13965-03-2; $[Ru(CH_3CN)_2(^{13}CO)_2(PPh_3)_2]^+$, 92937-79-6; $Pt(py)(C_2H_4)Cl_2$, 12078-66-9; $PtCl_3(C_2H_4)^-$, 12275-00-2; $CpFe(CO)_2(B)^+$ (B = 1-decene), 92937-80-9; $CpFe(CO)_2(H_2C{=}CHOC_2H_5)^+$, 55337-28-5; $Pt(Me_2NC_2H_4NMe_2)(C_2H_4)Cl^+$, 71639-55-9; $[Pd(py)Cl_2]_2$, 92937-81-0; $KN^{18}O_2$, 34745-31-8; $Ag^{15}NO_2$, 92957-38-5; $K^{15}NO_2$, 92937-66-1; O_2, 7782-44-7; 1-decene, 872-05-9; cycloheptene, 628-92-2; *cis*-cyclooctene, 931-87-3; *trans*-cyclooctene, 931-89-5; norbornene, 498-66-8; bicyclo[2.2.2]octene, 931-64-6; cycloheptene epoxide, 286-45-3; 2-cyclohepten-1-ol, 4096-38-2; 2-cyclohepten-1-one, 1121-66-0; cycloheptanone, 502-42-1; *cis*-cyclooctene epoxide, 4925-71-7; cyclooctanone, 502-49-8; *exo*-norbornene epoxide, 57378-36-6; bicyclo[2.2.2]octene epoxide, 278-84-2.