interactions between the donor and acceptor molecules. In this regard, the Curie–Weiss magnetic susceptibility behavior of $\mathrm{POZ{-}Ni(tfd)_2}$ argues against coupling of the unpaired electrons of the donor and acceptor ions, but the esr spectrum (single line, g value approximately the average of those of the cation and anion)[7] suggests that weak exchange interactions do occur between D^+ and A^-. The weak absorption observed in the electronic spectrum of $\mathrm{POZ{-}Ni(tfd)_2}$ in a KBr pellet[7] might then be seen as a charge-transfer transition between weakly overlapping $\mathrm{POZ^+}$ and $\mathrm{Ni(tfd)_2^-}$.

Summary

The strong intermolecular interactions previously reported[7] between the donor and acceptor radical ions in the $\mathrm{PTZ{-}Ni(tfd)_2}$ complex have been shown to arise from the relative orientation of the ions in the structure and a favorable DA intermolecular separation, which, taken together, ensure appreciable overlap of the donor and acceptor π orbitals. Although the ionic moieties in the analogous $\mathrm{POZ{-}Ni(tfd)_2}$ complex have been shown to have a similarly favorable relative orientation of their molecular π systems, the intermolecular distance (3.66 Å) is apparently too great to allow appreciable overlap of the π systems and a greatly diminished intermolecular interaction occurs.

Registry No. $\mathrm{PTZ{-}Ni(tfd)_2}$, 53142-51-1; $\mathrm{POZ{-}Ni(tfd)_2}$, 53142-52-2.

Supplementary Material Available. Listings of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$5.00 for photocopy or \$2.00 for microfiche, referring to code number AIC40410A.

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Preparation and Reactions of μ-Oxido-bis[triphenylphosphinenitrosyliridium(0)]

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The details of the preparation of the complex $\mathrm{[Ir(NO)PPh_3]_2O{\cdot}C_6H_6}$ are reported. Some chemical reactions of this complex are described, limited primarily to those reactions in which the oxygen bridge is retained. Two series of complexes, $\mathrm{[IrX(NO)PPh_3]_2O}$ and $\mathrm{[IrX(NO)PPh_3]_2O{\cdot}HgX_2}$ (where X = Cl, Br, or I), are reported, as well as 1:1 addition products formed by reaction of the complex $\mathrm{[Ir(NO)PPh_3]_2O}$ with tetracyanoethylene and the p-fluorophenyldiazonium cation.

Introduction

The crystal and molecular structure of the benzene solvate of μ-oxido-bis[triphenylphosphinenitrosyliridium(0)] was the subject of a previous communication;[1] in this paper we now report the preparation and some chemical reactions of this complex. The molecule contains two formally zerovalent iridium atoms which are linked by an oxygen bridge atom and a bent metal–metal bond.

The most common reaction of the compound is one of oxidation of the metal–metal bond by various species giving rise to two square-planar iridium(I) entities linked by the oxygen bridge. These products do not appear to undergo oxidative addition reactions which are common for such systems.[2] Other observed reactions involve cleavage of the oxygen bridge system.

Experimental Section

The complex *trans*-[$IrCl(CO)(PPh_3)_2$] was prepared from $IrCl_3 \cdot 3H_2O$ by a standard method.[3] All other reagents and solvents were of Analar grade.

Infrared spectra were recorded using a Beckman IR 12 spectrophotometer calibrated with a polystyrene film, accurate to ±2 cm^{-1}. Molecular weight measurements were obtained with a Hewlett-Packard Mechrolab 302 vapor phase osmometer. Thermogravimetric measurements were made with an R. L. Stone furnace and a Cahn electrobalance.

Elemental analyses were performed by A. Bernhardt Laboratory, Mülheim, West Germany. Analysis for halide in the presence of iridium, or mercury and iridium, always necessitated a special separation step to avoid interference which tended to reduce the accuracy of the analysis.

Preparations. 1. [$Ir(NO)PPh_3]_2O \cdot C_6H_6$. (a) The complex *trans*-[$IrCl(CO)(PPh_3)_2$] (1.0 g) and sodium nitrite (2.4 g) were refluxed under a nitrogen atmosphere for 48 hr in a 1:1 mixture by volume of benzene and aqueous (90%) ethanol (200 ml). On cooling the solution, a pale orange powder precipitated. It was collected, washed with water, ethanol, and ether, and dried in air; yield 0.10 g (15%).

(b) The complex *trans*-[$IrCl(CO)(PPh_3)_2$] (1.0 g) and excess sodium nitrite (5.0 g) were refluxed under an atmosphere of nitrogen for 12 hr in a 5:4:1 mixture, by volume, of ethanol, toluene, and water (175 ml). On cooling, a bright orange solid precipitated and was recovered by filtration. It was washed with water, ethanol, and ether and dried in air; yield 0.11 g (17%).

The complex [$Ir(NO)PPh_3]_2O \cdot C_6H_6$ was obtained by dissolving the product from either of the above reactions (0.40 g) in a minimum of boiling benzene (120 ml) under an atmosphere of nitrogen. After filtration, cooling gave a precipitate of pale orange crystals which were recovered and dried in air; yield 0.21 g (50%). *Anal.* Calcd for [$Ir(NO)PPh_3]_2O \cdot C_6H_6$: C, 47.4; H, 3.4; N, 2.6. Found: C, 47.9; H, 3.4; N, 2.6.

A similar recrystallization of crude product from tetrahydrofuran solution gave pale orange crystals of [$Ir(NO)PPh_3]_2O \cdot C_4H_8O$. *Anal.* Calcd for [$Ir(NO)PPh_3]_2O \cdot C_4H_8O$: C, 45.5; H, 3.6; N, 2.7. Found: C, 44.7; H, 3.5; N, 2.9.

Thermogravimetric analysis of the two solids showed that each exhibited weight loss on being heated above 90°. In the case of the benzene solvate, 16.6 mg of solid lost 1.5 mg in weight (calcd 1.2 mg). In the case of the tetrahydrofuran solvate, 19.5 mg of solid lost 1.3 mg in weight (calcd 1.4 mg). The weight loss observed was in each case consistent with there being one molecule of solvent present in the crystal per molecule of the complex. The product after heating in each case was a pale orange crystalline solid. In the benzene solvate case, the sample was analyzed. *Anal.* Calcd for [$Ir(NO)PPh_3]_2O$: C, 43.90; H, 3.07. Found: C, 43.92; H, 2.92.

2. [$IrCl(NO)PPh_3]_2O$. The complex [$Ir(NO)PPh_3]_2O \cdot C_6H_6$ (0.256 g) was suspended in dichloromethane (30 ml) under an atmosphere of nitrogen, and an equimolar amount of mercuric chloride (0.066 g) in solution in aqueous (95%) ethanol (20 ml) was added at room temperature with stirring. An immediate white precipitate formed which became gray and then gray-black during 15 min. Filtration under gravity gave a red solution which was allowed to evaporate during 1 day, when bright red crystals were deposited. The crystals were collected, washed with ethanol and ether, and dried in air; yield 0.160 g (63%).

The complex was recrystallized as large, deep red plates from dichloromethane–hexane. *Anal.* Calcd for [$IrCl(NO)PPh_3]_2O$: C, 40.9; H, 2.8; N, 2.7; Cl, 6.7. Found: C, 41.3; H, 2.9; N, 2.6; Cl, 6.9.

3. [$IrBr(NO)PPh_3]_2O$. Equimolar amounts of the complex [$Ir(NO)PPh_3]_2O \cdot C_6H_6$ (0.147 g) and mercuric bromide (0.050 g) were allowed to react at room temperature in a mixture of CH_2Cl_2 (20 ml) and aqueous (95%) ethanol (15 ml) exactly as in part 2. Deep red crystals of the product were collected, washed with ethanol and ether, and dried in air; yield 0.125 g (76%).

The complex was recrystallized as large, deep red plates from dichloromethane–petroleum ether. *Anal.* Calcd for [$IrBr(NO)PPh_3]_2O$: C, 37.3; H, 2.6; N, 2.5; Br, 14.0. Found: C, 37.5; H, 2.6; N, 2.8; Br, 16.6.

4. [$IrI(NO)PPh_3]_2O$. A solution of iodine (0.039 g) in chloroform (10 ml) was added to an equimolar amount of the complex [$Ir(NO)PPh_3]_2O \cdot C_6H_6$ (0.151 g) in $CHCl_3$ (15 ml). After stirring for several minutes, filtration gave a deep red solution which was diluted with petroleum ether (60 ml). Dark red crystals were recovered after 1 day. These were washed with ether and dried in air; yield 0.130 g (75%).

The complex was recrystallized as very dark red plates from chloroform–ether. *Anal.* Calcd for [$IrI(NO)PPh_3]_2O$: C, 34.9; H, 2.4; N, 2.3; I, 20.5. Found: C, 35.5; H, 2.5; N, 2.2; I, 20.1.

5. [$IrCl(NO)PPh_3]_2O \cdot HgCl_2$. The complex [$IrCl(NO)PPh_3]_2O$ (0.085 g) was dissolved in CH_2Cl_2 (10 ml) at room temperature, and a solution of excess mercuric chloride (0.060 g) in aqueous (95%) ethanol (10 ml) was added. The solution was allowed to evaporate slowly in a stream of nitrogen during several hours, when small orange-red needles were deposited. These were collected, washed with ethanol, and dried in air; yield 0.080 g (75%). *Anal.* Calcd for [$IrCl(NO)PPh_3]_2O \cdot HgCl_2$: C, 32.5; H, 2.3; N, 2.1; Cl, 10.7; Hg, 15.1. Found: C, 31.7; H, 2.2; N, 2.6; Cl, 11.8; Hg, 13.8.

6. [$IrBr(NO)PPh_3]_2O \cdot HgBr_2$. This complex was prepared from the complex [$IrBr(NO)PPh_3]_2O$ (0.090 g) and excess mercuric bromide (0.140 g) exactly as described in part 5. Orange-red needles were collected, washed with ethanol, and dried in air; yield 0.083 g (70%). *Anal.* Calcd for [$IrBr(NO)PPh_3]_2O \cdot HgBr_2$: C, 28.7; H, 2.0; N, 1.9; Br, 21.2; Hg, 13.3. Found: C, 27.4; H, 1.9; N, 1.3; Br, 24.1; Hg, 15.6.

7. [$IrI(NO)PPh_3]_2O \cdot HgI_2$. The complex [$IrI(NO)PPh_3]_2O$ (0.100 g) was treated with excess mercuric iodide (0.20 g) in $CHCl_3$ solution (25 ml) at room temperature. The resulting deep red solution was filtered, and ether (50 ml) was slowly added. Orange needles were rapidly deposited, which were collected after 1 day, washed with ether, and dried in air; yield 0.108 g (80%).

The complex was recrystallized as orange-red needles from chloroform–ether. *Anal.* Calcd for [$IrI(NO)PPh_3]_2O \cdot HgI_2$: C, 25.5; H, 1.8; N, 1.7; I, 30.0; Hg, 11.9. Found: C, 25.5; H, 1.7; N, 1.7; I, 32.8; Hg, 13.2.

8. {[$Ir(NO)PPh_3]_2O$-*p*-$FC_6H_4N_2$}X (Where X = BF_4 or PF_6). The complex [$Ir(NO)PPh_3]_2O \cdot C_6H_6$ (0.185 g) and slightly more than 1 equiv of the salt (*p*-$FC_6H_4N_2$)X (where X = BF_4 or PF_6) were added together to deoxygenated CH_2Cl_2 (30 ml) under an atmosphere of nitrogen, at room temperature. After stirring for a few minutes, the resulting deep red solution was filtered and diluted with ether (200 ml). The product, a pale orange solid in both cases, was precipitated over a period of 2 days; yield approximately 75% in each case.

Both complexes were recrystallized as deep red needles from dichloromethane–toluene. *Anal.* Calcd for {[$Ir(NO)PPh_3]_2O$-*p*-$FC_6H_4N_2$}BF_4: C, 42.2; H, 2.9; N, 4.7; F, 8.0. Found: C, 42.4; H, 2.9; N, 4.5; F, 6.3. Calcd for {[$Ir(NO)PPh_3]_2O$-*p*-$FC_6H_4N_2$}PF_6: C, 40.2; H, 2.7; N, 4.5; F, 10.6. Found: C, 40.5; H, 2.9; N, 4.3; F, 11.6.

Reaction of [$Ir(NO)PPh_3]_2O$ with Excess PPh_3. The complex [$Ir(NO)PPh_3]_2O \cdot C_6H_6$ (0.098 g) was treated with excess PPh_3 (0.211 g) in deoxygenated benzene (30 ml) under an atmosphere of nitrogen. After refluxing for 2 days, the solvent was removed under vacuum, and the residual solid was washed several times with deoxygenated ethanol. The dried product, an orange powder, was identified by elemental analysis and infrared spectrum as the known complex $Ir(NO)(PPh_3)_3$;[4] yield 0.175 g (94%). Removal of solvent from the combined ethanol washings produced a white powder, the infrared spectrum of which contained absorptions characteristic of both PPh_3 and Ph_3PO.[5] *Anal.* Calcd for $Ir(NO)(PPh_3)_3$: C, 64.2; H, 4.5; N, 1.4. Found: C, 64.5; H, 5.1; N, 1.9.

Reaction of [$IrCl(NO)PPh_3]_2O$ with Excess PPh_3. The complex [$IrCl(NO)PPh_3]_2O$ (0.080 g) was treated with a large excess of PPh_3 (0.40 g) in solution in CH_2Cl_2 (10 ml) at room temperature under an atmosphere of nitrogen. Slow evaporation of the solvent in a stream of nitrogen produced a mustard yellow precipitate which was collected by filtration. Evaporation of the filtrate to dryness gave a mixture of deep red crystals and more yellow solid. The red crystals were separated mechanically and washed with cold benzene to remove excess phosphine. The yellow and red solids were identified by elemental analysis and infrared spectra as the known complexes $IrCl_2(NO)(PPh_3)_2$[6] and $Ir(NO)(PPh_3)_3$,[4] respectively. *Anal.* Calcd for $IrCl_2(NO)(PPh_3)_2$: C, 52.8; H, 3.7; N, 1.7; Cl, 8.7. Found: C, 52.9; H, 3.7; N, 1.6; Cl, 8.7. Calcd for $Ir(NO)(PPh_3)_3$: C, 64.2; H, 4.5; N, 1.4. Found: C, 63.0; H, 4.6; N, 1.8.

Reaction of [$IrBr(NO)PPh_3]_2O$ with Excess PPh_3. The complex

Table I. Infrared Absorptions (cm^{-1})[a]

Compd	Nitrosyl str	Metal–oxygen str	Metal–halide str
$[Ir(NO)PPh_3]_2O{\cdot}C_6H_6$	1770 vs, 1738 s		
$[IrCl(NO)PPh_3]_2O$	1854 vs, 1832 vvs	797 vs	310 ms
$[IrBr(NO)PPh_3]_2O$	1848 s, 1824 vvs	823 ms	215 ms
$[IrI(NO)PPh_3]_2O$	1837 s, 1821 vvs	856 sh, 850 sh, 844 s	
$[IrCl(NO)PPh_3]_2O{\cdot}HgCl_2$	1858 vs, 1837 vvs	823 vs	344 s, 281 m[b]
$[IrBr(NO)PPh_3]_2O{\cdot}HgBr_2$	1858 vs, 1838 vvs	816 vs	280 w, 240 w[b]
$[IrI(NO)PPh_3]_2O{\cdot}HgI_2$	1849 m, 1831 vvs	825 vs	
$[Ir(NO)PPh_3]_2O{\cdot}C_2(CN)_4$	1853 sh, 1840 vvs	775 vs	
$\{[Ir(NO)PPh_3]_2O\text{-}p\text{-}FC_6H_4N_2\}BF_4$	1871 vvs, 1858 vs		
$\{[Ir(NO)PPh_3]_2O\text{-}p\text{-}FC_6H_4N_2\}PF_6$	1877 sh, 1871 vvs, 1857 vs		

[a] All spectra were recorded as Nujol mulls of the solids: v, very; s, strong; m, medium; w, weak; sh, shoulder. [b] A more specific assignment is not possible without knowledge of the molecular structure of these complexes.

$[IrBr(NO)PPh_3]_2O$ was treated with excess PPh_3 exactly as described above for the chloro complex. As above, yellow and red solids were identified by elemental analysis and infrared spectra as the known complexes $IrBr_2(NO)(PPh_3)_2$[6] and $Ir(NO)(PPh_3)_3$,[4] respectively. *Anal.* Calcd for $IrBr_2(NO)(PPh_3)_2$: C, 47.7; H, 3.3; N, 1.5; Br, 17.6. Found: C, 47.8; H, 3.5; N, 1.9; Br, 21.1. Calcd for $Ir(NO)(PPh_3)_3$: C, 64.2; H, 4.5; N, 1.4. Found: C, 66.4; H, 4.4; N, 1.3.

Results

Preparation of $[Ir(NO)PPh_3]_2O{\cdot}C_6H_6$. The complex $[Ir(NO)PPh_3]_2O$ is obtained as a benzene solvate in low yield (15%) when the complex *trans*-$[IrCl(CO)(PPh_3)_2]$ and excess sodium nitrite are refluxed for 48 hr in the absence of oxygen in a mixture of aqueous ethanol and benzene. The product obtained with a shorter reaction time is found to be a mixture of $[Ir(NO)PPh_3]_2O{\cdot}C_6H_6$ and *trans*-$[Ir(NO_2)(CO)(PPh_3)_2]$; with longer reaction times (3 days), decomposition to an uncharacterized black material occurs. The complex *trans*-$[Ir(NO_2)(CO)(PPh_3)_2]$, which had been the intended product, is obtained quantitatively by the same reaction in acetone solution.[7]

In the absence of water, or using alcohols other than ethanol or methanol, none of the complex $[Ir(NO)PPh_3]_2O$ is produced, but only uncharacterized black products. This is also the case if nonaromatic solvents (*e.g.*, *N*,*N*-dimethylformamide) are substituted for benzene. The use of toluene in place of benzene allows a shorter reaction time, but the yield is not affected. Reaction with several equivalents of PPh_3 present produces only *trans*-$[Ir(NO_2)(CO)(PPh_3)_2]$ in high yield and eliminates decomposition.

The complex $[Ir(NO)PPh_3]_2O{\cdot}C_6H_6$ is a diamagnetic orange crystalline solid which is stable in air, but solutions when exposed to air decompose rapidly. It is sparingly soluble in such solvents as benzene, tetrahydrofuran, acetone, and dimethyl sulfoxide, depositing crystals from many of the solutions. The crystals obtained from benzene and tetrahydrofuran were treated thermogravimetrically and were observed to lose weight corresponding to the loss of 1 molecule of solvent per molecule of the complex. For the benzene solvate, nitrosyl stretching frequencies are observed in the infrared spectrum at 1770 and 1738 cm^{-1}.

Reactions of the Complex $[Ir(NO)PPh_3]_2O$. (i) Oxidative Addition. The preceding complex was treated with a number of reagents known to give oxidative addition products with iridium(I) species.[2] With hydrogen gas, no reaction is observed under any conditions employed. With chlorine and bromine, reaction occurs readily, but the products are intractable black solids which could not be characterized.

Reaction was then attempted with less strongly oxidizing reagents (*e.g.*, iodine and mercuric halides), but in these cases, instead of oxidative additions to the individual iridium atoms occurring, oxidation of the metal–metal bond was observed.

(ii) Oxidation of the Metal–Metal Bond. The complex $[Ir(NO)PPh_3]_2O$ reacts readily with 1 equiv of mercuric chloride, mercuric bromide, or iodine, resulting in oxidation of the metal–metal bond without disruption of the oxygen bridge, according to the equations given below. In the reaction with mercuric salts, the other product is mercury metal. This simple reaction is not found to occur with mercuric iodide; *i.e.*

$$[Ir(NO)PPh_3]_2O + HgX_2 \rightarrow [IrX(NO)PPh_3]_2O + Hg$$

where X = Cl or Br, and

$$[Ir(NO)PPh_3]_2O + I_2 \rightarrow [IrI(NO)PPh_3]_2O$$

The crystal and molecular structure of μ-oxido-bis[chlorotriphenylphosphinenitrosyliridium(I)] has been determined by an X-ray diffraction study, and the details of the structure are given in the following paper. The molecule is found to contain two identical square-planar iridium(I) entities, linked by a common oxygen bridge atom, the two planes being skewed to minimize steric crowding. This reaction thus represents an oxidation of the metal–metal bond by chlorine.

The complexes $[IrX(NO)PPh_3]_2O$ (X = Cl, Br, or I) are air stable as solids and are sparingly soluble in solvents such as chloroform and dichloromethane, from which they may be crystallized unchanged. The solubilities are so low ($\simeq 5 \times 10^{-3}$ *M*) that reliable molecular weights could not be obtained by osmometry. The details of the infrared spectra of all these complexes are given in Table I.

Reaction of the complex $[Ir(NO)PPh_3]_2O$ with excess $HgCl_2$ or $HgBr_2$ or reaction of the complexes $[IrX(NO)PPh_3]_2O$ with excess HgX_2 (where X = Cl, Br, or I) is found to result in the formation of another series of compounds. It was thought initially that these products were the result of oxidative addition to the iridium(I) atoms, but elemental analysis results indicate that in each case only 1 mol of mercuric halide has been added. The stoichiometry of the reactions is given in the equations

$$[Ir(NO)PPh_3]_2O + 2HgX_2 \rightarrow [IrX(NO)PPh_3]_2O{\cdot}HgX_2 + Hg$$

where X = Cl or Br, and

$$[IrX(NO)PPh_3]_2O + HgX_2 \rightarrow [IrX(NO)PPh_3]_2O{\cdot}HgX_2$$

where X = Cl, Br, or I.

The complexes are formulated as $[IrX(NO)PPh_3]_2O{\cdot}HgX_2$ (where X = Cl, Br, or I) for convenience only, since the structures are presently unknown. All three complexes are air stable as solids. The complexes where X = Cl or Br are insoluble in all solvents tried, but that in which X = I is sparingly soluble in $CHCl_3$ and CH_2Cl_2. The solutions are air stable, and $[IrI(NO)PPh_3]_2O{\cdot}HgI_2$ may be recrystallized unchanged, but the solubility is too low for reliable molecular weight measurements to be obtained by osmometry.

The infrared spectral details for the three complexes are given in Table I; they are very similar to the spectra observed for the complexes $[IrX(NO)PPh_3]_2O$ (where X = Cl, Br, or I).

The complex $[Ir(NO)PPh_3]_2O$ also reacts readily with tetracyanoethylene to form a 1:1 adduct which is obtained as air-stable orange crystals. The preparation and crystal structure of this complex is being reported elsewhere.[8] The structure shows that the olefin has inserted into the metal–metal bond with one carbon atom bound to each iridium atom. Like the dichloro complex, the molecule thus contains two basically square-planar iridium(I) entities linked by a common oxygen atom, but in this case it is the carbon–carbon bridge which has oxidized the metal–metal bond. The solid is soluble in chloroform and dichloromethane, giving air-stable solutions from which it may be recovered unchanged. The molecular weight measured by osmometry at a concentration of 8×10^{-3} *M* in chloroform solution was 1050 (calcd 1113). Infrared details of the complex are given in Table I.

Reaction was attempted with other olefins. With ethylene, alkyl-substituted ethylenes, acrylonitrile, and fumaronitrile, no reaction was observed to occur under any of the conditions tried. With tetrafluoroethylene a rapid reaction occurred, producing a brown intractable solid which could not be characterized.

(iii) Reaction at the Bridge System. The complex $[Ir(NO)PPh_3]_2O$ is found to react in benzene with excess PPh_3, the products being the complex $Ir(NO)(PPh_3)_3$ and triphenylphosphine oxide, as given by

$$[Ir(NO)PPh_3]_2O + 5PPh_3 \rightarrow 2Ir(NO)(PPh_3)_3 + Ph_3PO$$

The complex $Ir(NO)(PPh_3)_3$ is produced quantitatively and was identified by elemental analysis and from its known nitrosyl infrared absorption[4] at 1600 cm^{-1}. The Ph_3PO was identified from its characteristic infrared absorption[5] at 1180 cm^{-1}. Under identical conditions, no reaction is observed with triphenylarsine.

Reactions of the complexes $[IrX(NO)PPh_3]_2O$ (where X = Cl or Br) with excess PPh_3, but in dichloromethane solutions, were also studied. These reactions resulted in the formation of two distinct products which were separated by fractional crystallization. In the case where X = Cl, the two products were identified by elemental analysis and their nitrosyl stretching frequencies in the infrared region as the known complexes[4,6] $IrCl_2(NO)(PPh_3)_2$ (ν(NO) at 1560 cm^{-1}) and $Ir(NO)(PPh_3)_3$ (ν(NO) at 1600 cm^{-1}). In the case where X = Br, the two products were similarly identified as $IrBr_2(NO)(PPh_3)_2$ (ν(NO) at 1560 cm^{-1}) and $Ir(NO)(PPh_3)_3$.

(iv) Other Reactions. The complex $[Ir(NO)PPh_3]_2O$ reacts readily in chloroform or dichloromethane solution with the tetrafluoroborate and hexafluorophosphate salts of the *p*-fluorophenyldiazonium cation to give 1:1 adduct complexes. The products are obtained as air-stable red crystals which are soluble in a variety of solvents. In ionizing solvents (acetone, tetrahydrofuran, acetonitrile, etc.) rapid decomposition occurs. Solutions in $CHCl_3$ or CH_2Cl_2 are stable. Molecular weight measurement by osmometry of the BF_4 salt in $CHCl_3$ solution gave anomalously high results: 1560 at 1.2×10^{-2} *F* and 1380 at 6.0×10^{-3} *F* (calcd 1195). Details of the infrared spectra of the two complexes are given in Table I.

Discussion

Infrared Spectra. The infrared absorptions which are observed in the spectra of the complexes reported are due to coordinated nitrosyl, halide, and triphenylphosphine ligands and to an iridium–oxygen–iridium bridge system.

The infrared absorptions of coordinated PPh_3 are well known,[5] and such absorptions appear in the spectra of all of the complexes prepared; these bands have been assigned but are omitted from Table I for simplicity.

Iridium–halogen stretching frequencies have been assigned in a variety of complexes.[6,9] Similarly the nitrosyl ligand stretching vibration has been assigned in several iridium complexes.[4,6] The iridium–halogen and nitrosyl stretching frequencies of the compounds prepared have been assigned in Table I.

The molecular structures of the complexes $[Ir(NO)PPh_3]_2O{\cdot}C_6H_6$,[1] $[Ir(NO)PPh_3]_2O{\cdot}C_2(CN)_4$,[8] and $[IrCl(NO)PPh_3]_2O$[10] are known. The first contains an Ir–O–Ir bridge with an angle close to 82°; the angles in the other two complexes are close to 131 and 134°, respectively. Nonlinear metal–oxygen–metal systems have been observed to exhibit an asymmetric stretching absorption (ν_2) in the infrared region at 700–900 cm^{-1}, and normal-coordinate analysis has shown that this absorption frequency will move toward higher energy as the bond angle increases.[11] The very strong bands observed at 775 and 797 cm^{-1} in the spectra of the complexes $[Ir(NO)PPh_3]_2O{\cdot}C_2(CN)_4$ and $[IrCl(NO)PPh_3]_2O$ are thus assigned to the ν_2(Ir–O–Ir) mode. Similar absorption between 800 and 850 cm^{-1} is observed in the spectra of all but three of the complexes reported. It is concluded that the appearance of this band indicates the presence of an Ir–O–Ir bridge.

In the spectrum of the complex $[Ir(NO)PPh_3]_2O{\cdot}C_6H_6$ no strong band is observed between 700 and 900 cm^{-1}; a weak absorption might be obscured by PPh_3 modes occurring at 700–750 cm^{-1}. However, the bridge system in this molecule is not comparable to the ones discussed above. The small bond angle (82°) is due to the presence of a bent metal–metal bond, giving rise to a three-atom ring system. The normal modes and the related absorption frequencies are likely to be very different in this ring as compared to the two complexes discussed above. In any case, no definite absorptions can be assigned to this mode.

The nitrosyl ligand stretching frequency in a metal complex can be related to the oxidation state of the metal atom,[12] higher frequencies implying increasing oxidation state, providing the M–N–O linkage remains linear. The nitrosyl stretching frequencies in the complexes $[IrX(NO)PPh_3]_2O$ (where X = Cl, Br, or I) are increased by 70–80 cm^{-1} from those observed in the complex $[Ir(NO)PPh_3]_2O{\cdot}C_6H_6$. In the case where X = Cl, the increase is compatible with the known structure,[10] since the metal–metal bond has been oxidized. Since the complexes where X = Br or I are similar in physical and chemical properties, it is suggested that all three complexes may have the same structure. Similarly the nitrosyl stretching frequencies in the infrared spectrum of the complex $[Ir(NO)PPh_3]_2O{\cdot}C_2(CN)_4$ appear some 85 cm^{-1} to higher energy than in the complex $[Ir(NO)PPh_3]_2O{\cdot}C_6H_6$.

The infrared spectra of the three complexes $[IrX(NO)PPh_3]_2O{\cdot}HgX_2$ are definitely distinct from those of the complexes $[IrX(NO)PPh_3]_2O$ (where X = Cl, Br, or I) but in all cases the observed nitrosyl stretching frequencies and the ν_2 oxygen bridge frequencies are shifted by only 10–20 cm^{-1}. Oxidative addition in a very similar iridium nitrosyl system[13] is known to increase the nitrosyl stretching frequency by at least 50 cm^{-1}. Very little if any relative oxidation of either iridium can have occurred, and thus the mercuric halide does not appear to have been oxidatively added in these complexes. It is possible to suggest a structure for the chloro complex, compatible with the observations, in which the two chlorine atoms attached to the iridium atoms are coordinated to the $HgCl_2$ molecule to give a pseudotetrahedral $HgCl_4$ system, which is well known in mercury(II) chemistry.[14] An X-ray diffraction study is currently being undertaken on the complex $[IrI(NO)PPh_3]_2O{\cdot}HgI_2$.

The structures of the salts $\{[Ir(NO)PPh_3]_2O$-*p*-$FC_6H_4N_2\}X$ (where X = BF_4 or PF_6) are also unknown. In both salts, the nitrosyl stretching frequencies are observed some 100 cm^{-1} to higher energy than in the complex $[Ir(NO)PPh_3]_2O{\cdot}C_6H_6$, indicating that oxidation of the metal–metal bond has occurred. No strong absorption is observed in the region 700–900 cm^{-1} for either salt, except for a band at 840 cm^{-1} in the PF_6 case, which is assigned as a mode of the anion.[15] The infrared spectra confirm that both anions are uncoordinated[15,16] and at present no explanation can be offered for the high molecular weight observed in $CHCl_3$ solution. An X-ray diffraction study on the PF_6 salt is currently under way.

Reactions with Excess Triphenylphosphine. The reaction of the complex $[Ir(NO)PPh_3]_2O$ with PPh_3 seems to involve the removal of the oxygen atom from the bridge and the addition of 2 mol of phosphine to each of the fragments $[Ir(NO)PPh_3]$. The final product contains only iridium(−1).

We suggest that the reactions of the complexes $[IrX(NO)PPh_3]_2O$ (where X = Cl or Br) with PPh_3 follow initially a similar pattern, with removal of the oxygen atom to leave the two fragments $[IrX(NO)PPh_3]^+$ and $[IrX(NO)PPh_3]^-$. Addition of 1 mol of phosphine to the former fragment would result in the formation of the cation $[IrX(NO)(PPh_3)_2]^+$ which is known[13] to accept halide ion readily, to form the complex $IrX_2(NO)(PPh_3)_2$, one of our observed products. This halide ion might be transferred from the other fragment $[IrX(NO)PPh_3]^-$ which on subsequent addition of 2 mol of phosphine would lead to the formation of our second observed product, $Ir(NO)(PPh_3)_3$.

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Registry No. $[Ir(NO)PPh_3]_2O$, 26317-79-3; $[IrCl(NO)PPh_3]_2O$, 53260-38-1; $[IrBr(NO)PPh_3]_2O$, 53260-39-2; $[IrI(NO)PPh_3]_2O$, 53260-40-5; $[IrCl(NO)PPh_3]_2O{\cdot}HgCl_2$, 53260-35-8; $[IrBr(NO)PPh_3]_2O{\cdot}HgBr_2$, 53260-36-9; $[IrI(NO)PPh_3]_2O{\cdot}HgI_2$, 53260-37-0; $[Ir(NO)PPh_3]_2O{\cdot}C_2(CN)_4$, 53260-33-6; $\{[Ir(NO)PPh_3]_2O{\cdot}p\text{-}FC_6H_4N_2\}BF_4$, 53449-42-6; $\{[Ir(NO)PPh_3]_2O{\cdot}p\text{-}FC_6H_4N_2\}PF_6$, 53352-74-2; *trans*-$[IrCl(CO)(PPh_3)_2]$, 15318-31-7; $HgCl_2$, 7487-94-7; $HgBr_2$, 7789-47-1; HgI_2, 7774-29-0; $(p\text{-}FC_6H_4N_2)BF_4$, 19578-37-1; $(p\text{-}FC_6H_4N_2)PF_6$, 53260-51-8; PPh_3, 603-35-0.

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Crystal and Molecular Structure of the Bridged Oxygen Complex μ-Oxido-bis[chlorotriphenylphosphinenitrosyliridium(I)]

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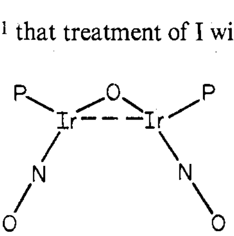
An X-ray crystal structure analysis has been carried out on μ-oxido-bis[chlorotriphenylphosphinenitrosyliridium(I)]. Crystals belong to the triclinic system, space group $P\bar{1}$, $a = 16.828$ (8) Å, $b = 11.515$ (6) Å, $c = 10.667$ (5) Å, $\alpha = 66.05$ (1)°, $\beta = 107.37$ (1)°, and $\gamma = 100.41$ (1)°, with two molecules per cell. The complex, which is prepared by treating μ-oxido-bis[triphenylphosphinenitrosyliridium(0)] with $HgCl_2$, has the Ir–O–Ir bridge intact (but with a more obtuse angle) and square-planar coordination about the iridium atoms.

Introduction

It has been shown[1] that treatment of I with 1 equiv of $HgCl_2$ yields $[IrCl(NO)PPh_3]_2O$. We report here a crystal structure analysis of this product confirming that the Ir–O–Ir bridge is left intact but that the Ir–Ir bond has undergone oxidative cleavage.



I

Experimental Section

Crystals of known elemental analysis were supplied by Professor A. Walker.[1]

Crystal data for $Ir_2C_{36}H_{30}N_2O_3Cl_2P_2$, of formula weight 1055.5, are as follows: triclinic, $P1$ or $P\bar{1}$ (latter confirmed); $a = 16.828$ (8), $b = 11.515$ (6), $c = 10.667$ (5) Å; $\alpha = 66.05$ (1), $\beta = 107.37$ (1), $\gamma = 100.41$ (1)°; $V = 1798.4$ (7) Å^3; $\rho_o = 1.94$ (1), $\rho_c = 1.95$ g cm^{-3} for $Z = 2$. No molecular symmetry required.

The crystal used for data collection was of approximate dimensions 0.12 × 0.12 × 0.03 mm mounted perpendicular to the plate. Intensities were collected on a computer-controlled Picker four-circle diffractometer equipped with pulse height analyzer using filtered Cu Kα radiation. Scanning was in θ–2θ mode at 2° min^{-1}. Background was determined for 30 sec at each end of the scan range of 2.2° adjusted for α splitting. The takeoff angle was 3.0°. Throughout the course of data collection there was no significant deviation in the standard reflections recorded after every 50 reflections. Counting statistics