Journal of Organometallic Chemistry, 347 (1988) 373–381
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

The reactivity of decacarbonylnitrosyltriruthenate: synthesis and characterization of $[Ru(CO)_3(NO)]^-$

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(Received September 8th, 1987)

Abstract

Decarbonylnitrosyltriruthenate, $[Ru_3(CO)_{10}(NO)]^-$, exhibits reactivity at both the nitrosyl ligand and the metal core. The N–O bond can be cleaved in a thermal reaction to give $[Ru_5N(CO)_{14}]^-$ in low yield, whereas $[Ru_3(NCO)(CO)_{11}]^-$ can be formed quantitatively when $[Ru_3(CO)_{10}(NO)]^-$ is photolyzed under CO. The carbonyl ligands of the cluster are readily substituted by triphenylphosphine and trimethylphosphite giving $[Ru_3(CO)_9L(NO)]^-$ (where L = PPh_3, $P(OCH_3)_3$). Under an atmosphere of ^{13}CO complete exchange with the carbonyl ligands is observed. The substituted clusters have been characterized by infrared and NMR spectroscopies as well as by their reactions with acids to give $HRu_3(CO)_9L(NO)$. With the anionic nucleophile, $PPN(NO_2)$, $[Ru_3(CO)_{10}(NO)]^-$ photochemically reacts under a CO atmosphere to form $[Ru(CO)_3NO)]^-$. This new nitrosyl carbonylmetalate can also be prepared from $PPN(NO_2)$ and $Ru(CO)_5$.

Introduction

Carbonylmetalates have proven to be among the most useful synthetic reagents in organometallic chemistry, as well as having many valuable applications in organic synthesis [1,2]. Modification of these anions by the formal replacement of CO with NO^+ will undoubtedly alter their reactivity and hopefully extend the value of these compounds. Recently, several reports of new nitrosyl carbonylmetalate monomers [3,4] and clusters [4] have appeared. Investigations of the reactivity of these compounds are necessary to delineate their synthetic utility in both organic and organometallic chemistry.

This paper details some of the diverse reactivity exhibited by $PPN[Ru_3(CO)_{10}(NO)]$. The nitrosyl ligand undergoes N–O bond cleavage to give both nitrido and isocyanato species. The metal–metal bonds can also be cleaved to give $[Ru(CO)_3(NO)]^-$, the first example of a mononuclear nitrosyl carbonylmetalate of a non first-row transition metal. Additional studies with ^{13}CO, PPh_3, and $P(OCH_3)_3$ show

0022-328X/88/$03.50

that the carbonyl ligands on the cluster are substitutionally labile. We have previously reported that the PPN[$Ru_3(CO)_{10}(NO)$] reacts with CH_3^+ and H^+ to give $Ru_3(NOCH_3)(CO)_{10}$ and $Ru_3(NOH)(CO)_{10}$, respectively [5].

Experimental

PPN(NO_2) [6], PPN($^{15}NO_2$) [4], $Ru_3(CO)_{12}$ [7], and PPN[$Ru_3(CO)_{10}(NO)$] [8] were prepared according to published procedures. ^{13}CO (99% enriched) was obtained from Merck, Sharp, and Dohme. All other reagents were obtained from commercial sources and used as received. Tetrahydrofuran (THF) and diethyl ether were dried by distillation from sodium benzophenone ketyl under N_2. Methylene chloride was dried by distillation from P_2O_5 under vacuum. Hexane was dried by distillation from sodium under N_2. All reactions were conducted under either a nitrogen or a carbon monoxide atmosphere. Chromatography was conducted on silica gel. A medium pressure Hanovia lamp with pyrex-filtered radiation was used in the photochemical experiments. The lamp was placed 5 cm from the reaction vessel which was immersed in a pyrex beaker filled with water to prevent overheating. Infrared spectra were obtained on a Beckman 4250 spectrophotometer, and the ^1H NMR spectra were recorded on a Varian CFT20 80 MHz-spectrophotometer. ^{31}P and ^{15}N NMR data were obtained on a Nicolet NTCFT-1180 300 MHz spectrophotometer. ^{31}P NMR chemical shifts were reported relative to H_3PO_4. ^{15}N NMR was conducted as described previously [4] and the data are reported relative to NH_3 (liquid, 25 ° C) [9]. Spectroscopic data are presented in Table 1.

Pyrolysis of PPN[$Ru_3(CO)_{10}(NO)$]. PPN[$Ru_3(CO)_{10}(NO)$] (179.7 mg, 0.156 mmol) was placed in a Schlenk tube and degassed. THF (20 ml) was added via syringe, and the solution was refluxed for 2 h. The solvent was removed under vacuum giving a deep red oil, which was extracted with diethyl ether (2 × 10 ml) and filtered giving an orange solution. The solution volume was reduced to 8 ml and hexane (10 ml) was layered on top. Slow diffusion gave PPN[$Ru_5N(CO)_{14}$] (12.3 mg, 0.008 mmol) in 5% overall yields as large red platelike crystals. Anal. Found: C, 41.38; H, 2.17; N, 1.91. $Ru_5P_2O_{14}N_2C_{50}H_{30}$ calcd.: C, 41.41; H, 2.08; N, 1.93%.

Photolysis of PPN[$Ru_3(CO)_{10}(NO)$] under CO. $Ru_3(CO)_{12}$ (82.0 mg, 0.128 mmol) and PPN$(NO)_2$ (76.5 mg, 0.131 mmol) were placed in a Schlenk tube and degassed. THF (30 ml) was added via syringe, and the reaction was stirred and saturated with a stream of CO. After 20 min infrared spectroscopy showed the solution to contain only $[Ru_3(CO)_{10}(NO)]^-$. The reaction was placed in a water bath and photolyzed for 20 h. The reaction was followed by infrared spectroscopy which showed a clean conversion of the $[Ru_3(CO)_{10}(NO)]^-$ to a new species with the evolution of carbon dioxide. The product was identified as $[Ru_3(NCO)(CO)_{11}]^-$ on the basis of both its infrared spectrum and reactivity [10].

Preparation of PPN[$Ru(CO)_3(NO)$]. a. From $Ru(CO)_5$. $Ru_3(CO)_{12}$ (125.7 mg, 0.197 mmol) was placed in the glass liner of a 350 ml stainless steel autoclave and slurried with THF (4 ml). The liner was then sealed in the autoclave, and the system was purged six times with N_2 (1000 psig) followed by 5 times with CO (500 psig). The reaction was then pressurized with CO (4100 psig), heated to 115 ° C, and rocked for 24 h. The reaction was cooled to room temperature, and the pressure was slowly released. The autoclave was opened in a nitrogen filled glove bag, and the pale yellow solution was quickly added to a slurry of PPN(NO_2) (368.0 mg, 0.629

Table 1

Spectroscopic data

Compound	ν(CO) (cm^{-1})	ν(NO) (cm^{-1})	^{1}H NMR (ppm) (CD$_2$Cl$_2$)	^{31}P NMR (ppm) (CD$_2$Cl$_2$)
PPN{$Ru_3(CO)_9[P(OMe)_3](NO)$}	2052m, 1997s, 1974vs, 1965sh (THF)		7.52m(30H), 3.92(d, J(PH) 11.0 Hz, 9H)	158.8
PPN[$Ru_3(CO)_9(PPh_3)(NO)$]	2050m, 1994s, 1975vs, 1959s (CH_2Cl_2)			49.6
$HRu_3(CO)_9[P(OMe)_3](NO)$	2096m, 2057vs, 2023vs, 2004s, 1990m (hexane)	1524w, br (hexane)	3.61(d, J(PH) 12.5, 9H) −12.10 (d, J(PH) 8.1 Hz, 1H)	135.8
$HRu_3(CO)_9(PPh_3)(NO)$ [11]	2094, 2056s, 2021vs, 2002m, 1991w (hexane)		7.37(m, 15H) −11.44(d, J(PH) 6.7 Hz, 1H)	33.8
$HRu_3(CO)_7[P(OMe)_3]_3(NO)$ [12]	2054m, 2018s, 1991vs, 1969m (hexane)		3.60m, −12.04m	140.3(2P) 153.7(1P)
PPN[$Ru(CO)_3(NO)$]	1978w, 1886vs (THF)	1597(ν(^{15}NO) 1561)(THF)		

mmol) in THF (30 ml). Gas evolution was observed as the solution turned deep yellow. The reaction vessel was removed from the glove bag and placed under nitrogen on the Schlenk line. The reaction was stirred in the dark for 1 h, after which the mixture was filtered to remove unreacted PPN(NO_2), and the solvent was removed under vacuum. The residue was extracted three times with 10 ml portions of diethyl ether to remove $[Ru_3(CO)_{10}(NO)]^-$. The remaining solid was extracted two times with 10 ml portions of THF to give a deep yellow-red solution and leaving behind residual PPN(NO_2). The product was precipitated with diethyl ether and recrystallized from THF/diethyl ether to give pale yellow, very air-sensitive microcrystals of PPN[$Ru(CO)_3(NO)$] (175.0 mg, 0.232 mmol) in 40% overall yield from $Ru_3(CO)_{12}$. Found: C, 62.05; H, 4.05; N, 3.70. $RuP_2O_4N_2C_{39}H_{30}$ calcd.: C, 62.14; H, 4.01; N, 3.72%.

b. From $[Ru_3(CO)_{10}(NO)]^-$. $Ru_3(CO)_{12}$ (102.6 mg, 0.160 mmol) and PPN(NO_2) (295.4 mg, 0.503 mmol) were placed in a 100 ml Schlenk tube under N_2, and THF (40 ml) was added by syringe. A vigorous evolution of gas followed and an infrared spectrum confirmed that $[Ru_3(CO)_{10}(NO)]^-$ had formed. At this point, the N_2 atmosphere was replaced with CO. After stirring for 2 h at room temperature under CO no reaction occurred so photolysis was initiated. Five hours later, the solid PPN(NO_2) had dissolved indicating that the reaction was complete. The THF solution was filtered and evaporated under vacuum. The infrared spectrum of the filtered THF solution had absorptions at 1975m, 1887s, and 1593m cm^{-1} due to the product, PPN[$Ru(CO)_3(NO)$]. Also present were weak to very weak absorptions at 2220br, 2185, 1775, and 1760 cm^{-1}, indicating that the product was slightly impure.

Substitution reactions of PPN[$Ru_3(CO)_{10}(NO)$] with ^{13}CO

PPN[$Ru_3(CO)_{10}(NO)$] (111.4 mg, 0.97 mmol) was placed in a Schlenk tube and degassed. THF (12 ml) was vacuum distilled into the tube and kept frozen in a liquid nitrogen bath. The tube was evacuated and refilled with an atmosphere of ^{13}CO. The apparatus was sealed, allowed to warm to room temperature and stirred overnight. After 14 h, the ^{13}CO was removed and infrared spectroscopy showed complete exchange by the shift of the absorption at 2069 to 2041 cm^{-1}. The solvent was removed under vacuum, and the product was extracted into diethyl ether and precipitated with hexane.

Substitution reactions of PPN[$Ru_3(CO)_{10}(NO)$] with $P(OCH_3)_3$ and PPh_3

PPN[$Ru_3(CO)_{10}(NO)$] (90 mg, 0.08 mmol) was placed in a Schlenk tube which was then evacuated and filled with nitrogen. Enough solvent (THF for the phosphite and CH_2Cl_2 for the phosphine) was added to completely dissolve the anion. One equivalent of the donor (dissolved in the appropriate solvent) was slowly added to the yellow-red solution causing an immediate color change to orange-red. Infrared spectroscopy indicated complete consumption of $[Ru_3(CO)_{10}(NO)]^-$. Removal of the solvent under vacuum gave an orange oil which was slightly soluble in ether and very soluble in THF. All attempts to crystallize these anions were unsuccessful.

Preparation of $HRu_3(CO)_9[(P(OCH_3)_3](NO)$. PPN[$Ru_3(CO)_{10}(NO)$] (85.9 mg, 0.075 mmol) was placed in a Schlenk tube, degassed, and dissolved in freshly distilled CH_2Cl_2 (8 ml). A solution of $P(OCH_3)_3$ (89.8 μl, 0.075 mmol) in CH_2Cl_2 (8 ml) was added dropwise to the stirred ruthenium solution causing a color change from yellow-red to orange. Infrared spectroscopy showed the replacement of the bands due to starting material with those due to $\{Ru_3(CO)_9[P(OCH_3)_3](NO)\}^-$. The volume of the orange solution was reduced to ~ 8 ml, and the solution was cooled to $-78\,^\circ C$ with a dry ice/isopropanol bath. CF_3CO_2H (9.0 μl, 0.117 mmol) was added via microsyringe, causing an immediate color change to red-orange with mixing. The solution was stirred and allowed to warm to room temperature. The solvent was removed under vacuum, and the residue was extracted with hexane (5 × 8 ml) and filtered. The hexane extract was chromatographed with hexane/CH_2Cl_2 (7/3) to give two bands. The first band was yellow-red and was identified as $HRu_3(CO)_{10}(NO)$ (20.0 mg, 0.033 mmol, 44% yield) by its infrared spectrum [11]. The second band was orange and gave $HRu_3(CO)_9[P(OCH_3)_3)](NO)$ (19.8 mg, 0.028 mmol) in 37% yield from PPN[$Ru_3(CO)_{10}(NO)$]. The product was isolable only as an orange-brown oil which failed to give satisfactory analysis.

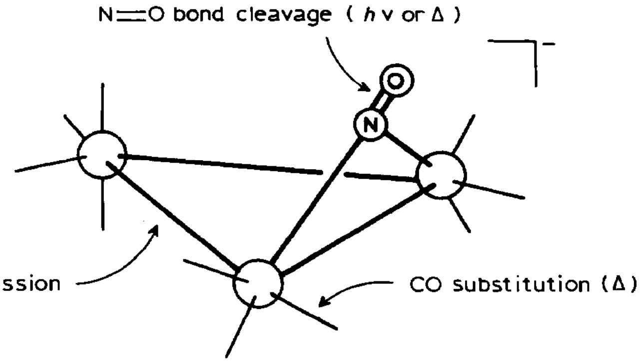
Preparation of $HRu_3(CO)_7[P(OCH_3)_3]_3(NO)$. $HRu_3(CO)_9[P(OCH_3)_3](NO)$ (15.4 mg, 0.022 mmol) was dissolved in hexane (15 ml) under nitrogen. $P(OCH_3)_3$ (12 μl, 0.102 mmol) was added via microsyringe, and the reaction was refluxed for 3 h during which time the color perceptively darkened from orange to orange-red. Infrared spectroscopy indicated completion of the reaction by the replacement of the 2096 cm^{-1} peak with a peak at 2055 cm^{-1}. The solution was cooled to room temperature, and the solvent was removed under vacuum. The residue was dissolved in hexane/CH_2Cl_2 (7/3) and chromatographed to give $HRu_3(CO)_7[P(OCH_3)_3]_3$-(NO) (13.0 mg, 0.012 mmol) in 56% yield as deep red crystals. The product was identified by its infrared spectrum [11].

Preparation of $HRu_3(CO)_9(PPh_3)(NO)$. PPN[$Ru_3(CO)_{10}(NO)$] (83.7 mg, 0.073 mmol) was placed in a Schlenk tube, degassed, and dissolved in CH_2Cl_2 (10 ml).

PPh_3 (21.0 mg, 0.080 mmol) was dissolved in CH_2Cl_2 (10 ml) in a pressure equalizing addition funnel and the resulting solution was added dropwise to the $PPN[Ru_3(CO)_{10}(NO)]$ solution over a 45 min period. Infrared spectroscopy showed replacement of the bands of the starting material with those of $[Ru_3(CO)_9(PPh_3)(NO)]^-$. The volume was reduced under vacuum to ~ 8 ml, and the solution was cooled to $-78°C$ with a dry ice/isopropanol bath. CF_3CO_2H (6.0 μl, 0.078 mmol) was added via microsyringe causing an immediate color change to light orange. An absorption at 1720 cm^{-1} appeared which was probably due to a μ_3-CO. The solution was allowed to warm to room temperature, and darkened to deep red-orange with time. After 2 h the 1720 cm^{-1} band had disappeared, and the solvent was removed under vacuum. The residue was extracted with diethyl ether and filtered giving a red-orange solution. The solution was evaporated to dryness on a rotary evaporator. The residue was dissolved in hexane/CH_2Cl_2 (7/3) and chromatographed to give one band identified by its infrared spectrum [11] to be $HRu_3(CO)_9(PPh_3)(NO)$ (6.2 mg, 0.007 mmol) recovered in 10% yield.

Results and discussion

The reactivity of the anionic nitrosyl-containing cluster, $[Ru_3(CO)_{10}(NO)]^-$, under a variety of conditions has been studied. The structure of this anion is shown below along with the sites of bond breaking observed in the various reactions.



The following sections are grouped according to the bond broken.

Thermally induced cleavage of the N–O bond. Pyrolysis of the nitrosyl anion for 2 h in THF results in the cleavage of the N–O bond and formation of a nitrido cluster, eq. 1. While the yield of this reaction is very low (5%), a high yield synthesis

$$[Ru_3(CO)_{10}(NO)]^- \xrightarrow[THF]{\Delta} [Ru_5N(CO)_{14}]^- \qquad (1)$$

has been discovered starting from $[Ru_6N(CO)_{16}]^-$ [12]. The formation of nitrido clusters from nitrosyl clusters has been well documented [13], and with $[FeRu_3(CO)_{12}(NO)]^-$ the reaction has been studied in detail [14].

Photochemically induced cleavage of the N–O bond. If $[Ru_3(CO)_{10}(NO)]^-$ is photolyzed under CO, not only is the N–O bond cleaved but a nitrogen–carbon bond is formed, eq. 2. Surprisingly, this reaction proceeds quantitatively over a 20 h

$$[Ru_3(CO)_{10}(NO)]^- + CO \xrightarrow[THF]{h\nu} [Ru_3(NCO)(CO)_{11}]^- + CO_2 \qquad (2)$$

period. $[Ru_3(NCO)(CO)_{11}]^-$ has been independently synthesized and characterized from the reaction of azide ion with $Ru_3(CO)_{12}$ [10], and the infrared spectrum of the product in eq. 2 is identical to $[Ru_3(NCO)(CO)_{11}]^-$ produced by the azide route. While this is the first report of a NO to NCO conversion on a metal cluster, such conversions have been previously observed with mononuclear nitrosyl complexes of Mo [15], W [16], and Pt [17]. Recently, an elegant matrix isolation study on a tungsten complex, $CpW(CO)_2(NO)$, has shown conclusively that the reaction involves intramolecular migration of a CO ligand to a metal nitrene, eq. 3 [16]. What

$$CpW(CO)_2(NO) \xrightarrow{h\nu} CpW(N)(CO)_x \xrightarrow{CO} CpW(CO)_3(NCO) \qquad (3)$$

we find interesting (and somewhat surprising) is that this photochemistry cleanly produces a trinuclear product. In light of the results described below, it is certainly possible that eq. 2 proceeds via mononuclear intermediates.

Photochemically induced formation of $[Ru(CO)_3(NO)]^-$. If nitrite is added to the solution of $[Ru_3(CO)_{10}(NO)]^-$ during the photolysis, no $[Ru_3(NCO)(CO)_{11}]^-$ is observed. Instead, absorptions in the infrared spectrum at 1978, 1886, and 1597 cm^{-1} indicated the formation of a new complex which has been identified as $[Ru(CO)_3(NO)]^-$. The original goal in studying this photochemistry was to develop a simple route to this mononuclear nitrosyl carbonylmetalate. Several studies of the photochemistry of $Ru_3(CO)_{12}$ have appeared [18–26], and under CO, photolysis of $Ru_3(CO)_{12}$ leads to $Ru(CO)_5$. As discussed below, $Ru(CO)_5$ reacts rapidly with $PPN(NO_2)$ to generate $PPN[Ru(CO)_3(NO)]$, eq. 4. If $Ru(CO)_5$ could be formed in the presence of $PPN(NO_2)$, we anticipated it would be trapped to form $PPN[Ru(CO)_3(NO)]$.

$$PPN(NO_2) + Ru(CO)_5 \rightarrow PPN[Ru(CO)_3(NO)] + CO + CO_2 \qquad (4)$$

A simple mixture of $Ru_3(CO)_{12}$, 3 equivalents of $PPN(NO_2)$, and CO leads immediately to the formation of $PPN[Ru_3(CO)_{10}(NO)]$. No further reaction occurs until photolysis is initiated. After 5 h of pyrex-filtered radiation from a Hanovia lamp, the formation of $PPN[Ru(CO)_3(NO)]$ is complete. This route has the drawback of being very sensitive to the reaction conditions. If the temperature increases during the reaction, varying amounts of an unidentified impurity also form. This impurity has an absorption at 2220 cm^{-1} which is characteristic of a coordinated isocyanate, however, we were unable to isolate or further characterize this species.

The alternative route shown in eq. 4 allows $PPN[Ru(CO)_3(NO)]$ (**1**) to be isolated as analytically pure material. A THF solution of $Ru(CO)_5$ was prepared [27] in a rocking autoclave using $Ru_3(CO)_{12}$ and CO (4100 psig) at 115 °C for 25 h. The resulting pale yellow solution was added to excess $PPN(NO_2)$ under N_2 and allowed to stir for 1 h in the dark. After filtration to remove unreacted $PPN(NO_2)$, the solvent was removed under vacuum. Extraction of the residue with diethyl ether removes $PPN[Ru_3(CO)_{10}(NO)]$. The solid $PPN[Ru(CO)_3(NO)]$ was then collected and recrystallized to give a 40% overall yield based on the original amount of $Ru_3(CO)_{12}$ charged in the autoclave. This moderate yield of 40% results in part from loss of $Ru(CO)_5$ when the high pressure of CO was vented since the autoclave could not be cooled below room temperature.

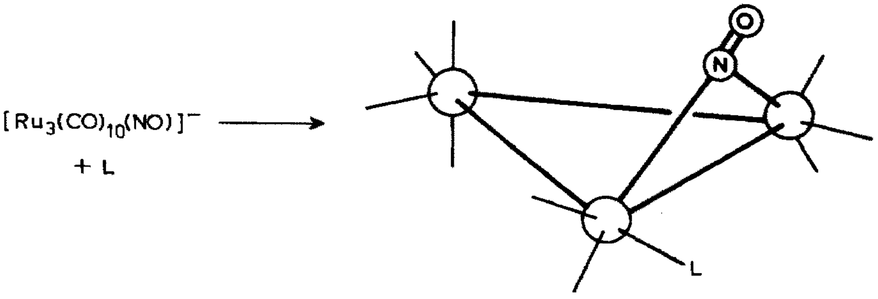
$PPN[Ru(CO)_3(NO)]$ is the first mononuclear complex of a second or third row transition element having only NO and CO ligands. This complex exhibits two absorptions in the carbonyl region of the infrared spectrum at 1978 and 1886 cm^{-1} and one ν(NO) at 1597 cm^{-1} in THF. Although the carbonyl absorptions are at similar energy to those found for PPN[$Fe(CO)_3(NO)$], the ν(NO) in $[Ru(CO)_3(NO)]^-$ is shifted 50 cm^{-1} to lower energy relative to $[Fe(CO)_3(NO)]^-$ [28]. The lowering in energy of the nitrosyl stretch is due to increased overlap between the $d\pi$ orbitals of the second row ruthenium atom with the π^* orbitals of the nitrosyl ligand. The increased overlap allows the additional electron density on the ruthenium to be exclusively delocalized onto the nitrosyl ligand, reducing the N–O bond order, and therefore the energy of the nitrosyl stretch.

The ^{15}N NMR resonance of $[Ru(CO)_3(NO)]^-$ appears at 404.7 ppm relative to NH_3 (25°C, 1). This is in the region typical for terminal, linear nitrosyl ligands [4,13,29–32] and can be compared to 398.0 ppm for the ferrate analog [13]. The ruthenium anion is also a paler yellow then the iron species as a result of the shift in the absorption maxima from 370 nm in $[Fe(CO)_3(NO)]^-$, to 318 nm for $[Ru(CO)_3(NO)]^-$.

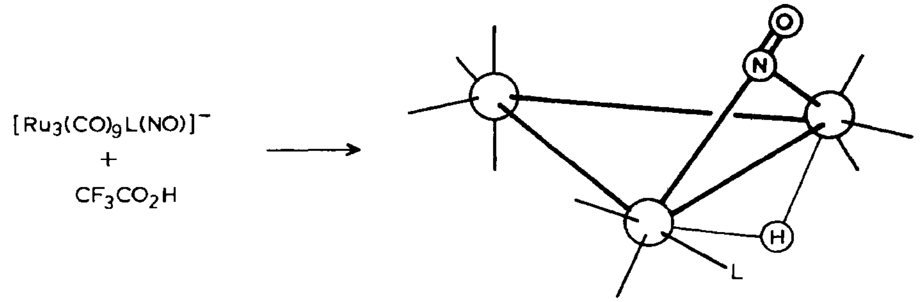
Substitution reactions. PPN[$Ru_3(CO)_{10}(NO)$] undergoes rapid ^{13}CO-exchange in THF at room temperature. After stirring overnight under 99%-enriched ^{13}CO, the infrared spectrum showed complete replacement of the bands of the starting material with the following absorptions: 2041w, 1982vs, 1955s, 1942s, 1923m, and 1908 m cm^{-1}. A control reaction using unenriched CO exhibited no change in the infrared spectrum after 48 h showing that isotopic exchange was the only reaction taking place under ^{13}CO.

$[Ru_3(CO)_{10}(NO)]^-$ reacts with phosphorus donor ligands to give substituted anions, eq. 5. Carbon monoxide is the only gas evolved in the reaction as shown by infrared spectroscopy. The product anions have been characterized by infrared and ^{31}P NMR spectroscopy (Table 1) as well as their conversion to $HRu_3(CO_9L(NO)$ via protonation. The infrared spectra of **2a** and **2b** are virtually superimpossible. They both show a lowering in the energy of the carbonyl stretches as expected from substitution of CO with a stronger σ-donor, weaker π-acceptor ligand.

Acceptable elemental analyses were not obtained because we were unsuccessful in forming crystalline products.



(**2a**, L = $P(OCH_3)_3$;
2b, L = PPh_3)



(6)

(**3a** , L = $P(OCH_3)_3$;
3b , L = PPh_3)

Although the products were isolable only as oils, in situ protonation of the materials allowed the isolated of the corresponding hydrido nitrosyl clusters, **3a**, **3b** eq. 6.

After separation of the neutral materials via column chromatography, the products are isolated in 37 and 10% yields for **3a** and **3b**, respectively. **3b** had been previously isolated from the reaction of PPh_3 with $HRu_3(CO)_{10}(NO)$ [11]. The infrared spectra of the two PR_3 substituted clusters are again very similar. The exception is the observation of ν(NO) at 1524 cm^{-1} for **3a** while the nitrosyl stretch was not observed for **3b** (due to solvent and ligand interference). The structure of the neutral species is proposed as **3** from the observation of *cis*-coupling between L and the bridging hydride: $L = P(OCH_3)_3$, J 8.1 Hz; $L = PPh_3$, J 6.7 Hz. The known structure of $HRu_3(CO)_7[P(OCH_3)_3]_3(NO)$ also supports the location of L in structure **3** [11]. **3a** can be converted into the previously characterized cluster. $HRu_3(CO)_7[P(OCH_3)_3]_3(NO)$, via substitution with excess $P(OCH_3)_3$ in refluxing hexane, providing further support for the formulation of the starting material.

Finally, we note that the ease of CO substitution of $[Ru_3(CO)_{10}(NO)]^-$ parallels that found for the isoelectronic cluster $[HRu_3(CO)_{11}]^-$ [33].

Acknowledgements

We gratefully acknowledge the National Science Foundation for support of this work.

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