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Conversion of Coordinated Carbon Monoxide into Carbon Dioxide via Oxygen-Atom Transfer from Coordinated Nitrite: Thermolysis of $Ru(NO_2)_2(CO)_2(PPh_3)_2$

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Abstract: The thermolysis (111 °C, toluene solution) of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ in the presence of excess PPh_3 proceeds according to the stoichiometry $Ru(NO_2)_2(CO)_2(PPh_3)_2 + PPh_3 \rightarrow Ru(NO)_2(PPh_3)_2 + CO_2 + CO + Ph_3PO$. Two highly selective oxygen-atom transfer processes are involved in the overall thermolysis reaction: (i) $Ru(NO_2)_2(CO)_2(PPh_3)_2 \rightarrow Ru(ONO)(CO)(NO)(PPh_3)_2 + CO_2$; (ii) $Ru(ONO)(CO)(NO)(PPh_3)_2 + PPh_3 \rightarrow Ru(NO)_2(PPh_3)_2 + CO + Ph_3PO$. The intermediate complex $Ru(ONO)(CO)(NO)(PPh_3)_2$ was synthesized independently and has been characterized by analytical and spectral methods. The thermolysis of $Ru(N^{18}O_2)_2(CO)_2(PPh_3)_2$ unambiguously establishes coordinated NO_2^- as the source of oxygen in the conversion of coordinated CO into CO_2. Moreover, the extent of ^{18}O enrichment in the CO_2 product indicates that *statistical* scrambling of oxygen occurs between nitrogen and carbon atoms prior to the loss of CO_2. The results of a double-label study involving the thermolysis of $Ru(N^{18}O_2)_2(CO)_2(PPh_3)_2$ and $Ru(NO_2)_2(^{13}CO)_2(PPh_3)_2$ are consistent with an *intermolecular* mechanism for oxygen-atom transfer from NO_2^- to CO. Additional mechanistic implications are discussed.

Introduction

The ability of CO to reduce coordinated NO_2^- to coordinated NO (eq 1) is well documented in the literature.[1-13] Although

$$M(NO_2)L_n + CO \rightarrow M(NO)L_n + CO_2 \tag{1}$$

the *synthetic* aspects of eq 1 have been recognized for some time,[1-17] *mechanistic* details were nonexistent until recently. A frequently invoked[4,6,9] mechanism for this type of reaction is the intramolecular oxygen-atom transfer process shown in Scheme I. Our recent ^{18}O-labeling study[10] of reaction 2 represents the

$$trans\text{-}Ni(NO_2)_2(PEt_3)_2 + CO \rightarrow Ni(NO_2)(NO)(PEt_3)_2 + CO_2 \tag{2}$$

first operational test of this mechanism. This study[10] provided unambiguous experimental confirmation of oxygen-atom transfer from coordinated NO_2^- to coordinated CO in the production of CO_2. However, the oxygen-atom transfer was found to be more complex than the simple *irreversible* process depicted in Scheme I. The observed ^{18}O enrichment of the CO_2 product from eq 2 indicated that significant—but not statistical—oxygen scrambling occurs between nitrogen and carbon atoms prior to the loss of CO_2. Thus, in this system at least, oxygen-atom transfer is appreciably reversible during the lifetime of the intermediate(s) involved. We have proposed[10] a minor modification of Scheme I which is sufficient to provide a mechanism consistent with the ^{18}O labeling results. It should be pointed out that suubsequent kinetic studies[11] of the closely related system in eq 3 are in complete accord with this modified mechanism.

$$Ni(NO_2)_2(dppe) + CO \rightarrow Ni(NO_2)(NO)(dppe) + CO_2 \tag{3}$$

In spite of the detailed studies of reactions 2 and 3, several important mechanistic features regarding the oxygen-atom transfer process have yet to be delineated. First, it was not possible to experimentally rule out an *intermolecular* mechanism for the nickel systems.[10,11] Moreover, it remains to be seen whether the oxygen-atom scrambling observed for eq 2 is a general feature of such reactions. In an effort to simultaneously address both of these essential mechanistic features, we have turned our attention to systems which—unlike the above nickel systems—involve isolable nitrocarbonylmetal complexes, $M(NO_2)(CO)L_n$ (see Scheme I). As shown in Figure 1, a double-label experiment involving two different isotopically labeled $M(NO_2)(CO)L_n$ derivatives would in principle provide a definitive method of distinguishing between intramolecular and intermolecular processes.

For our initial study we have carried out a detailed investigation of the reported[4] thermolysis of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ (eq 4).

$$Ru(NO_2)_2(CO)_2(PPh_3)_2 \xrightarrow{PPh_3} Ru(NO)_2(PPh_3)_2 + CO_2 + CO + Ph_3PO \tag{4}$$

The choice of this system was dictated primarily by the rather limited number[18] of isolable complexes which contain both NO_2^- and CO ligands. We report here a determination of the stoichiometry of this novel reaction and the results of a series of ^{18}O- and ^{13}C-labeling experiments designed to examine the associated oxygen-atom transfer process.

Experimental Section

General Procedures. Unless otherwise specified all operations, including the purification of solvents, were carried out under an atmosphere of dry nitrogen. Schlenk-type apparatus was used for all benchtop re-

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[18] In view of the ease with which oxygen-atom transfer generally occurs in such systems, it is not surprising that NO_2^- and CO are mutually incompatible ligands in all but a few cases. We note in this regard that the corresponding osmium analogue, $Os(NO_2)_2(CO)_2(PPh_3)_2$, has also been briefly mentioned.[4]

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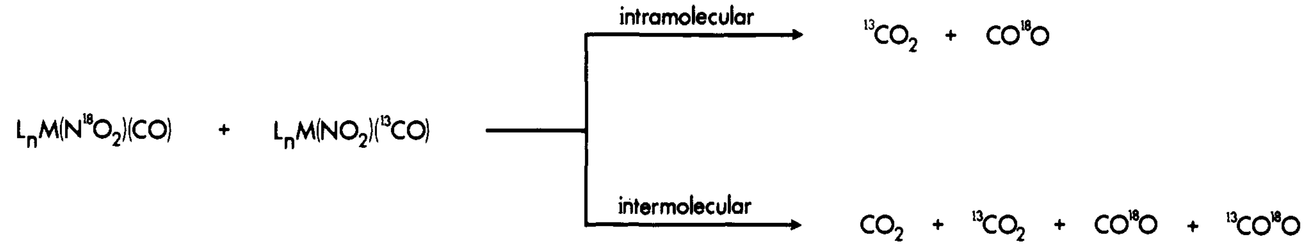
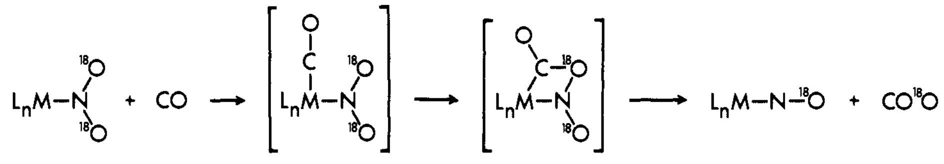


Figure 1. Isotopically labeled CO_2 species resulting from double-label experiment.

Scheme I



actions. Vacuum manipulations were carried out in a conventional glass vacuum line. Samples of $C^{18}O$ were transferred by means of a Toepler pump. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

Materials. All solvents (reagent grade) were dried by appropriate methods and distilled immediately prior to use. The following compounds were purchased from the indicated commercial source and were used without further purification: $RuCl_3 \cdot xH_2O$ (Englehard); $AgPF_6$ (Ozark-Mahoning); Ph_3PO (Aldrich); AgCN, KNO_2, KNO_3 (MCB). Triphenylphosphine (Pressure Chemical Co.) was purified by recrystallization from ether/*n*-heptane. Water enriched in ^{18}O at the nominal level of 1.5% was purchased from YEDA (Rehovoth, Israel). Carbon monoxide enriched in either ^{13}C (94%) or ^{18}O (99%) was purchased from Monsanto Research Corp. and Prochem, respectively.

The complexes $RuCl_2(CO)_2(PPh_3)_2$,[19] $RuCl_2(PPh_3)_3$,[19] and $Ru(OH)(CO)(NO)(PPh_3)_2$[20] were synthesized by literature methods. The method of Samuel and Wasserman[21] was used to prepare $KN^{18}O_2$ by exchange with $H_2{}^{18}O$.

Spectra. Infrared spectra were obtained on a Perkin-Elmer 180 spectrophotometer or a Perkin-Elmer 237 spectrophotometer equipped with a Moseley Model 7101A external recorder. The instruments were calibrated with carbon monoxide and polystyrene. Solution spectra were run in NaCl cells using CH_2Cl_2 as solvent. Mull spectra were recorded in Nujol and hexachlorobutadiene between NaCl plates.

Proton, $^{31}P\{^1H\}$, and ^{13}C NMR spectra were obtained at 90.00, 36.43, and 22.62 MHz, respectively, on a Bruker WH-90DS spectrometer operating in the FT mode. For the $^{31}P\{^1H\}$ measurements a CH_2Cl_2 solution of the sample was placed in a nitrogen-filled 8-mm NMR tube held coaxially in a 10-mm NMR tube. The outer tube contained D_2O which served as an external lock. ^{31}P chemical shifts are referenced to an external sample of 85% H_3PO_4; positive chemical shifts are *downfield* from H_3PO_4.

The ^{13}C NMR spectra were obtained in 10-mm NMR tubes using $CDCl_3$ as solvent. The spectra were referenced internally to the solvent and ^{13}C chemical shifts were converted to the TMS scale by taking the chemical shift of $CDCl_3$ as +77.0 ppm. Positive ^{13}C chemical shifts are *downfield* from TMS.

Preliminary mass spectrometry measurements were carried out on a Hitachi Perkin-Elmer RMU-6 mass spectrometer. Mass spectrometric analysis of ^{18}O- and ^{13}C-enriched CO_2 samples were carried out on a Nuclide Analysis Associates RMS-11 isotope ratio mass spectrometer using the double collector procedure.[22,23]

Preparation of Complexes. a. $RuCl_2(^{13}CO)_2(PPh_3)_2$ was prepared by a modification of the literature method.[19] Solid $RuCl_2(PPh_3)_3$ (4.07 g, 4.24 mmol) was placed in a 50-mL, round-bottomed flask which was equipped with a ball joint and a Teflon valve for vacuum line manipulation. The flask was evacuated and ^{13}CO (~400 Torr) was admitted. Dichloromethane (~15 mL) was added via syringe through a serum cap port on the side of the flask and the flask was brought to ambient pressure by addition of more ^{13}CO. The solution was vigorously stirred for 6–7 h, during which time ^{13}CO was periodically added to maintain ambient pressure. The dark brown solution gradually became lighter as CO uptake continued. The resulting pale yellow solution and white precipitate were transferred to a larger flask and dissolved in additional CH_2Cl_2. This solution was heated for 20 min to convert any remaining *all-trans*-$RuCl_2(^{13}CO)_2(PPh_3)_2$ to the more stable cis isomer.[19,24] Addition of ethanol gave the desired product as a white microcrystalline solid which was recrystallized from CH_2Cl_2/ethanol (yield 3.11 g, 97%): IR (CH_2Cl_2) ν(CO) 2015 (s), 1954 (s) cm^{-1}.

$RuCl_2(^{13}CO)_2(PPh_3)_2$ of lower (~20–25%) ^{13}C enrichment was prepared in the same manner by diluting the ^{13}CO with an appropriate amount of unlabeled CO.

b. $RuCl_2(C^{18}O)_2(PPh_3)_2$ was prepared similarly from $RuCl_2(PPh_3)_3$ and $C^{18}O$: IR (CH_2Cl_2) 2013 (s), 1950 (s) cm^{-1}.

c. $Ru(NO_2)_2(CO)_2(PPh_3)_2$. A solution of $RuCl_2(CO)_2(PPh_3)_2$ (10.2 g, 13.6 mmol) and $AgPF_6$ (6.98 g, 27.6 mmol) in 250 mL of CH_3CN was heated under reflux for 4 h. The resulting suspension was filtered and solvent was removed in vacuo from the filtrate to afford solid $[Ru(CH_3CN)_2(CO)_2(PPh_3)_2](PF_6)_2$.[25] In practice this material was not purified further. Methanol (250 mL) and KNO_2 (3.54 g, 41.6 mmol) were added and the suspension was heated at 50–60 °C for 4 h to give a gray precipitate. Solvent was evaporated in vacuo and the solid residue was extracted with CH_2Cl_2. Addition of methanol to the filtered extracts, followed by concentration in vacuo, gave an off-white solid. Recrystallization from CH_2Cl_2/methanol afforded pure $Ru(NO_2)_2(CO)_2(PPh_3)_2$ as a white microcrystalline solid (8.44 g, 80%). Anal. Calcd for $C_{38}H_{30}O_6N_2P_2Ru$: C, 58.99; H, 3.92; N, 3.62. Found: C, 58.97; H, 4.02; N, 3.52. IR (CH_2Cl_2) ν(CO) 2050 (s), 1992 (s) cm^{-1}; IR (mull) ν(CO) 2054 (w), 2042 (s), 1996 (w), 1983 (s) cm^{-1}; $\nu(NO_2)$ 1406, 1060, 1390, 1310, 820 cm^{-1}; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) 27.3 (singlet), 23.4 (singlet) ppm with relative intensities ~5:1, respectively.

d. $Ru(NO_2)_2(^{13}CO)_2(PPh_3)_2$ was prepared similarly from $RuCl_2(^{13}CO)_2(PPh_3)_2$: IR ($CH_2Cl_2$) ν(CO) 2003 (s), 1949 (s) cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$) 26.0 (triplet, J_{PC} = 10.9 Hz), 21.6 (triplet, J_{PC} = 10.6 Hz) ppm with relative intensities ~5:1, respectively; ^{13}C NMR ($CDCl_3$) 198.6 (triplet, J_{PC} = 10.9 Hz), 195.6 (triplet, J_{PC} = 10.6 Hz), 195.3 (triplet, J_{PC} = 10.6 Hz) ppm with relative intensities ~32:1:1, respectively.

e. $Ru(NO_2)_2(C^{18}O)_2(PPh_3)_2$ was prepared similarly from $RuCl_2(C^{18}O)_2(PPh_3)_2$: IR ($CH_2Cl_2$) ν(CO) 2004 (s), 1948 (s) cm^{-1}.

f. $Ru(N^{18}O_2)_2(CO)_2(PPh_3)_2$ was prepared similarly from $RuCl_2(CO)_2(PPh_3)_2$ and $KN^{18}O_2$.

g. $Ru(NO_3)_2(CO)_2(PPh_3)_2$. Treatment of $RuCl_2(CO)_2(PPh_3)_2$ (2.03 g, 2.70 mmol) with $AgPF_6$ (1.38 g, 5.45 mmol) and KNO_3 (0.630 g, 6.23 mmol) by a similar method afforded the product as a white microcrystalline solid (1.88 g, 87%): IR (CH_2Cl_2) ν(CO) 2067 (s), 2010 (s) cm^{-1} [lit.[26] (Nujol) 2068 (s), 2012 (s) cm^{-1}]; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) 26.5 (singlet) ppm [lit.[26] ($CDCl_3$) 27.2 (singlet) ppm].

h. $Ru(ONO)(CO)(NO)(PPh_3)_2 \cdot 0.5CH_2Cl_2$. A solution of KNO_2 (1.39 g, 16.4 mmol) in 10 mL of aqueous ethanol was added to a solution of $Ru(OH)(CO)(NO)(PPh_3)_2$ (3.39 g, 4.85 mmol) in 40 mL of CH_2Cl_2. The resulting yellow-brown mixture was stirred at room temperature for 30 min and solvent was removed in vacuo. The solid residue was extracted with CH_2Cl_2 and ethanol was added to the filtered solution. Concentration in a nitrogen stream afforded yellow-brown crystals which

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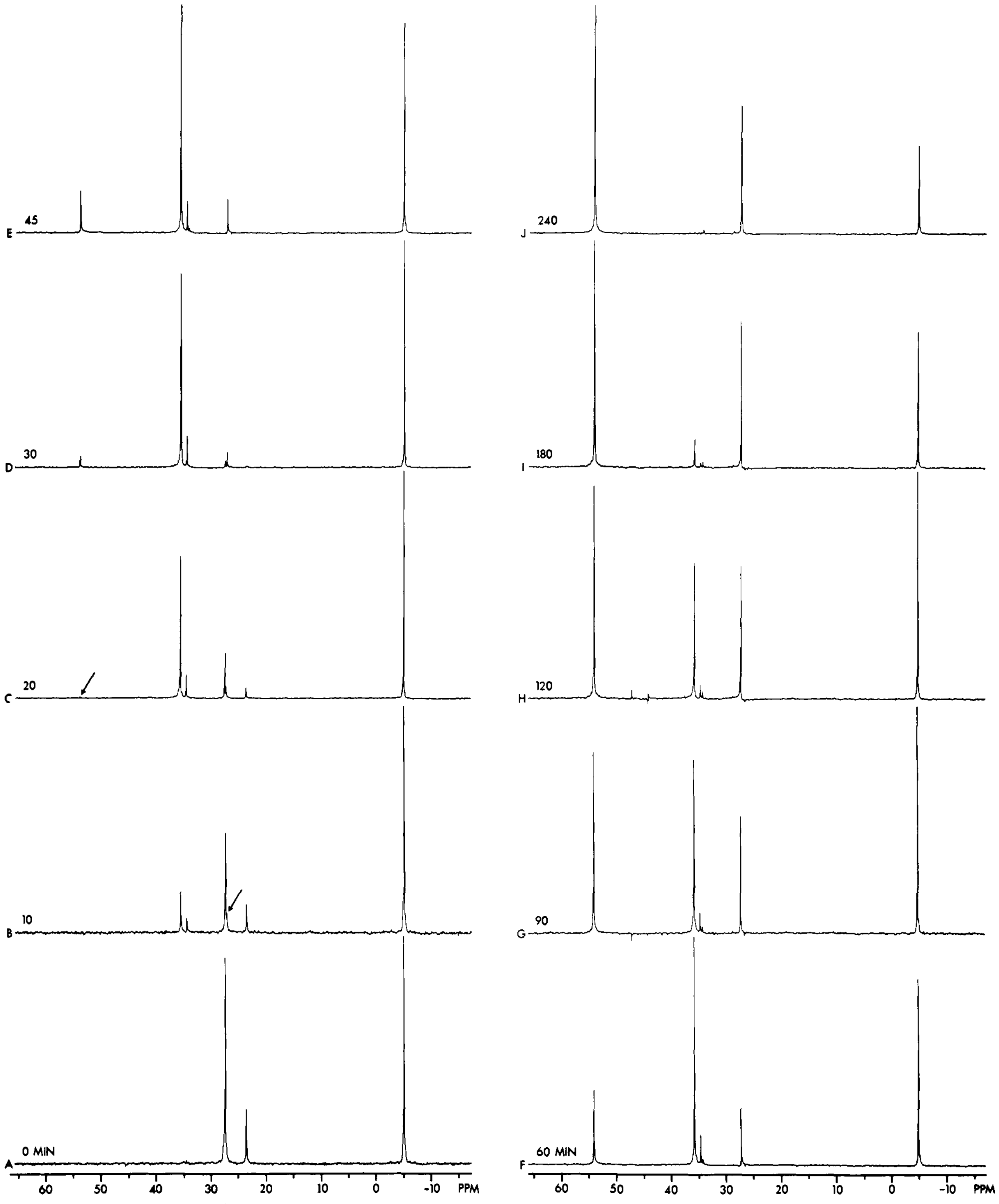

Figure 2. Selected time-dependent $^{31}P\{^1H\}$ NMR spectra of the thermolysis of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ in the presence of PPh_3 (111 °C, toluene solution). Arrows denote the partially obscured resonances due to Ph_3PO (spectrum B) and $Ru(NO)_2(PPh_3)_2$ (spectrum C); see text.

turned olive green after washing with hexane (yield 2.86 g, 76%). Anal. Calcd for $C_{37.5}H_{31}O_4N_2P_2ClRu$: C, 58.33; H, 4.05; N, 3.63; P, 8.02; Cl, 4.59. Found: C, 57.99; H, 4.21; N, 3.42; P 8.08; Cl, 4.72. IR (CH_2Cl_2) $\nu(CO)$ 1935 (s) cm^{-1}; $\nu(NO)$ 1572 cm^{-1}; IR (mull) $\nu(NO_2)$ 1311, 1072 cm^{-1}; ^1H NMR ($CDCl_3$) τ 7.39 (C_6H_5, complex multiplet), 5.29 (CH_2Cl_2, single) with relative intensities 30:1, respectively; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) 35.6 (singlet) ppm.

i. **$Ru(^{18}ON^{18}O)(CO)(NO)(PPh_3)_2 \cdot 0.5CH_2Cl_2$** was prepared similarly from $Ru(OH)(CO)(NO)(PPh_3)_2$ and $KN^{18}O_2$.

Thermolysis of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ in the Presence of PPh_3. General Considerations. In a typical experiment, a solution of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ (0.958 g, 1.24 mmol) and PPh_3 (0.436 g, 1.66 mmol), in 100 mL of toluene was heated under reflux for 4 h. Solvent was removed in vacuo from the intense red-orange solution. Crystallization of the residue from CH_2Cl_2/ethanol afforded $Ru(NO)_2(PPh_3)_2$ as a brick red crystalline solid (0.802 g, 95%): IR (CH_2Cl_2) $\nu(NO)$ 1667 (s), 1619 (s) cm^{-1} [lit.[4] (Nujol) $\nu(NO)$ 1665 (s), 1619 (vs) cm^{-1}].

^{31}P NMR Studies. a. Thermolysis of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ in the Presence of PPh_2. Time Study. A solution of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ (1.54 g, 2.00 mmol) and PPh_3 (0.816 g, 3.12 mmol) in 150 mL of toluene was heated under reflux. Aliquots (10 mL) were withdrawn at suitable time intervals, evaporated in vacuo, and redissolved in 2 mL of CH_2Cl_2 for ^{31}P NMR analysis. A series of representative $^{31}P\{^1H\}$ NMR spectra is shown in Figure 2. The reaction was observed to be complete after

~4 h, at which time the ^{31}P NMR spectrum showed three major resonances attributable to Ru(NO)$_2$(PPh$_3$)$_2$, Ph$_3$PO, and unreacted PPh$_3$.

A similar experiment was carried out at 85 ± 2 °C in order to more closely examine the early stages of the reaction. The ^{31}P {^{1}H} NMR spectra showed the same features observed in the previous study.

b. Thermolysis of Ru(NO$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$ in the Presence of PPh$_3$. Product Analysis. In a typical experiment, a solution of Ru(NO$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$ (~100 mg) and a weighed amount of PPh$_3$ (1-4 equiv) in 20 mL of toluene was heated under reflux for 11 h to ensure complete reaction. Solvent was removed in vacuo from the homogeneous red-orange solution. The solid residue was dissolved in CH$_2$Cl$_2$ and the resulting solution was transferred to a 8-mm NMR tube for ^{31}P {^{1}H} NMR measurements. The relative amounts of Ru(NO)$_2$(PPh$_3$)$_2$ and Ph$_3$PO were determined by integration of the appropriate peaks. A constant set of instrumental parameters was maintained for all integration measurements. Identical analysis of a series of standard Ru(NO)$_2$(PPh$_3$)$_2$/Ph$_3$PO solutions established the validity of this method for the concentration range studied. The mean value of the Ru(NO)$_2$(PPh$_3$)$_2$/Ph$_3$PO molar ratio was 1.07 ± 0.13 for seven different reactions.

Reactions carried out in the presence of *less than* 1 mol of free PPh$_3$/mol of Ru(NO$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$ led to *substantial* decomposition during the 11-h reflux period. Although Ru(NO)$_2$(PPh$_3$)$_2$ and Ph$_3$PO were still the only products detected by ^{31}P NMR spectroscopy, their relative amounts were quite altered from above.

c. Thermolysis of Ru(ONO)(CO)(NO)(PPh$_3$)$_2$ in the Presence of PPh$_3$. Product Analysis. The reaction of Ru(ONO)(CO)(NO)(PPh$_3$)$_2$·0.5CH$_2$Cl$_2$ and PPh$_3$ (1-4 equiv) was examined in a similar manner. The mean value of the Ru(NO)$_2$(PPh$_3$)$_2$/Ph$_3$PO molar ratio was 1.06 ± 0.08.

Mass Spectrometry Data Treatment. a. Single-Label Studies. The following symbols are used in this paper.

$^{46}E_X$ is a measure of the ^{18}O enrichment in the species X relative to a normal sample of species X. $^{46}E_X$ is determined experimentally from the (mass 46)/(mass 44 + mass 45 + mass 47) ratio ($^{46}R_X$) for an ^{18}O-enriched CO$_2$ sample derived from species X compared to that ($^{46}R_{\text{standard}}$) for a standard CO$_2$ sample of natural isotopic abundance. Thus,

$$^{46}E_X = {}^{46}R_X/{}^{46}R_{\text{standard}}$$

For a substance X of natural isotopic abundance, $^{46}E_X = 1.000$.

n_t represents the number of oxygen atoms per CO$_2$ molecule which derive from the nitrite ligands in Ru(N^{18}O$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$. Values of n_t can be calculated from the relationship

$$n_t = \left[\frac{^{46}E_{CO_2} - {}^{46}E_{CO}}{^{46}E_{NO_2^-} - {}^{46}E_{CO}}\right](2.00)$$

where $^{46}E_{CO_2}$ is the ^{18}O enrichment of the CO$_2$ produced from Ru(N^{18}O$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$ and $^{46}E_{CO}$ and $^{46}E_{NO_2^-}$ are the ^{18}O enrichments of the carbonyl and nitrite groups, respectively, in Ru(N^{18}O$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$.

b. Double-Label Studies. The quantities $^{46}E_X$ and $^{46}R_X$ are defined as before. By analogy with the single-label case, $^{47}R_X$ is defined as the experimentally measured (mass 47)/(mass 44 + mass 45 + mass 46) ratio for an ^{18}O/^{13}C-enriched CO$_2$ sample derived from species X. $^{47}R_{\text{standard}}$ is the corresponding ratio for a standard CO$_2$ sample of natural isotopic abundance. $^{47}E_X$ is defined by

$$^{47}E_X = {}^{47}R_X/{}^{47}R_{\text{standard}}$$

and is thus related to the ^{18}O/^{13}C enrichment in the species X relative to a normal sample of species X.

For all label studies, the amount of ^{17}O present was assumed to be negligible and isotope effects were considered to be unimportant.

Determination of ^{18}O and ^{13}C Enrichment. The ^{18}O enrichment of KN^{18}O$_2$ and Ru(N^{18}O$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$ was determined by mass spectrometry after conversion of the oxygen in the samples to CO$_2$ with AgCN according to the method of Shakhashiri and Gordon.[27] The ^{18}O enrichment of the CO$_2$ produced is taken as identical with that of the parent compound. The mean value of $^{46}E_{\text{complex}}$ for Ru(N^{18}O$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$ was 4.913 ± 0.012 for three determinations. The mean value of $^{46}E_{KNO_2}$ for the KN^{18}O$_2$ used to prepare the complex was 6.694 ± 0.064 for three determinations. The precision of both sets of measurements lies within the expected uncertainty associated with the AgCN method.[27] The experimental value of $^{46}E_{\text{complex}}$ for Ru(N^{18}O$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$ is in acceptable agreement with the value (4.796 ± 0.065) calculated from the measured value of $^{46}E_{KNO_2}$. In view of this agreement, $^{46}E_{\text{complex}}$ for Ru(^{18}ON^{18}O)(CO)(NO)(PPh$_3$)$_2$ was calculated from $^{46}E_{KNO_2}$ rather than measured directly.

Single-label studies indicated that the oxygen atoms in Ru(NO$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$ are statistically scrambled during the production of CO$_2$ (see Results and Discussion). Thus, values of ^{46}E and ^{47}E for Ru(NO$_2$)$_2$(^{13}CO)$_2$(PPh$_3$)$_2$ and ^{47}E for Ru(N^{18}O$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$ were obtained by mass spectrometry of the CO$_2$ produced in the thermolysis of the individual complexes. That is, no AgCN degradation was necessary. The ^{18}O and ^{13}C enrichments of both complexes were calculated from the values of ^{46}E and ^{47}E by solving the simultaneous equations which result from the definitions of ^{46}E and ^{47}E and consideration of the isotopically labeled species present (see Supplementary Material).

Vacuum Line and Labeling Studies. a. Thermolysis of Ru(NO$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$ in the Presence of PPh$_3$. In a typical experiment, Ru(NO$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$ (300 mg, 0.388 mmol) and PPh$_3$ (150 mg, 0.572 mmol) were placed in a 100-mL, round-bottomed flask. The flask was sealed by means of an O-ring joint to a Dewar condenser which was attached to a vacuum line. The entire apparatus was evacuated to <10^{-5} Torr for at least 12 h, and toluene (~35 mL), previously degassed by several freeze-pump-thaw cycles, was introduced by vacuum distillation. The apparatus was isolated from the vacuum line and nitrogen (~600 Torr) was admitted. Dry ice was added to the Dewar condenser and the toluene solution was heated under reflux for ~4 h. Volatile material was condensed in a trap cooled at -196 °C, purified by a series of trap to trap distillations, and transferred to an evacuated storage tube for mass spectrometric analysis.

Preliminary studies were carried out with unenriched Ru(NO$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$. Mass spectrometric analysis established CO$_2$ as the only condensable volatile product of the reaction. Pressure-volume measurements indicated that ~1 mol of CO$_2$ was produced per mole of Ru(NO$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$ reacted. Qualitative measurement of the pressure changes in the reaction system indicated that a noncondensable gas (presumably CO) was also produced.

Studies involving ^{18}O-labeled complex were carried out similarly except that mass spectrometric measurements were performed only on the RMS-11 instrument. For double-label experiments, samples of Ru(N^{18}O$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$, Ru(NO$_2$)$_2$(^{13}CO)$_2$(PPh$_3$)$_2$, and PPh$_3$ were weighed directly into the reaction flask. Alternatively, a homogeneous mixture of the ^{18}O- and ^{13}C-labeled complexes was prepared by recrystallization. A portion of this mixture and the PPh$_3$ sample were weighed directly into the reaction flask. In either case, the remainder of the procedure was identical with that described above.

b. Thermolysis of Ru(ONO)(CO)(NO)(PPh$_3$)$_2$ in the Presence of PPh$_3$. In a similar experiment, a solution of Ru(ONO)(CO)(NO)(PPh$_3$)$_2$·0.5CH$_2$Cl$_2$ (276 mg, 0.358 mmol) and PPh$_3$ (249 mg, 0.950 mmol) in ~35 mL of toluene was heated under reflux for ~4 h. The solution was thoroughly degassed by several freeze-pump-thaw cycles and condensable material was retained in a trap cooled at -196 °C. This material was shown to be CO$_2$ by mass spectrometry of the purified sample. The amount of CO$_2$ produced, as measured by standard pressure-volume techniques, was 0.034 mmol.

c. Reversibility Studies. Two studies of this type were carried out. In the first experiment, a solution of Ru(N^{18}O$_2$)(CO)(NO)(PPh$_3$)$_2$·0.5CH$_2$Cl$_2$ (209 mg, 0.271 mmol) and PPh$_3$ (108 mg, 0.412 mmol) in ~35 mL of toluene was prepared as in part a. The solution was frozen at -196 °C and unenriched CO$_2$ (0.258 mmol) was condensed into the reaction vessel. Subsequent operations followed the procedure outlined in part a except that CO$_2$ was *not* trapped during the 4-h reflux period. The solution was cooled and CO$_2$ was trapped, purified, and transferred to a storage tube for mass spectrometric analysis ($^{46}E_{CO_2} = 1.266$).

In the second experiment, the unenriched CO$_2$ was generated in situ by thermolysis of Ru(NO$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$. Samples of Ru(N^{18}O$_2$)(CO)(NO)(PPh$_3$)$_2$·0.5CH$_2$Cl$_2$ (212 mg, 0.275 mmol), PPh$_3$ (212 mg, 0.809 mmol), and Ru(NO$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$ (202 mg, 0.261 mmol) were placed in the reaction vessel described above. All subsequent operations were carried out according to the procedure in part a. Mass spectrometric analysis of the recovered purified CO$_2$ sample showed $^{46}E_{CO_2} = 1.345$.

d. Investigation of the Role of Free NO$_2^-$. Samples of Ru(NO$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$ (322 mg, 0.416 mmol), PPh$_3$ (164 mg, 0.626 mmol), and KN^{18}O$_2$ (62 mg, 0.73 mmol) were placed in the reaction vessel described above. The remainder of the experimental procedure was identical with that in part a. Mass spectrometric analysis of the purified CO$_2$ sample showed no incorporation of ^{18}O ($^{46}E_{CO_2} = 0.994$).

Results and Discussion

Preparation and Structure of Ru(NO$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$. It is not clear in the very brief original report[4] of Ru(NO$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$ whether the complex was actually isolated and characterized. While exploring alternative synthetic routes to this complex, we found that Ru(NO$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$ could be readily prepared in

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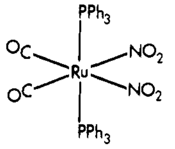
(27) Shakhashiri, B. Z.; Gordon, G. *Talanta* **1966**, *13*, 142.

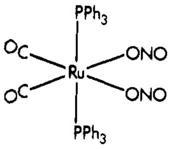
80% yield by a two-step process. Reaction of $RuCl_2(CO)_2(PPh_3)_2$ with $AgPF_6$ in acetonitrile afforded $[Ru(CH_3CN)_2(CO)_2(PPh_3)_2](PF_6)_2$, which in turn was converted to the desired product upon reaction with KNO_2 in methanol.

The Nujol mull infrared spectrum of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ in the ν(CO) region showed two strong bands at 2042 and 1983 cm^{-1} and two weak bands at 2054 and 1996 cm^{-1}. The latter are not resolvable in solution and the infrared spectrum in CH_2Cl_2 exhibited only two strong bands at 2050 and 1992 cm^{-1}. The ^{31}P {^{1}H} NMR spectrum of the complex consists of two singlets at 27.3 and 23.4 ppm (CH_2Cl_2) having relative intensities ~5:1, respectively. Since the infrared and ^{31}P NMR spectra were unaltered by repeated crystallization of the sample, it is apparent that two isomers of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ are present. Clearly, a large number of isomers are possible in principle when both geometrical isomerism and linkage isomerism involving the nitrite ligand are taken into account. In order to identify the major and minor isomers a sample of ^{13}C-enriched $Ru(NO_2)_2(^{13}CO)_2(PPh_3)_2$ was prepared from 94% ^{13}CO. The ^{31}P {^{1}H} resonances at 26.0 and 21.6 ppm ($CDCl_3$) were observed as triplets with ^{31}P–^{13}C coupling constants of 10.9 and 10.6 Hz, respectively. Satellites due to the species (~10% abundance) containing a single ^{13}CO group, i.e., $Ru(NO_2)_2(^{12}CO)(^{13}CO)(PPh_3)_2$, were also observed. The ^{13}C NMR spectrum of the enriched complex exhibited an intense triplet (J_{PC} = 10.9 Hz) at 198.6 ppm and an overlapping pair of weak triplets at 195.6 (J_{PC} = 10.6 Hz) and 195.3 (J_{PC} = 10.6 Hz) ppm having equal intensity.

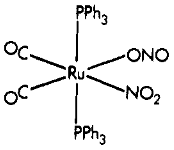
The ^{31}P and ^{13}C NMR results indicate that the major isomer contains magnetically equivalent pairs of PPh_3 and CO groups. In addition, the observation of two strong ν(CO) bands in the infrared spectrum of this isomer reveals that the two CO groups adopt a mutual cis arrangement. Only two structures (**1** and **2**) are compatible with these spectroscopic data. A tentative distinction between these structural alternatives can be made from ^{31}P NMR spectroscopy. The ^{31}P chemical shift (27.3 ppm) of the major isomer of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ is quite similar to that (26.5 ppm) observed under identical conditions for the isostructural *nitrate* complex $Ru(NO_3)_2(CO)_2(PPh_3)_2$, in which the anionic ligands are required to be O-bonded.[28] On this basis we favor structure **2** for the major isomer.



1



2



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Similarly, the ^{31}P and ^{31}C NMR and ν(CO) infrared data indicate that the minor isomer of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ contains a pair of magnetically equivalent PPh_3 ligands and two nonequivalent, mutually cis CO groups. Structure **3**, which contains both N-bonded and O-bonded nitrite ligands, is the only isomer consistent with the spectral data. The presence of linkage isomerism in the isomeric mixture of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ is also suggested by infrared bands characteristic[29] of both O-bonded (1406, 1060 cm^{-1}) and N-bonded (1390, 1310 cm^{-1}) nitrite ligands. The weaker intensity of the latter pair of bands is consistent with our formulation of the isomeric mixture.

Thermolysis of $Ru(NO_2)_2(CO)_2(PPh_3)_2$. Products and Stoichiometry.[30] As reported by Roper and co-workers[4] the thermolysis of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ in the presence of PPh_3 affords excellent yields of $Ru(NO)_2(PPh_3)_2$ (eq 4). Our studies of this reaction were carried out in refluxing (111 °C) toluene, a more innocent solvent than the previously[4] used dimethylformamide. Under these conditions the reaction proceeded quite readily to completion in ~4 h, and virtually quantitative yields of $Ru(NO)_2(PPh_3)_2$ were obtained. Reaction progress can be followed by the series of color changes which accompanies the reaction. Thus, the originally colorless solution sequentially turned yellow-green, dark-green, and orange during the first 45 min of heating. Eventually, the solution became the characteristic intense red-orange color of $Ru(NO)_2(PPh_3)_2$. The ^{31}P {^{1}H} NMR spectrum of the final reaction mixture exhibited three singlets at 54.0, 27.1, and −5.50 ppm which are assigned, respectively to $Ru(NO)_2(PPh_3)_2$, Ph_3PO, and unreacted PPh_3 by comparison with authentic samples. The infrared spectrum of this solution in the ν(CO) and ν(NO) regions showed only two strong ν(NO) bands at 1667 and 1619 cm^{-1}, in excellent agreement with the literature[4,31] values for $Ru(NO)_2(PPh_3)_2$.

Mass spectrometric analysis of the purified volatile material produced and trapped during the reaction showed CO_2 as the only detectable product. Conventional pressure–volume measurements established that ~1 mol of CO_2 was produced per mole of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ reacted. Evidence for the production of a noncondensable gas (presumably CO) was also noted qualitatively, but the amount of this product was not measured.

Infrared analysis of the solution during the early stages of the reaction indicated the presence of an intermediate species having a single ν(CO) band at 1935 cm^{-1} and a single ν(NO) band at 1572 cm^{-1}. A logical formulation of this intermediate would be the five-coordinate complex $Ru(ONO)(CO)(NO)(PPh_3)_2$—or its linkage isomer $Ru(NO_2)(CO)(NO)(PPh_3)_2$—since it would derive from $Ru(NO_2)_2(CO)_2(PPh_3)_2$ by oxygen-atom transfer and subsequent loss of CO_2. This assumption was indeed confirmed by independent synthesis and characterization of the intermediate.[32] Reaction of the labile hydroxo complex[20] $Ru(OH)(CO)(NO)(PPh_3)_2$ with KNO_2 in a mixture of dichloromethane and aqueous ethanol afforded the proposed intermediate as an olive-green crystalline dichloromethane solvate, $Ru(ONO)(CO)(NO)(PPh_3)_2 \cdot 0.5CH_2Cl_2$. Yields (76%) are comparable with those obtained previously[20] in the preparation of related $RuX(CO)(NO)(PPh_3)_2$ derivatives from $Ru(OH)(CO)(NO)(PPh_3)_2$.

Both elemental analysis and ^{1}H NMR spectroscopy confirmed the indicated solvate formulation. The infrared spectrum of $Ru(ONO)(CO)(NO)(PPh_3)_2$ showed ν(CO) (1935 cm^{-1}) and ν(NO) (1572 cm^{-1}) bands identical with those observed for the reaction intermediate in the thermolysis of $Ru(NO_2)_2(CO)_2(PPh_3)_2$. An infrared band at 1072 cm^{-1} is consistent[29] with the presence of O-bonded nitrite in the complex. The ^{31}P {^{1}H} NMR spectrum exhibited a singlet at 35.6 ppm.

The thermolysis of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ was also monitored as a function of time by ^{31}P NMR spectroscopy. A series of representative ^{31}P {^{1}H} NMR spectra is reproduced in Figure 2. Spectrum A is that of the intial solution of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ (isomer **2**, 27.4 ppm; isomer **3**, 23.4 ppm) and PPh_3 (−5.50 ppm) prior to heating. After 10 min of heating (spectrum B), a pair of resonances attributable to $Ru(ONO)(CO)(NO)(PPh_3)_2$ and a second intermediate are seen at 35.6 and 34.5 ppm, respectively. A weak resonance due to Ph_3PO (27.1 ppm) appears as a high-field shoulder on the resonance of isomer **2**. Interestingly, no resonance attributable to $Ru(NO)_2(PPh_3)_2$ is detected at this point. Spectrum C indicates that $Ru(ONO)(CO)(NO)(PPh_3)_2$ is the predominant complex in solution after 20 min of heating.

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[28] In $CDCl_3$ solution the ^{31}P chemical shifts of the major isomer of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ and $Ru(NO_3)_2(CO)_2(PPh_3)_2$ are +26.0 and +27.2[26] ppm, respectively.

[29] (a) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1978; pp 220–225. (b) Assignment of infrared bands involving nitrite ligands was aided by comparing spectra of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ with spectra of the corresponding *chloride* $RuCl_2(CO)_2(PPh_3)_2$. The reported bands are the *only* bands which could be attributed with certainty to O-bonded or N-bonded nitrite ligands. All other bands in the infrared spectrum (1600–800 cm^{-1}) of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ are also common to the infrared spectrum of $RuCl_2(CO)_2(PPh_3)_2$.

[30] Unless otherwise stated, the single formula $Ru(NO_2)_2(CO)_2(PPh_3)_2$ is used for simplicity to refer to the isomeric mixture of $Ru(ONO)_2(CO)_2(PPh_3)_2$ (**2**) and $Ru(ONO)(NO_2)(CO)_2(PPh_3)_2$ (**3**).

[31] Levison, J. J.; Robinson, S. D. *J. Chem. Soc. A* **1970**, 2947.

[32] We have also isolated $Ru(ONO)(CO)(NO)(PPh_3)_2$ directly from solution during the initial stages of the thermolysis reaction. In view of the complexity of the thermolysis reaction (see text and Figure 2), this direct method does not represent the optimum synthesis of $Ru(ONO)(CO)(NO)(PPh_3)_2$.

A very weak resonance due to $Ru(NO)_2(PPh_3)_2$ (54.0 ppm) is barely discernible. After 30 min (spectrum D) the areas of the $Ru(NO)_2(PPh_3)_2$ and Ph_3PO resonances are approximately equal, and the resonances due to $Ru(NO_2)_2(CO)_2(PPh_3)_2$ have practically disappeared.

Spectrum E shows that the conversion of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ into intermediates is complete within 45 min. Moreover, the areas of the $Ru(NO)_2(PPh_3)_2$ and Ph_3PO resonances have attained a 2:1 ratio that remains constant throughout the rest of the reaction. Subsequent spectra (F–J) illustrate the gradual conversion of the two intermediates into $Ru(NO)_2(PPh_3)_2$ and Ph_3PO, a process that is complete after ~4 h total reaction time (spectrum J). Note that $Ru(ONO)(CO)(NO)(PPh_3)_2$ remains as the major complex in solution until the reaction time exceeds 90 min (spectra G and H). One extra very weak resonance is detected at 34.1 ppm in the final spectrum. The origin of this minor resonance, whose appearance is first noted after 45 min (spectrum E), is unknown at present.

A number of additional features regarding reaction 1 are apparent from this ^{31}P NMR study. These features and their implications may be summarized as follows.

(1) The existence of *two* intermediates is clearly indicated by the growth and subsequent disappearance of resonances at 35.6 and 34.5 ppm. Although the more intense resonance (35.6 ppm) can be unambiguously assigned to $Ru(ONO)(CO)(NO)(PPh_3)_2$, assignment of the other resonance is more tenuous. It is possible that the second intermediate is the N-bonded linkage isomer of $Ru(ONO)(CO)(NO)(PPh_3)_2$. The ^{31}P NMR data are not inconsistent with this contention since the ^{31}P chemical shift of $Ru(NO_2)(CO)(NO)(PPh_3)_2$ might be expected to occur *upfield* of that in $Ru(ONO)(CO)(NO)(PPh_3)_2$ in view of the trend noted for **2** and **3**. Further support for this contention comes from the observation that the 34.5-ppm resonance was also detected during the thermolysis of $Ru(ONO)(CO)(NO)(PPh_3)_2$ and PPh_3 under identical conditions. Thus, the second intermediate—whatever its nature—is derivable from $Ru(ONO)(CO)(NO)(PPh_3)_2$.

(2) The resonances due to $Ru(NO)_2(PPh_3)_2$ (54.0 ppm) and Ph_3PO (27.1 ppm) grow in simultaneously, except initially when a small amount of Ph_3PO is detectable prior to the appearance of $Ru(NO)_2(PPh_3)_2$. The most obvious conclusion to be drawn from this observation is that there are two different processes which give rise to Ph_3PO. The major process thus appears to be linked to the formation of $Ru(NO)_2(PPh_3)_2$. In contrast, the second process leading to Ph_3PO is not directly related to the production of $Ru(NO)_2(PPh_3)_2$ and occurs to a much lesser extent. A logical conclusion is that this second process is related to the formation of the intermediates.

(3) The resonances attributable to intermediates (35.6, 34.5 ppm) grow in at a faster rate than does the resonance due to Ph_3PO (27.1 ppm). This further suggests that the intermediate complexes and most of the Ph_3PO are formed by independent processes.

(4) The conversion of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ into intermediates is necessarily a faster process than the subsequent conversion of intermediates into the ultimate products $Ru(NO)_2(PPh_3)_2$ and Ph_3PO. Note that under the conditions used the former process requires only ~45 min of the total ~4-h reaction time.

(5) The **2**/**3** isomer ratio remains essentially unaltered, within experimental error, as $Ru(NO_2)_2(CO)_2(PPh_3)_2$ is converted into intermediates.[33] This observation suggests that the rate of any linkage isomerization process involving **2** and **3** must be comparable to (or greater than) the rate of conversion of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ into intermediates.

(6) Such is clearly *not* the case for the two intermediates since the relative amounts of these species undergo considerable change as the reaction proceeds. The area ratio increases steadily from ~3:1 (spectrum B) to ~11:1 (spectrum E) during the first 45 min of the reaction. This ratio remains essentially constant at ~11:1 over the next 75 min (spectra F–H) but decreases to ~7:1 during the subsequent 1-h period (spectrum I) prior to complete conversion of intermediates into products. The implications of these observations are unclear, and extensive speculation is probably unwarranted in the absence of detailed kinetic studies.

An additional ^{31}P NMR study was carried out to determine the stoichiometry of reaction 4 with respect to the phosphorus-containing reactants and products. In a series of seven experiments the $PPh_3/Ru(NO_2)_2(CO)_2(PPh_3)_2$ molar ratio was systematically varied over the range from 1:1 to 4:1 and the thermolysis reactions were effected as before. The seven solutions were analyzed for the relative amounts of $Ru(NO)_2(PPh_3)_2$ and Ph_3PO by integration of the appropriate ^{31}P resonances. Within experimental error, these products were observed to be formed in *equal* amounts ($Ru(NO)_2(PPh_3)_2/Ph_3PO$ molar ratio = 1.07 ± 0.13), independent of the quantity of free PPh_3 used in the reaction.

Similar experiments carried out in the presence of *less than* 1 mol of PPh_3/mol of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ also showed $Ru(NO)_2(PPh_3)_2$ and Ph_3PO as the only products detectable by ^{31}P NMR spectroscopy. However, these reactions were accompanied by *substantial* decomposition as evidenced by the formation of dark-brown insoluble residue and metallic ruthenium, in contrast to the red-orange *homogeneous* solutions observed in the presence of at least 1 equiv of PPh_3. Moreover, the relative amounts of $Ru(NO)_2(PPh_3)_2$ and Ph_3PO formed under these conditions were greatly dependent on the quantity of free PPh_3 used. For example, the $Ru(NO)_2(PPh_3)_2/Ph_3PO$ molar ratio was 0.78 when 0.60 mol of PPh_3 was used per mole of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ whereas this ratio decreased to 0.27 in the absence of free PPh_3.

It is clear from the above ^{31}P NMR studies that *at least* 1 equiv of PPh_3 is necessary for the thermolysis of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ to proceed cleanly. Furthermore, our combined results indicate that under these conditions the overall stoichiometry reaction 4 is correctly described by eq 5. The identification of $Ru(ONO)(CO)(NO)(PPh_3)_2$ as the predominant intermediate in this reaction necessarily requires that eq 5 take place in a stepwise fashion. Two of the more likely alternatives are shown in eq 6 and 7.[34]

$$Ru(NO_2)_2(CO)_2(PPh_3)_2 + PPh_3 \rightarrow Ru(NO)_2(PPh_3)_2 + CO_2 + CO + Ph_3PO \tag{5}$$

$$Ru(NO_2)_2(CO)_2(PPh_3)_2 \rightarrow Ru(ONO)(CO)(NO)(PPh_3)_2 + CO_2 \tag{6a}$$

$$Ru(ONO)(CO)(NO)(PPh_3)_2 + PPh_3 \rightarrow Ru(NO)_2(PPh_3)_2 + Ph_3PO + CO \tag{6b}$$

$$Ru(NO_2)_2(CO)_2(PPh_3)_2 + PPh_3 \rightarrow Ru(ONO)(CO)(NO)(PPh_3)_2 + Ph_3PO + CO \tag{7a}$$

$$Ru(ONO)(CO)(NO)(PPh_3)_2 \rightarrow Ru(NO)_2(PPh_3)_2 + CO_2 \tag{7b}$$

In order to experimentally distinguish between these two (or other) alternatives, the thermolysis of $Ru(ONO)(CO)(NO)(PPh_3)_2$ was studied under conditions identical with those used for eq 5. In the presence of 1–4 equiv of PPh_3 such reactions proceeded cleanly to yield equimolar amounts ($Ru(NO)_2(PPh_3)_2/Ph_3PO$ molar ratio = 1.06 ± 0.08) of $Ru(NO)_2(PPh_3)_2$ and Ph_3PO as determined by ^{31}P NMR spectroscopy. Vacuum line measurements indicated that ~0.1 mol of CO_2 (identified by mass spectrometry) was produced per mole of $Ru(ONO)(CO)(NO)(PPh_3)_2$ reacted. Qualitative evidence for the formation of a noncondensable gas (presumably CO) was also obtained.

Since Ph_3PO and CO_2 are *both* observed as products in the thermolysis of $Ru(ONO)(CO)(NO)(PPh_3)_2$, it is apparent that neither of the competitive processes given in reactions 6 and 7 by itself represents the *exclusive* pathway for eq 5. However, the

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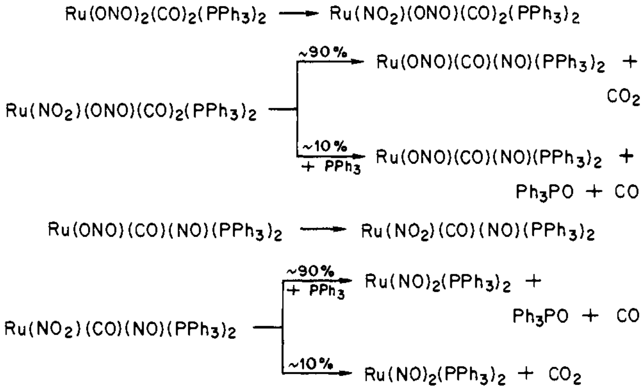
(33) A similar result was observed when the reaction was carried out at 85 ± 2 °C in order to more closely examine the early stages of the reaction. Under these conditions the **2**/**3** isomer ratio was unchanged, within experimental error, during the ~6.5-h period required for complete conversion of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ into intermediates.

(34) For simplicity, only the major observed intermediate, $Ru(ONO)(CO)(NO)(PPh_3)_2$, is indicated in eq 6 and 7.

Scheme II



amount of CO_2 produced is such that reaction 7 can account for only ~10% of the total reaction. This is consistent with the ^{31}P NMR study of reaction 5 (Figure 2) in which appreciable amounts of Ph_3PO were *not* detected *prior to* the formation of $Ru(NO)_2(PPh_3)_2$. We therefore conclude that reaction 6 is by far the *predominant* pathway for eq 5. It is important to note that the thermolysis of $Ru(NO_2)_2(CO)_2(PPh_3)_2$ (eq 5) thus involves *two highly selective* oxygen-atom transfer processes which occur from NO_2^- ligands to, in turn, CO (eq 6a) and PPh_3 (eq 6b) ligands. Oxygen-atom transfer from coordinated NO_2^- to PPh_3 has been observed previously[35] in the reaction of $[Ru(NO_2)(Cl)(bpy)_2]^+$ with PPh_3. In earlier work,[36] the formation of Ph_3PO from the reaction of $NiX_2(PPh_3)_2$ (X = Cl, Br, I) and PPh_3 with $NaNO_2$ was attributed to a side reaction. Such is clearly not the case in the system at hand.

Throughout this discussion little attention has been paid to the mechanistic involvement of the O-bonded and N-bonded isomers of the starting material and intermediate. Although the exact role of these complexes in the overall reaction mechanism is uncertain, the reasonable sequence shown in Scheme II can be proposed. Consistent with experimental observations on a variety of related systems,[1-13] the assumption is made in Scheme II that oxygen-atom transfer from N-bonded NO_2^- is preferred over transfer from O-bonded NO_2^-. Note also that it is conceptually easier to envision the former process leading to the conversion of coordinated NO_2^- to coordinated NO. Scheme II is particularly attractive because it provides a logical way to account for all the species observed—or presumed to exist—in solution from the ^{31}P NMR and infrared studies, In view of the observed complexity of the reaction, kinetic studies designed to examine the proposed mechanism would likely be a nontrivial task.

^{18}O Single-Label Studies. An ^{18}O-labeling study of reaction 5 was carried out in order to determine the nature of the oxygen-atom transfer process leading to the formation of CO_2. The thermolysis reaction was effected under the usual conditions except that ^{18}O-enriched $Ru(N^{18}O_2)_2(CO)_2(PPh_3)_2$ was used. Pertinent ^{18}O enrichment data for the CO_2 product from eight separate experiments are listed in Table I.

The presence of a substantial amount ($n_t > 1.00$) of ^{18}O in the CO_2 produced in reaction 5 unambiguously establishes NO_2^- as the source of transferred oxygen. It is important to note that the degree of enrichment ($n_t = 1.33$) is significantly larger than that expected ($n_t = 1.00$) for the simple oxygen-atom transfer process depicted in Scheme I. In fact, the observed value of n_t is exactly the value which would be predicted on the basis of *statistical* scrambling of all oxygen atoms in the molecule.[37] Such scrambling could in principle arise from several sources. Exchange between free CO_2 and either $Ru(^{18}ON^{18}O)(CO)(N^{18}O)(PPh_3)_2$ or $Ru(N^{18}O)_2(PPh_3)_2$ is one possibility. It is also possible that CO_2 could exchange with free $N^{18}O_2^-$ that might be present in solution. Alternatively, oxygen scrambling could be an intrinsic part of the oxygen-atom transfer process itself, as was the case for the nickel system[10] in eq 2. A series of control experiments was conducted in order to examine these possibilities.

Table I. ^{18}O Enrichment of CO_2 Derived from the Thermolysis of $Ru(N^{18}O_2)_2(CO)_2(PPh_3)_2$[a]

trial	$^{46}E_{CO_2}$	n_t
1	4.714	1.30
2	4.733	1.31
3	4.768	1.32
4	4.776	1.33
5	4.801	1.34
6	4.814	1.34
7	4.747	1.32
8	4.840	1.35
mean	4.774 ±0.043	1.33 ±0.02

[a] See Experimental Section for explanation of terms; $^{46}E_{NO_2^-} = 6.694 \pm 0.064$.

Two experiments demonstrated that the observed ^{18}O enrichment was not merely due to exchange between free CO_2 and the reaction intermediates or products. For both studies, CO_2 of normal isotopic abundance was brought into contact with an approximately equimolar amount of $Ru(^{18}ON^{18}O)(CO)(NO)(PPh_3)_2$ under reaction conditions. In one case, a measured sample of CO_2 was frozen into the reaction solution, and, in the second case, the CO_2 was generated in situ by the simultaneous thermolysis of unenriched $Ru(NO_2)_2(CO)_2(PPh_3)_2$. For both experiments only a small amount of ^{18}O enrichment was detected in the recovered CO_2 ($^{46}E_{CO_2} = 1.266$, 1.345, respectively). This is not surprising since it has already been established that ~0.1 equiv of CO_2 is produced during the thermolysis of $Ru(ONO)(CO)(NO)(PPh_3)_2$ (eq 7b). Thus, the thermolysis of $Ru(^{18}ON^{18}O)(CO)(NO)(PPh_3)_2$ introduces some labeled CO_2 into the system regardless of whether or not exchange takes place. The extent of this enrichment can, in fact, be estimated since the amount of unenriched CO_2 admitted to the system is known and the ^{18}O enrichment of the CO_2 formed in reaction 7b can be calculated from the known enrichment of $Ru(^{18}ON^{18}O)(CO)(NO)(PPh_3)_2$. The calculated values of $^{46}E_{CO_2}$ (1.28, 1.29, respectively) are in reasonable agreement with the experimental values if it is assumed that 10% of the $Ru(^{18}ON^{18}O)(CO)(NO)(PPh_3)_2$ reacts to form CO_2 (eq 7b) and that CO_2 does not exchange with $Ru(^{18}ON^{18}O)(CO)(NO)(PPh_3)_2$ or the reaction products.

It should be noted that these calculations do not depend on the extent of oxygen scrambling in the production of CO_2 by the intermediate $Ru(ONO)(CO)(NO)(PPh_3)_2$. It can be shown that the CO_2 produced by this intermediate will have the same ^{18}O enrichment in the presence or absence of scrambling.[38] Thus, for both experiments the observed enrichment of the CO_2 product is consistent with the formation of ~0.1 equiv of labeled CO_2 by the thermolysis of $Ru(^{18}ON^{18}O)(CO)(NO)(PPh_3)_2$. It would, therefore, seem that any exchange process involving free CO_2 and $Ru(ONO)(CO)(NO)(PPh_3)_2$ is insufficient to account for the ^{18}O enrichment observed in the labeling studies. Since the $Ru(N^{18}O)(NO)(PPh_3)_2$ and $Ph_3P^{18}O$ produced in the thermolysis of $Ru(^{18}ON^{18}O)(CO)(NO)(PPh_3)_2$ are also in contact with the CO_2, any possibility of substantial exchange between CO_2 and

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(37) Since four of the six oxygen atoms in the complex are labeled, the value of n_t for the limiting case of statistical scrambling is given by $n_t = (4/6)(2.00) = 1.33$.

(38) For $Ru(^{18}ON^{18}O)(CO)(NO)(PPh_3)_2$, $^{46}E_{NO_2^-} = 6.69$ and $^{46}E_{CO} = {}^{46}E_{NO} = 1.00$. If oxygen is transferred from $N^{18}O_2^-$ to CO, the enrichment of the CO_2 in the absence of scrambling is given by

$$^{46}E_{CO_2} = \frac{^{46}E_{NO_2^-} + {}^{46}E_{CO}}{2} = \frac{6.69 + 1.00}{2} = 3.85$$

If statistical scrambling occurs,

$$^{46}E_{CO_2} = \frac{2(^{46}E_{NO_2^-}) + {}^{46}E_{CO} + {}^{46}E_{NO}}{4} = \frac{2(6.69) + 1.00 + 1.00}{4} = 3.85$$

Table II. Observed and Calculated Mass 47 Enrichments for CO_2 Derived from Double-Label Study[a]

				$^{47}E_{CO_2}$(calcd)	
trial	A,[b] mmol	B,[c] mmol	$^{47}E_{CO_2}$(obsd)[d]	intramolecular	intermolecular
1	1.186	0.601	27.7	22.6	27.8
2	0.376	0.188	26.4	22.4	27.5
3	0.196	0.446	45.8	42.2	47.1
4	0.186	0.370	44.9	40.6	45.8

[a] See Experimental Section for explanation of terms. [b] A = $Ru(N^{18}O_2)_2(CO)_2(PPh_3)_2$; $^{47}E_A = 4.17$. [c] B = $Ru(NO_2)_2(^{13}CO)_2(PPh_3)_2$; $^{47}E_B = 59.0$. [d] Estimated uncertainty ±2%.

either of these products is similarly eliminated.

An experiment was also conducted to examine the possibility of NO_2^- dissociation from $Ru(NO_2)_2(CO)_2(PPh_3)_2$. The thermolysis reaction was conducted in the usual way with unlabeled $Ru(NO_2)_2(CO)_2(PPh_3)_2$ except that excess $KN^{18}O_2$ was added to the solution. The recovered CO_2 showed no ^{18}O enrichment ($^{46}E_{CO_2} = 0.994$), indicating that NO_2^- does not dissociate from the complex during the reaction. Thus, free NO_2^- cannot be involved in the exchange of ^{18}O.

It can thus be concluded from this series of control experiments that oxygen scrambling is an inherent feature of the oxygen-atom transfer process itself rather than the result of an independent simple exchange process. In other words, scrambling takes place *prior to* the loss of CO_2 and the formation of $Ru(ONO)(CO)(NO)(PPh_3)_2$. The rate of oxygen scrambling must necessarily be faster than the rate of CO_2 loss since *statistical* distribution of the ^{18}O label is observed in the CO_2 product.

It should be noted that these conclusions are not altered by the fact that ~10% of the CO_2 is formed in the second step (eq 7b) of the thermolysis reaction. Since statistical oxygen scrambling must occur prior to loss of CO_2 and formation of $Ru(ONO)(CO)(NO)(PPh_3)_2$ (eq 6a), this intermediate will necessarily contain statistically scrambled oxygen atoms having the same enrichment as the CO_2. Thus, any CO_2 produced from $Ru(ONO)(CO)(NO)(PPh_3)_2$ by reaction 7b must also have statistical ^{18}O content.

^{18}O and ^{13}C Double-Label Study. A double-label study was carried out in an effort to determine whether the oxygen-atom transfer in eq 6a is an intramolecular or intermolecular process. Weighed amounts of the isotopically labeled complexes $Ru(N^{18}O_2)_2(CO)_2(PPh_3)_2$ and $Ru(NO_2)_2(^{13}CO)_2(PPh_3)_2$ were mixed and allowed to undergo thermolysis as usual. Figure 1 shows the various isotopically labeled CO_2 species predicted on the basis of intramolecular and intermolecular reaction mechanisms. In particular, it should be noted that $^{13}CO^{18}O$ (mass 47) can only be produced by means of an intermolecular mechanism. However, Figure 1 clearly represents a vast oversimplification of the actual experiment in two ways. The scheme does not take into account the statistical scrambling of oxygen atoms which occurs during the thermolysis reaction. In addition, the experiment is complicated by the fact that a significant amount of ^{18}O label exists in $Ru(NO_2)_2(^{13}CO)_2(PPh_3)_2$ since the 94% ^{13}CO used to prepare the complex is also enriched in ^{18}O. Thus, this complex is perhaps better represented as $Ru(NO_2)_2(^{13}C^{18}O)_2(PPh_3)_2$. Fortunately, both of these factors can be taken into account in the detailed calculations, and the general principle remains that intramolecular and intermolecular mechanisms predict *different* amounts of the species $^{13}CO^{18}O$.

The results of the double-label study are listed in Table II together with the values of $^{47}E_{CO_2}$ calculated for *general* intramolecular and intermolecular oxygen-atom transfer mechanisms. These calculations[39] were made on a purely statistical basis using only the known ^{18}O and ^{13}C enrichments of the two labeled forms of $Ru(NO_2)_2(CO)_2(PPh_3)_2$. The calculations are thus independent of both the microscopic details of the mechanistic process by which oxygen-atom transfer and scrambling occur and the formulation of the associated intermediates or activated complexes. The only restriction built into the calculations is that prior to the loss of CO_2 the six oxygen atoms within each molecule (intramolecular) or the 12 oxygen atoms within each dimeric unit (intermolecular) must become indistinguishable. This restriction is, in fact, required for the *intramolecular* case by the results of the single-label studies. However, it is important to note that intermolecular scrambling of oxygen is *not* necessarily required by the single-label studies. The single-label results can be explained by simply requiring that statistical scrambling occur only *within* each molecule, independent of any mechanistic assumptions.

The latter point raises the interesting possibility of an alternative intermolecular oxygen-transfer mechanism in which statistical scrambling of oxygen occurs only on an *intramolecular* basis prior to *intermolecular* transfer of oxygen and concomitant loss of CO_2. It can be shown[40] that this model yields calculated $^{47}E_{CO_2}$ values which are indistinguishable from those of the intermolecular mechanism proposed earlier.

The experimental results (Table II) are not consistent with an intramolecular oxygen-atom transfer process, but are in excellent agreement with the values calculated on the basis of an intermolecular mechanism. The only restriction is that the intermolecular mechanism requires the statistical scrambling of either (1) all 12 oxygen atoms within the dimeric unit, or alternatively, (2) all 6 oxygen atoms within each molecule *prior to* formation of the dimeric unit. In the latter case, further scrambling within the dimeric unit is not required.

Unfortunately, our results afford little insight into either the nature of the dimeric unit involved in oxygen-atom *transfer* or the mechanistic details necessary to achieve statistical oxygen-atom *scrambling*. Indeed, it is not evident that a simple rearrangement, either before or after formation of the dimeric unit, would lead to both statistical distribution of the oxygen atoms and retention of one *O-bonded* NO_2^- ligand on each metal center. Clearly, the mechanistic process involved is complicated, and further speculation must await more experimental detail.

Regardless, the results of our labeling studies clearly establish that the irreversible *intramolecular* oxygen-atom transfer mechanism depicted in Scheme I is inadequate for the system at hand. Any correct mechanism must involve *intermolecular* oxygen-atom transfer via an intermediate (or intermediates) sufficiently long-lived to undergo statistical oxygen scrambling between nitrogen and carbon prior to the loss of CO_2. Based upon these results and the results of our previous study[10] of the nickel system (eq 2), oxygen scrambling would appear to be the rule rather than the exception. Thus, irreversible intramolecular oxygen-atom transfer from coordinated NO_2^- to coordinated CO (Scheme I) has yet to be demonstrated experimentally.

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Supplementary Material Available: Calculations used in the double-label study (14 pages). Ordering information is given on any current masthead page.

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(39) See Supplementary Material.

(40) See Supplementary Material. This result is an artifact of the low ^{18}O enrichment used in order to achieve high sensitivity and precision on the RMS-11 isotope ratio mass spectrometer.