Journal of Organometallic Chemistry, 287 (1985) 133–143
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

DOUBLE DEOXYGENATION OF PPN(NO_2) USING METAL CARBONYL CLUSTERS OF COBALT, RHODIUM, AND IRIDIUM

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(Received November 15th, 1984)

Summary

The reaction of PPN(NO_2) with $M_4(CO)_{12}$ (M = Co, Rh) gives the nitrido clusters $[M_6N(CO)_{15}]^-$ in 13 and 21% yields, respectively. A high yield synthesis (77%) of $[Rh_6N(CO)_{15}]^-$ directly from $Rh_6(CO)_{16}$ and PPN(NO_2) is also presented. PPN(NO_2) reacts with $Ir_4(CO)_{12}$ to give the new isocyanato cluster, $[Ir_4(NCO)(CO)_{11}]^-$ in 34% yield, while the direct synthesis of this isocyanate product occurs in 77% yield from PPN(N_3) and $Ir_4(CO)_{12}$. Modifications of published procedures for the preparation of $[N(C_2H_5)_4]_2$ $[Ir_6(CO)_{15}]$ and $Ir_6(CO)_{16}$ are reported that allow shorter reaction times and give higher yields. The reaction of $Ir_6(CO)_{16}$ with one equivalent of PPN(NO_2) generates a new cluster, PPN[$Ir_6(CO)_{15}(NO)$], in 57% yield which is proposed to contain a bent nitrosyl ligand. An additional equivalent of PPN(NO_2) gives $(PPN)_2[Ir_6(CO)_{15}]$ in 84% yield with the evolution of N_2O as well as CO_2.

Introduction

Since the primary source of the nitrogen atom in nitrido clusters is usually a metal-bound nitrosyl ligand [1], the common nitrosylating reagents, NO gas and NO^+, have also been used in the preparation of nitrido clusters (eqs. 1 and 2) [2].

$$[Co_6(CO)_{15}]^{2-} + NOBF_4 \xrightarrow{THF} Co^{2+} + Co(CO)_3(NO) + Co_4(CO)_{12} + [Co_6N(CO)_{15}]^- \quad (1)$$

$$[Rh_7(CO)_{16}]^{3-} + NO/CO \xrightarrow{MeOH} [Rh_6N(CO)_{15}]^- \quad (2)$$

The use of PPN(NO_2) as a source of metal nitrosyl carbonyl clusters is well-docu-

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[*] Fellow of the Alfred P. Sloan Foundation (1983–85).

mented [3–7]. This paper discusses the reactions of PPN(NO_2) with carbonyl clusters of the cobalt triad to produce compounds containing either a nitrosyl, nitrido, or an isocyanato ligand.

Experimental section

PPN(NO_2) [8], PPN($^{15}NO_2$) [4], PPN(N_3) [8], $Co_4(CO)_{12}$ [9], $Rh_4(CO)_{12}$ [10], and $Rh_6(CO)_{16}$ [12], were prepared according to published procedures. $Ir_4(CO)_{12}$ was purchased from Strem Chemical Company and used without further purification. Trifluoromethanesulfonic acid was purchased from Aldrich Chemicals and was distilled under nitrogen prior to use. Tetrahydrofuran (THF) and diethyl ether were dried by distillation from sodium benzophenone ketyl under N_2. Hexane was dried by distillation from sodium metal under N_2, and methylene chloride was dried by distillation from P_2O_5 under N_2. All reactions and crystallizations were carried out under either a nitrogen or carbon monoxide atmosphere. Infrared spectra were obtained on a Beckman 4250 spectrophotometer, and the Fourier transform infrared spectra were obtained on a Nicolet 60SX. The NMR data were obtained on a Nicolet NTCFT-1180 300 MHz spectrometer. Each ^{15}N NMR spectrum was conducted using CH_2Cl_2 as the solvent (~ 3.5 ml) in a 12-mm tube at a sample concentration of approximately 0.03 *M* and Cr(acac)$_3$ (53 mg) added. The referencing was done externally with use of CH_3NO_2 in $CHCl_3$ with 0.03 *M* Cr(acac)$_3$ set at 379.60 ppm downfield from NH_3 (liquid, 25°C) [12]. All ^{15}N shifts are reported relative to NH_3. Fast atom bombardment mass spectrometry was performed at the Midwest Center for Mass Spectrometry at the University of Nebraska-Lincoln.

Reaction of PPN(NO_2) with $Co_4(CO)_{12}$

$Co_4(CO)_{12}$ (217.1 mg, 0.380 mmol) and PPN(NO_2)(133.9 mg, 0.229 mmol) were placed in a Schlenk tube under nitrogen, and THF (30 ml) was added via syringe. Immediate gas evolution was observed, and the solution turned deep brown as the reaction was refluxed. After 2 h the solvent and $Co(CO)_3(NO)$, identified by its infrared spectrum [13] were removed under vacuum. The crude product was first extracted with hexane (40 ml) to remove the unreacted $Co_4(CO)_{12}$ (5 mg, 0.009 mmol) which was recovered in 2% yield. Extraction with diethyl ether (3 × 10 ml) gave a yellow-orange solution from which PPN[$Co_6N(CO)_{15}$] (24.9 mg, 0.032 mmol) was precipitated with hexane as orange-red crystals in 13% yield. Its identity was confirmed by its infrared spectrum [2]. The remaining residue was extracted with THF (15 ml), filtered, and pale yellow crystals of PPN[$Co(CO)_4$] (79.8 mg, 0.113 mmol), identified by its infrared spectrum [14], were obtained via precipitation with diethyl ether in 7% yield.

Reaction of PPN(NO_2) with $Rh_4(CO)_{12}$

$Rh_4(CO)_{12}$ (84.6 mg, 0.113 mmol) and PPN$(NO)_2$ (66.0 mg, 0.113 mmol) were placed in a Schlenk tube, degassed, and put under a CO atmosphere. THF (40 ml), previously saturated with CO for 20 min, was added via syringe. Gas evolution was observed as the solution turned deep red. After stirring for 14 h, the solution changed to a yellow green color. The volume of the solution was reduced under vacuum to ~ 2 ml, and diethyl ether (30 ml) was added causing precipitation of a dark solid. The solution was filtered, and the precipitate was washed with diethyl ether (2 × 5 ml). The product was crystallized by slow diffusion of hexane into diethyl ether giving PPN[$Rh_6N(CO)_{15}$] (37.5 mg, 0.024 mmol) in 21% yield. The product was identified by its infrared spectrum [2].

Preparation of PPN[$Rh_6N(CO)_{15}$]

$Rh_6(CO)_{16}$ (79.0 mg, 0.074 mmol) and PPN(NO_2) (43.6 mg, 0.077 mmol) were placed in a Schlenk tube and degassed. THF (20 ml) was added via syringe, causing gas evolution as the solution turned deep red. After 5 min, the solution was saturated with CO and then was stirred for an additional 5 h, eventually turning deep violet. The volume of the solution was reduced to 2 ml under vacuum, and diethyl ether (40 ml) was added via syringe precipitating a dark solid, which was removed by filtration. The residue was washed with diethyl ether (10 ml), and the product was crystallized from a slow solvent diffusion of hexane into the ether giving deep golden crystals of PPN[$Rh_6N(CO)_{15}$] (90.8 mg, 0.057 mmol) in 77% yield. Anal. Found: C, 38.14; H, 2.08; N, 1.70. $Rh_6P_2O_{15}N_2C_{51}H_{30}$ calcd.: C, 38.52; H, 1.90; N, 1.76%.

Reaction of PPN(NO_2) with $Ir_4(CO)_{12}$

$Ir_4(CO)_{12}$ (55.2 mg, 0.050 mmol) and PPN(NO_2) (30.2 mg, 0.052 mmol) were placed in a Schlenk tube, degassed, and THF (15 ml) was added via syringe. Gas evolution was observed as the solution first turned pink-orange, then deep red, and finally brown. After 3 h the solvent was removed under vacuum giving a deep red oil. The oil was extracted with diethyl ether (2 × 10 ml) and filtered giving a golden solution and leaving some red-brown oil. PPN[$Ir_4(NCO)(CO)_{11}$] (27.6 mg, 0.017 mmol) was precipitated with hexane in 34% yield, and was identified by its infrared spectrum. The remaining ether insoluble red-brown oil was extracted with THF (10 ml) and filtered to give a deep red-brown solution. Infrared spectroscopy showed the solution contained a mixture of $[Ir_6(CO)_{15}]^{2-}$ and $[Ir_8(CO)_{22}]^{2-}$ [15].

Preparation of PPN[$Ir_4(NCO)(CO)_{11}$]

$Ir_4(CO)_{12}$ (34.0 mg, 0.031 mmol) and PPN(N_3) (19.3 mg, 0.032 mmol) were placed in a Schlenk tube under an N_2 atmosphere. THF (20 ml) was added via syringe and the mixture was stirred at room temperature for 1 h as the cloudy solution slowly turned to a clear yellow. The volume was reduced to 1 ml, and diethyl ether (25 ml) was added to give a yellow solution and a light brown residue. The solution was filtered, and the residue was washed with diethyl ether (5 ml). The volume of the solution was reduced to 15 ml, and PPN[$Ir_4(NCO)(CO)_{11}$] (39.3 mg, 0.024 mmol) was precipitated with hexane (30 ml) as lemon yellow crystals in 77% yield. Found: C, 35.39; H, 2.16; N, 1.63. $Ir_4P_2O_{12}N_2C_{48}H_{30}$ calcd.: C, 34.78; H, 1.82; N, 1.69%.

Preparation of $[N(C_2H_5)_4]_2[Ir_6(CO)_{15}]$

$Ir_4(CO)_{12}$ (180.0 mg, 0.163 mmol) and Na (sand) (120 mg, 5.2 mmol) were placed in a Schlenk tube in a nitrogen-filled drybox. The Schlenk tube was removed from the drybox, evacuated, and filled with CO. THF (20 ml) that had been previously saturated with CO was then added to the solids under CO. The reaction was stirred at room temperature under a CO atmosphere until infrared spectroscopy showed the presence of only $[Ir(CO)_4]^-$ and $[Ir_6(CO)_{15}]^{2-}$ (~ 14 h) [16]. The brown solution was filtered under CO into a CO filled Schlenk tube containing $Ir_4(CO)_{12}$ (175.1 mg, 0.158 mmol). The brown residue was washed with THF (2 × 3 ml) and discarded. The red-brown solution was heated to 60°C in an oil bath and stirred under a CO atmosphere. The reaction was monitored by infrared spectroscopy which showed complete consumption of the $[Ir(CO)_4]^-$ after 24 h. The reaction was allowed to cool to room temperature, after which the volume was reduced to ~ 5 ml under vacuum. An absolute ethanol solution of $[N(C_2H_5)_4]Br$ (3.4 g, 16.2 mmol), previously saturated with CO, was added to the THF solution which was stirred for 3 h. The solvent was removed under vacuum, leaving a red-brown solid. Under nitrogen, the solid was extracted with THF (4 × 8 ml) and filtered to separate the red solution from the tan solid. The volume of the solution was reduced under vacuum to 5 ml, causing a trace of $Ir_4(CO)_{12}$ to precipitate. The solution was refiltered, and the product was precipitated with ethanol/diethyl ether giving red-orange crystals of $[N(C_2H_5)_4]_2[Ir_6(CO)_{15}]$ (254.2 mg, 0.139 mmol) in 65% yield based on iridium. The product was identified by its infrared spectrum [15].

Preparation of $Ir_6(CO)_{16}$

$[N(C_2H_5)_4]_2[Ir_6(CO)_{15}]$ (252.0 mg, 0.137 mmol) was placed in a Schlenk tube, degassed, and then placed under a CO atmosphere. Methylene chloride (25 ml), previously saturated with CO, was added to give a pale orange solution with most of the starting material remaining as a solid. CF_3SO_3H (25.0 μl, 0.282 mmol) was added via syringe, and the solution turned deep red. After stirring approximately 60 s an orange crystalline solid precipitated and the solution turned a pale orange. The volume was reduced to ~ 2 ml, and the solution was decanted. The crystals were washed with absolute ethanol (2 × 10 ml), filtered in air, washed with petroleum ether, and air-dried giving $Ir_6(CO)_{16}$ (206.9 mg, 0.129 mmol) in 94% yield. Anal. Found: C, 12.32; H, 0.19. $Ir_6O_{16}C_{16}$ calcd.: C, 12.00; H, 0.00%.

Reaction of $PPN(NO)_2$ *with* $Ir_6(CO)_{16}$

$Ir_6(CO)_{16}$ (76.0 mg, 0.047 mmol) was placed in a 25 ml three-neck round-bottom flask, degassed, and slurried in THF (10 ml). $PPN(NO_2)$ (23.7 mg, 0.047 mmol) was placed in a pressure-equalizing addition funnel degassed, and slurried in THF (15 ml). The $PPN(NO_2)$ slurry was added slowly to the $Ir_6(CO)_{16}$ slurry over a period of 1.5 h, during which the reaction turned from an orange slurry to clear brown solution. The solvent was removed under vacuum, and the residue was extracted with diethyl ether (3 × 10 ml). This was filtered giving a clear red-brown solution and leaving a brown oil. The volume was reduced under vacuum to ~ 10 ml, and hexane (15 ml) was layered on the diethyl ether solution. Solvent diffusion gave $PPN[Ir_6(CO)_{15}(NO)]$ (57.4 mg, 0.027 mmol) as deep red crystals in 57% yield, however it was not possible to obtain a sample that was completely free of $Ir_6(CO)_{16}$ and/or $(PPN)_2[Ir_6(CO)_{15}]$. Anal. Found: C, 26.95; H, 1.52; N, 1.24. $Ir_6P_2O_{16}N_2C_{51}H_{30}$ calcd.: C, 28.60; H, 1.41; N, 1.31%. Fast atom bombardment mass spectroscopy in the negative ion mode shows a peak at m/z 1575; the parent was not observed.

Preparation of $(PPN)_2[Ir_6(CO)_{15}]$

$Ir_6(CO)_{16}$ (44.5 mg, 0.028 mmol) and $PPN(NO_2)$ (33.0 mg, 0.057 mmol) were placed in a Schlenk tube and degassed. THF (20 ml) was added via syringe, and the reaction was stirred. Gas evolution was observed as the reaction turned first brown and then red brown. Infrared spectroscopy of the gases above the solution showed the presence of CO_2 and N_2O; no CO was evolved in the reaction. After 40 min, the solvent was removed under vacuum. The red brown solid was washed with diethyl ether (10 ml) and dried under vacuum. The solid was extracted with THF (2 × 8 ml) to give a red-brown solution. The volume was reduced under vacuum to ~ 3 ml, and the product was precipitated with diethyl ether (10 ml). The red microcrystalline product was filtered in air, washed with diethyl ether, and air dried to give $(PPN)_2[Ir_6(CO)_{15}]$ (62.2 mg, 0.024 mmol) in 84% yield. Anal. Found: C, 39.61; H, 2.63; N, 1.01. $Ir_6P_4O_{15}N_2C_{87}H_{60}$ calcd.: C, 39.42; H, 2.28; N, 1.06%. Fast atom bombardment mass spectroscopy in the negative ion mode shows a peak at m/z 2112 corresponding to the $\{PPN[Ir_6(CO)_{15}]\}^-$ ion pair.

Reaction of $PPN[Ir_6(CO)_{15}(^{15}NO)]$ *with* $PPN(^{14}NO_2)$

A sample of $PPN[Ir_6(CO)_{15}(^{15}NO)]$ was prepared by the above procedure using 90–95% ^{15}N enriched nitrite (114 mg, 0.195 mmol) and $Ir_6(CO)_{16}$ (330 mg, 0.206 mmol). After attempting to observe the ^{15}N NMR spectrum of $PPN[Ir_6(CO)_{15}(^{15}NO)]$ in CH_2Cl_2, the solution (including $Cr(acac)_3$) was returned to a Schlenk flask and the solvent was removed. $PPN(^{14}NO_2)$ (77.6 mg, 0.113 mmol) was added to the flask which was then equipped with an evacuated gas IR cell. THF (5 ml) was distilled into the flask under vacuum, the solution was warmed to room temperature, and the gases were sampled by opening the cell. Infrared spectroscopic analysis revealed peaks at 2234, 2212, 2195, and 2172 cm^{-1} in the N_2O region.

Fourier transform infrared spectroscopy

Equal concentration solutions of PPN(Cl), $PPN[Ir_6(CO)_{15}(NO)]$, and $PPN[Ir_6(CO)_{15}(^{15}NO)]$ in chloroform were prepared. The spectra were recorded on a Nicolet 60SX spectrophotometer in a 0.1 mm sealed NaCl cell. Subtraction of the absorptions due to the PPN^+ cation resulted in the observation of a very weak $\nu(NO)$ at 1457 cm^{-1} for the hexairidium cluster. An observed isotopic shift of $\nu(^{15}NO)$ to 1430 cm^{-1} for $[Ir_6(CO)_{15}(^{15}NO)]^-$ supports the assignment of this band.

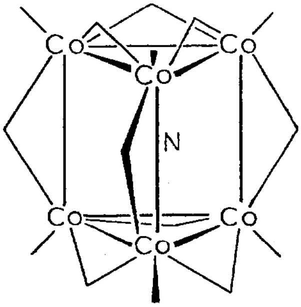
Results and discussion

Dodecacarbonyltetracobalt

$Co_4(CO)_{12}$ reacts with $PPN(NO_2)$ in THF to generate $Co(CO)_3(NO)$, $PPN[Co_6N(CO)_{15}]$, and $PPN[Co(CO)_4]$. These three species are readily separable due to the volatility of $Co(CO)_3(NO)$, and the solubility differences between the hexamer and the monomer. The nitrido cluster was previously synthesized by Martinengo and coworkers [2] from the reaction shown in eq. 1. In that study, the Co cluster was obtained in 40–50% yields after metathesis to the PPN^+ salt and characterized both spectroscopically and structurally (**1**).

Although the yield of **1** from the $PPN(NO_2)$ reaction is only 13%, the reaction represents an easier preparative method for the nitrido cluster due to the difficulty of preparing $K_2[Co_6(CO)_{15}]$ [17], the ready availability of $Co_4(CO)_{12}$, and the absence of a metathesis step.

The observed cluster fragmentation of $Co_4(CO)_{12}$ in the reaction to generate mononuclear complexes was not totally unexpected because of the weakness of



(1)

metal–metal bonds for the first row carbonyl clusters. For example, $Fe_3(CO)_{12}$ is fragmented to $[Fe(CO)_3(NO)]^-$ in its reaction with $PPN(NO_2)$ [4].

Dodecacarbonyltetrarhodium

$Rh_4(CO)_{12}$ reacts with $PPN(NO_2)$ in THF under CO to ultimately give $PPN[Rh_6N(CO)_{15}]$ in 21% yield. The reaction however, occurs in several steps. Immediately after addition of the solvent, CO_2 is evolved and the infrared spectrum of the deep red solution showed peaks at 2077w, 2043vs, and 2011s cm^{-1} in the terminal carbonyl region and 1875m, 1842m, and 1787ms cm^{-1} in the bridging carbonyl region. This spectrum is very similar to that reported for $[Rh_5(CO)_{15}]^-$ [18]. With stirring and time, the absorptions for $[Rh_6N(CO)_{15}]^-$ grow in along with a broad peak at 1984 cm^{-1} which could be due to $[Rh_6(CO)_{15}]^{2-}$ [19]. In contrast to the cobalt reaction, at no time during the reaction was any evidence found for the presence of any mononuclear fragments such as $[Rh(CO)_4]^-$ [20].

The nuclearity change observed here from four to six is not unique. $Rh_4(CO)_{12}$ itself converts readily to $Rh_6(CO)_{16}$ at 130°C under nitrogen. $Rh_4(CO)_{12}$ also reacts with certain nucleophiles to form $[Rh_6(CO)_{15}X]^-$ (X = Cl, Br, I, CN, SCN) in good yields [22].

Hexadecacarbonylhexarhodium

$Rh_6(CO)_{16}$ reacts with $PPN(NO_2)$ under CO to generate $PPN[Rh_6N(CO)_{15}]$ in 77% yield, eq. 3.

$$Rh_6(CO)_{16} + PPN(NO_2) \rightarrow PPN[Rh_6N(CO)_{15}] + 2CO_2 \qquad (3)$$

The nitrido cluster had been previously prepared and characterized from two different reactions, eqs. 2 and 4 [2].

$$K_2[Rh_6(CO)_{15}] + NOBF_4 \rightarrow K[Rh_6N(CO)_{15}] \ (<10\%) \qquad (4)$$

A number of intermediates were observed in the $PPN(NO_2)$ reaction. Immediately after solvent addition under N_2, the deep red solution exhibited infrared absorptions at 2079ms, 2060m, 2039vs, 2008m, 1810m(sh), 1783ms, and 1700mw cm^{-1} in the carbonyl nitrosyl region. This infrared spectrum is strikingly similar to the reported spectrum of $[Rh_6(CO)_{14}(allyl)]^{1-}$ [23] with the exception of the absorption at 1700 cm^{-1} which could be due to a terminal nitrosyl ligand for the expected isoelectronic product $[Rh_6(CO)_{14}(NO)]^-$. Interestingly, the main product of eq. 4 is reported to give "the infrared spectrum expected for a substituted $[Rh_6(CO)_{14}(NO)]^-$

species", although no details were given [22]. The intermediate observed here unfortunately decomposes under either CO or N_2 to give a second species with an infrared spectrum similar to the intermediate observed in the $Rh_4(CO)_{12}$ reaction. Distinct absorptions attributable to the final product, $[Rh_6N(CO)_{15}]^-$, do not appear until 4 h after solvent addition.

Due to the availability of $Rh_6(CO)_{16}$ and the high yield obtained, this reaction is the preferred method of synthesis of the nitrido cluster.

Dodecacarbonyltetrairidium

$Ir_4(CO)_{12}$ reacts with $PPN(NO_2)$ in THF to generate $PPN[Ir_4(NCO)CO)_{11}]$, $(PPN)_2[Ir_6(CO)_{15}]$, and $(PPN)_2[Ir_8(CO)_{22}]$, eq. 5.

$$Ir_4(CO)_{12} + PPN(NO_2) \rightarrow PPN[Ir_4(NCO)(CO)_{11}] + (PPN)_2[Ir_6(CO)_{15}] + (PPN)_2[Ir_8(CO)_{22}] + CO_2 \quad (5)$$

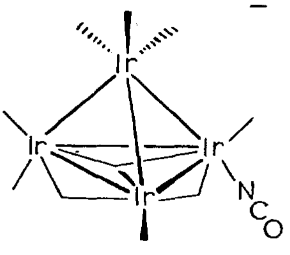
Infrared spectroscopy of the gases evolved in the reaction showed mostly CO_2; very little CO was given off. Removal of the solvent under vacuum, extraction of the residue with diethyl ether, and precipitation of the product with hexane gave $PPN[Ir_4(NCO)(CO)_{11}]$ in 34% yield. The characterization of this material is described below. Infrared spectroscopy of the diethyl ether insoluble material showed a mixture of $[Ir_6(CO)_{15}]^{2-}$ and $[Ir_8(CO)_{22}]^{2-}$ [15].

After the ether-soluble product of the $PPN(NO_2)$ reaction (eq. 5) was identified as an isocyanate, a high yield synthesis of the cluster was developed using $PPN(N_3)$, eq. 6, which gives a 77% yield of the the product. Fast atom bombardment mass

$$Ir_4(CO)_{12} + PPN(N_3) \rightarrow PPN[Ir_4(NCO)(CO)_{11}] + N_2 \quad (6)$$

spectroscopy in the positive ion mode gave a parent peak at m/z 538 corresponding to the PPN^+ cation. In the negative ion mode a parent peak at 1122 daltons, corresponding to $[Ir_4(NCO)(CO)_{11}]^-$, was observed. This peak was followed by a peak at m/z 1077 corresponding to loss of NCO and peaks indicating successive loss of six carbonyls. The infrared spectrum of the cluster has weak and broad absorption at 2210 cm^{-1} in the isocyanate region. It has been reported for $[Ru_3(NCO)(CO)_{11}]^-$ and $[Ru_3(NCO)(CO)_{10}]^-$ that the terminally bound isocyanate has a weak and broad absorption at 2230 cm^{-1} while a bridging isocyanate has a strong, sharp absorption at lower energy [24]. Therefore, both the shape and intensity of the stretch indicate that the isocyanate is terminally bound.

The carbonyl region of the spectrum exhibits peaks at 2078w, 2049vs, 2038s, 2019m, 2004s, and 1836m cm^{-1} indicating the presence of both terminal and



(2)

bridging carbonyls. The similarity of this spectrum to that of the structurally characterized $[Ir_4(CO)_{11}Br]^-$ [25] combined with the above analysis of the isocyanate stretch allows the assignment of structure **2** to $[Ir_4(NCO)(CO)_{11}]^-$.

Hexadecacarbonylhexairidium

The synthesis of $[N(C_2H_5)_4]_2[Ir_6(CO)_{15}]$ via eq. 7 has been reported to proceed in 43% yield [15], however, simple modifications of this procedure allow the isolation of the product in 65% yield.

$$2[Ir(CO)_4]^- + Ir_4(CO)_{12} \rightarrow [Ir_6(CO)_{15}]^{2-} \qquad (7)$$

The dissolution of $Ir_4(CO)_{12}$ in THF seems to be the rate limiting step, and heating to 60°C under CO greatly reduces the reaction time. Fast crystallization from THF/ethanol/diethyl ether enhances the recovery of the product from solution. $Ir_6(CO)_{16}$ can be prepared in basically quantitative yields from the protonation of $[N(C_2H_5)_4]_2[Ir_6(CO)_{15}]$ under CO, eq. 8.

$$[Ir_6(CO)_{15}]^{2-} + 2H^+ \overset{CO}{\rightarrow} Ir_6(CO)_{16} + H_2 \qquad (8)$$

This reaction had been previously reported using glacial acetic acid as both the acid and the solvent [15]. Under those conditions the reaction is reported to take 2 d. By using a stronger acid, CF_3SO_3H, and going to CH_2Cl_2 as a solvent it is possible to reduce the reaction time to approximately 2 min. The insolubility of $Ir_6(CO)_{16}$ in CH_2Cl_2 allows simple isolation procedures, and the product is recovered in 94% yield.

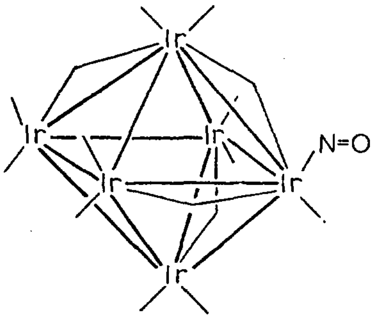
$Ir_6(CO)_{16}$ reacts with one equivalent of $PPN(NO_2)$ in THF to give a species tentatively identified as $PPN[Ir_6(CO)_{15}(NO)]$, eq. 9. Analysis of the gas released in the reaction by infrared spectroscopy showed only CO_2; no CO was evolved.

$$Ir_6(CO)_{16} + PPN(NO_2) \rightarrow PPN[Ir_6(CO)_{15}(NO)] + CO_2 \qquad (9)$$

Slow addition of $PPN(NO_2)$ to $Ir_6(CO)_{16}$ in THF gives a brown solution with the following infrared spectrum in the carbonyl region: 2069w, 2022vs, 2012s, 1982w, and 1821m cm^{-1}. The 2069 cm^{-1} peak is due to unreacted $Ir_6(CO)_{16}$, and the 1983 cm^{-1} peak is due to $[Ir_6(CO)_{15}]^{2-}$. Upon isolation of the product, the final spectrum shows absorptions at 2069vw, 2022vs, 1982vw,br, 1821m cm^{-1} in the $\nu(CO)$ region, however, small amounts of $Ir_6(CO)_{16}$ and/or $(PPN)_2[Ir_6(CO)_{15}]$ were usually present. Examination of the Fourier transform infrared spectra of both $PPN[Ir_6(CO)_{15})(^{14}NO)]$ and $PPN[Ir_6(CO)_{15}(^{15}NO)]$ after removal of the PPN^+ peaks (by subtraction of the PPN(Cl) spectrum) revealed a very weak absorption at 1457 cm^{-1} (^{14}NO) and 1430 cm^{-1} (^{15}NO) attributable to the nitrosyl ligand. The energy of this nitrosyl absorption is indicative of a bridging or a bent nitrosyl ligand. Since the final spectrum in the $\nu(CO)$ region is very similar to the reported spectrum of $[Ir_6(CO)_{15}(COEt)]^-$ [26], we suggest that the nitrosyl ligand is coordinated to one metal in a bent fashion formally donating one electron to the cluster.

A satisfactory elemental analysis was never obtained apparently owing to the difficulties of isolating $PPN[Ir_6(CO)_{15}(NO)]$ that was completely free of $(PPN)_2[Ir_6(CO)_{15}]$ and $Ir_6(CO)_{16}$. The analytical data provided confirmation of the presence of a nitrogen in the cluster.

Fast atom bombardment mass spectroscopy in the negative ion mode shows a high mass peak centered at m/z 1575 which corresponds to $[Ir_6(CO)_{14}(NO)]^-$. The parent peak may simply be unobserved due to a low energy bent-to-linear conversion of the nitrosyl ligand with loss of CO. The proposed structure of $[Ir_6(CO)_{15}(NO)]^-$ is shown as **3**, based on comparison to the known structure of $[Ir_6(CO)_{15}(COEt)]^-$ [26].



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Reaction of $Ir_6(CO)_{16}$ with two equivalents of $PPN(NO_2)$

The appearance of a diethyl ether insoluble "dianion" species in the reaction of $Ir_6(CO)_{16}$ with one equivalent of $PPN(NO_2)$ suggested that two equivalents of nitrite might drive the reaction to completion. When the gases above the reaction of this stoichiometry were quantitatively analyzed by infrared spectroscopy it was found that three equivalents of carbon dioxide were liberated together with one equivalent of nitrous oxide, and that no carbon monoxide was released. Elemental analysis of the isolated product indicated its formulation as $(PPN)_2[Ir_6(CO)_{15}]$, but its infrared spectrum was different from that found for either $[N(C_2H_5)_4]_2[Ir_6(CO)_{15}]$ [15] or the structurally characterized $[N(CH_3)_3(CH_2C_6H_5)]_2[Ir_6(CO)_{15}]$ [27]. In particular, only one $\nu(CO)$ is found (at 1769 cm^{-1}) in the bridging region for the PPN^+ salt, while the others exhibit two absorptions (at 1770 and 1745 cm^{-1} for $N(C_2H_5)_4{}^+$).

In order to confirm the formulation indicated by elemental analysis, the product was analyzed by NMR spectroscopy and fast atom bombardment mass spectrometry. NMR showed neither any hydride resonances in the proton spectrum nor any ^{15}N resonance in the ^{15}N NMR of material prepared from ^{15}N-enriched $PPN(NO_2)$. Fast atom bombardment mass spectrometry in the negative ion mode showed a parent ion centered at m/z 2112 which corresponds to the $\{PPN[Ir_6(CO)_{15}]\}^-$ ion pair. This peak was followed by peaks corresponding to successive loss of nine of the fifteen carbonyls. Also observed was a peak centered at m/z 1574 from the formal loss of PPN from the parent ion pair, followed again by peaks indicating successive loss of 9 of the 15 carbonyls. Final proof for the formulation of the material as $(PPN)_2[Ir_6(CO)_{15}]$ was obtained from direct metathesis to the PPN^+ salt from the tetraethylammonium salt. The dependence of the infrared spectrum, particularly in the bridging CO region, on the cation must be due to ion-pairing effects.

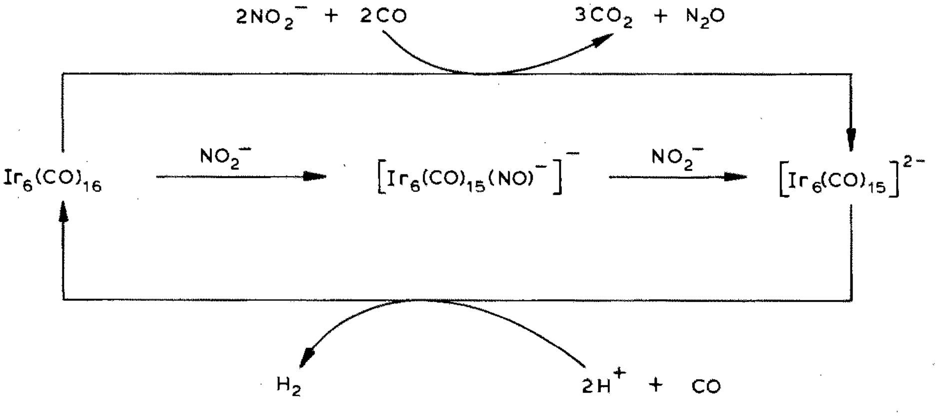
A simple experiment was designed to probe the nature of the initial intermediate in the reaction between $[Ir_6(CO)_{15}(NO)]^-$ and $NO_2{}^-$ that leads to N_2O formation. A solution of enriched $[Ir_6(CO)_{15}(^{15}NO)]^-$ was allowed to react with $PPN(^{14}NO_2)$, and the gases above solution were analyzed by infrared spectroscopy. The energies of the absorptions of the various N_2O isotopomers are: $^{14}N_2O$, 2223.9 cm^{-1}; $^{15}N^{14}NO$, 2202.5 cm^{-1}; $^{14}N^{15}NO$, 2177.6 cm^{-1}; $^{15}N_2O$, 2156.2 cm^{-1} [28]. While these values are well-separated, the two maxima that occur 12–13 cm^{-1} on either side of the centroid for each isotopomer do overlap with the adjacent species. Although this prevented a quantitative determination of the isotope distribution, the qualitative appearance of the infrared spectrum allows two important conclusions. First, the two most prominent absorptions occur at 2212 and 2195 cm^{-1}. The former results from $^{15}N^{14}NO$ and some $^{14}N_2O$, and the latter results from the combination of $^{15}N^{14}NO$ and $^{14}N^{15}NO$. This clearly shows that both the nitrogen on the starting cluster, $[Ir_6(CO)_{15}(^{15}NO)]^-$, and the $^{14}NO_2^-$ end up in the N_2O. Second, the very weak shoulder at ~ 2145 cm^{-1} due to $^{15}N_2O$ suggests that N_2O formation occurs on one cluster (i.e., without the formation of significant amounts of the crossover product $^{15}N_2O$). While some $^{14}N_2O$ is found (as measured by the absorption at 2234 cm^{-1}), this can in part be traced to the 5–10% ^{14}N present in the $Na^{15}NO_2$ and to the small amount of $Ir_6(CO)_{16}$ remaining with the $[Ir_6(CO)_{15}(^{15}NO)]^-$.

If this reaction proceeded as did the first step, eq. 9, one possible intermediate could be $[Ir_6(CO)_{14}(NO)_2]^{2-}$. Deoxygenation of one of the NO ligands could occur before or after N–N bond formation. In the former case the intermediate would contain a nitride, while in the latter situation a hyponitrite ligand would be present. While the formation of N_2O from a nitrido cluster has not been observed, it has been shown that N_2O can be produced from coordinated hyponitrite [29].

The overall stoichiometry of the reaction is shown in eq. 10, where the CO necessary to balance the reaction must come from sacrificial decomposition of an intermediate cluster. Alternatively, CO can be added to the system to improve the yield.

$$Ir_6(CO)_{16} + 2PPN(NO_2) \rightarrow (PPN)_2[Ir_6(CO)_{15}] + 3CO_2 + N_2O \qquad (10)$$

SCHEME 1



If the reactions (eqs. 8 and 10) of the hexameric Ir clusters discussed in the study are examined, the net reaction is shown in eq. 11.

$$2HNO_2 + 3CO \rightarrow H_2 + N_2O + 3CO_2 \qquad (11)$$

The overall cycle is shown in Scheme 1. This cycle, while not particularly useful, is interesting due to the formation of the nitrogen–nitrogen bond on the surface of the cluster, and the similarity this bears to the surface-catalyzed oxidation of CO with NO [30].

Acknowledgement

We gratefully acknowledge the National Science Foundation for supporting this research (Grant Number CHE8410999).

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