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Radiation induced reactions of some platinum metal nitrosyl complexes containing tertiary phosphine, arsine and stibine ligands

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Abstract

Photochemical reactions of complexes of the stoichiometric type $M(NO)X_3(Ph_3Y)_2$ for M = Ru, Os; Y = P, As, Sb; X = Cl, Br, I and $M(NO)X_2(Ph_3Y)_2$ for M = Rh, Ir; Y = P, As; X = Cl, Br, I, have been investigated. In many of the reactions one of the organo-pnictide ligands (Ph_3Y) is oxidized and remains coordinated (through the oxygen) to the transition metal. In the case of rhodium and iridium complexes, however, different reactions occur with complete loss of NO from the metal centre. Oxidation studies of the free ligands, and mass spectrometric analysis of gaseous reaction products have been used to elucidate the nature of the oxidizing agent for the complexes. The photochemical reactions of the complexes $Ru(NO)X_3(Et_2PhP)_2$ for X = Cr, Br, I have also been studied and they differ from the others in that isomerization occurs from the *trans* isomer to the *cis–meridional* isomer.

Introduction

Bis-organosulfide nitrosyl complexes of ruthenium and osmium such as $[Ru(NO)Br_3(Et_2S)_2]$ have been reported to undergo photochemical oxidation reactions [1–4]. One of the organosulfide ligands is oxidized to organosulfoxide, which then coordinates to the metal centre through the oxygen. In the present work the investigations have been extended to tertiary phosphine, arsine and stibine nitrosyl complexes of ruthenium, osmium, rhodium and iridium.

Experimental

Identification of the starting materials and their reaction products

The compounds prepared and their reaction products were identified by means of their elemental analysis (obtained from the Micro-analytical Laboratory, University of Otago, Dunedin) and spectroscopic properties. IR spectra of the compounds (as KBr discs) were recorded on a Pye Unicam SP3-300 spectrophotometer. The ^1H and ^{13}C NMR spectra were obtained in deuterated chloroform or d_6-dimethyl sulfoxide, using a Varian XL300 spectrometer operating at 299.93 MHz. Gaseous products were analysed using a SMS DATAQUAD mass spectrometer, and an AEI MS 902 mass spectrometer for high resolution studies. X-ray powder diffraction patterns were obtained with a Philips PW X-ray generator, a Philips PW 1710 control unit and Cu Kα radiation.

Preparation of the compounds

Ligands were obtained from commercial sources and used without further purification. The complexes $[M(NO)X_3(Ph_3Y)_2]$: M = Ru, Os; X = Cl, Br, I; Y = P, As, Sb; and $[M(NO))X_2(Ph_3Y)_2]$: M = Rh, Ir; X = Cl, Br, I; Y = P, As were prepared by reported methods [5–9] with modifications as outlined below. Yields of $[Ru(NO))X_3(PPh_3)_2]$ were increased if the intermediate species '$[Ru(NO)X_3]$' formed from the reaction of NO gas on $RuCl_3nH_2O$ was allowed to stand overnight in solvent saturated with NO prior to the addition of PPh_3. The complex $[Os(NO)Br_3(PPh_3)_2]$ was readily prepared using $(H_3O)_2[OsCl_6]$ as the starting material, (generated from the ammonium salt using cation exchange [10]). The compounds gave satisfactory elemental analytical results and spectroscopic data, which agreed with published results. The diethylphenylphosphine complexes $[Ru(NO)X_3(Et_2PhP)_2]$, X = Cl, Br and I were prepared according to reported methods [11].

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Oxidation of the ligands

The oxidation of the free ligands using reaction conditions and the apparatus described previously [2, 3] was investigated by treating solutions of the compounds with either NO, NO_2 or O_2. The results are summarized in Table 1.

Triphenylphosphine is readily oxidized by both oxides of nitrogen in reagent grade chloroform (the solvent used in the photochemical studies) as reported to occur in other solvents [12–17]. The rate of oxidation, as estimated by the appearance of triphenylphosphineoxide, was faster using the nitrogen oxides compared with using O_2 and UV radiation. Triphenylphosphineoxide was identified from its ^1H NMR spectrum; $\delta = 7.62$ ppm (shifted from 7.35 ppm), and new absorbances in the IR spectrum at 1120 and 1180 cm^{-1} [18–24]. The mass spectrum of gaseous products, when NO was used, showed an increase in peak of mass 44 accompanied by a reduction in peak of mass 30 during the reaction. From this it was deduced that NO oxidized the phosphine and was itself reduced to nitrous oxide

$$2NO + PPh_3 \longrightarrow N_2O + OPPh_3$$

Diethylphenylphosphine was readily oxidized using dioxygen together with either UV radiation or heating [19]. The ^1H NMR spectrum of the product had resonances at $\delta = 1.22$ (triplet), 3.69 (quartet) and 7.70 (multiplet) ppm and new absorbances in the IR spectrum at 1120 and 1190 cm^{-1} [18, 19]. The reaction contrasts with that of triphenylphosphine which is not oxidized by O_2 and heating. Diethylphenylphosphine was also oxidized with NO. A more complex reaction occurs when NO_2 is used and an adduct of the form $Et_2PhPO \cdot N_2O_4$ was produced. Extra absorbances in the IR spectrum at 1300 and 1650 cm^{-1} are attributable to N_2O_4 [16–18].

Triphenylarsine was readily oxidized with both NO and NO_2, but the latter reagent also produces a dinitrogen tetraoxide adduct, $Ph_3AsO \cdot N_2O_4$. The spectral features were: ^1H NMR, $\delta = 7.60$ ppm [16–18], $\nu(AsO) = 880$ cm^{-1} [21, 25, 26], and absorptions due to N_2O_4 1350, 1665 cm^{-1} [16, 18]. No reaction occurred with dioxygen even with UV radiation. In contrast triphenylstibine was readily oxidized with dioxygen under UV radiation ($\nu(SbO) = 660$ cm^{-1} [26]), but not with NO or NO_2 or O_2 alone.

TABLE 1. Oxidation of Ph_3Y (Y = P, As, Sb) and Et_2PhP with NO, NO_2 and O_2

Ligand	Oxidizing agents				
	NO	NO_2	O_2	O_2+UV	O_2+heat
Ph_3P	readily	readily	no	slower	no
Et_2PhP	yes	yes + adduct	[a]	readily	readily
Ph_3As	readily	readily + adduct	no	no	no
Ph_3Sb	no	no	no	yes	[a]

[a] No reaction carried out.

Photochemical reactions of the complexes

Solutions of the complexes were stable under reflux and in the absence of light. In light, however, the complexes undergo chemical changes at ambient temperatures. The changes were investigated using both sunlight and a mercury discharge lamp as radiation sources. No attempt was made to define the radiation intensity and the critical wavelength. Reactions in sunlight generally took many hours to several weeks, whereas in the presence of the more intense Hg lamp the reactions proceeded in a few hours. The majority of the reactions reported in this work were carried out using sunlight as the changes could be monitored more readily. Solutions or suspensions of the complexes in glass tubes were placed in direct sunlight. The course of the reactions was monitored spectroscopically (NMR and IR) and stopped when there was no evidence for remaining starting material. A summary of the reactions investigated and the results obtained are given in Table 2.

$[Ru(NO)X_3(PPh_3)_2]$ (X = Cl, Br)

The chloro and bromo complexes are insoluble in reagent grade chloroform, and suspensions were exposed to sunlight for varying periods of time (1–2 days to 2–3 weeks). No visible changes occurred but the materials left after removal of the solvent displayed different infrared spectra to that of the starting materials. The new absorptions at 1120, 720 and 540 cm^{-1} were assigned to $\nu(PO)$, $\delta(PO)$ and $\delta(RuO)$ respectively [18, 19]. There was no evidence of an absorption at 1180 cm^{-1} which would be expected for uncoordinated $OPPh_3$ [18, 19]. Mass spectrometric analysis of the gaseous products indicated peaks at masses 44 and 30, which were assigned to N_2O and NO, respectively. The addition of free PPh_3 to the suspension inhibited the formation of the peak at mass 30. Elemental analytical results on the solid products isolated were consistent with the stoichiometry $[Ru(NO)X_3(PPh_3)(OPPh_3)]$ (X = Cl and Br). *Anal.* for the chloro complex: Found: C, 55.6; H, 4.6. Calc. for $[Ru(NO)Cl_3(PPh_3)(OPPh_3)]$ ($C_{36}H_{30}Cl_3NO_2P_2Ru$): C, 55.6; H, 3.9%. For the bromo-complex: Found: C, 47.6; H, 4.1. Calc. for $[Ru(NO)Br_3(PPh_3)(OPPh_3)]$ ($C_{36}H_{30}Br_3NO_2P_2Ru$): C, 47.4; H, 4.1%. The low solubility of the starting materials and products precluded doing NMR measurements.

$[Ru(NO)X_3(Et_2PhP)_2]$ (X = Cl, Br, I)

The complexes, dissolved in chloroform, changed from orange to dark green solutions within a few hours of irradiation. No evidence was obtained from either mass

TABLE 2. Summary of the photochemical reactions of nitrosyl complexes of ruthenium, osmium, rhodium, and iridium

Starting material	Solubility in $CHCl_3$	Products of irradiation	Probable oxidant	Evidence[a]
Ruthenium $[Ru(NO)X_3(R_2S)_2]$[b] X = Cl, Br, I	soluble	$[Ru(NO)X_3(R_2S)(R_2SO)]$, $[Ru(NO)X_3(R_2SO)]_2$, free R_2SO, R_2SO_2	NO_2	MS, IR, NMR, UV, XRS, EA
$[Ru(NO)X_3(Ph_3P)_2]$ X = Cl, Br	insoluble	$[Ru(NO)X_3(Ph_3P)(Ph_3PO)]$, free Ph_3PO for X = Br	NO	MS, IR, EA
t-$[Ru(NO)X_3(Et_2PhP)_2]$ X = Cl, Br, I	soluble	isomerization *c*-$[Ru(NO)X_3(Et_2PhP)_2]$	none	MS, IR, NMR, XRS, EA
$[Ru(NO)X_3(Ph_3As)_2]$ X = Cl, Br	insoluble	$[Ru(NO)X_3(Ph_3As)(Ph_3AsO)]$, free Ph_3AsO	NO, NO_2	IR, NMR
$[Ru(NO)Cl_3(Ph_3Sb)_2]$	soluble	*trans*-$[Ru(NO)Cl_3(Ph_3SbO)_2]$	O_2	IR, NMR, EA
Osmium $[Os(NO)X_3(Ph_3P)_2]$ X = Cl, Br	insoluble	$[Os(NO)X_3(Ph_3P)(Ph_3PO)]$, free Ph_3PO	NO, NO_2	IR, NMR, EA
Rhodium $[Rh(NO)X_2(Ph_3P)_2]$ X = Cl, Br, I	sparingly soluble	NO lost completely, mixture of products, free Ph_3PO	NO, NO_2	IR, NMR
$[Rh(NO)X_2(Ph_3As)_2]$ X = Cl, Br, I	sparingly soluble	NO lost completely, mixture of products, evidence for coordinated and free Ph_3AsO	NO, NO_2	IR, NMR
Iridium $[Ir(NO)X_2(Ph_3P)_2]$ X = Cl, Br, I	sparingly soluble	NO lost completely, mixture of products, free Ph_3PO	NO, NO_2	IR, NMR

[a] MS = mass spectrometry, IR = infrared spectroscopy, NMR = nuclear magnetic resonance spectroscopy, UV = Ultraviolet and visible spectroscopy, XRS = single crystal diffraction analysis, EA = elemental analysis. [b] Refs. 1–4.

spectrometric or IR spectral data for any obvious change in the starting material, and this was verified by the elemental analytical results on the solid obtained after irradiation. *Anal.* Found: C, 34.6; H, 5.1. Calc. for [Ru(NO)Br_3(Et_2PhP)$_2$] ($C_{20}H_{30}Br_3NOP_2Ru$): C, 34.2; H, 4.3%. However, there were major differences in the ^1H and ^{13}C NMR spectra of the starting and product materials. For the bromo complex the ^1H NMR spectrum of the starting material has three main features: phenyl resonances at 7.48 and 7.53 ppm, a quintet at 1.25 ppm assigned to the methyl protons, and two 13 peak multiplets at 2.75 and 3.05 ppm assigned to the inequivalent methylene protons [27]. The spectrum also shows evidence for virtual coupling [28–31], which occurs when two organophosphine ligands are in the *trans* configuration. The methyl quintet is due to the overlap of three triplets, split by the methylene protons and the two phosphorus nuclei. The thirteen peak multiplet, observed for the methylene protons, arises from the overlap of two octets. These octets arise from the splitting of triplets (by the phosphorus nuclei) into three quartets (by the methyl protons) which overlap to give an octet. Decoupling of the methyl protons leaves two doublets of triplets, and decoupling of one of the methylene protons leads to the collapse of the methyl quintet into a sextet. The ^{13}C NMR spectrum shows two triplets due to coupling between the carbon atoms and the virtually coupled phosphorous nuclei consistent with equivalent magnetic environments for the two diethylphenylphosphine ligands. The molecular structure of the bromo complex, to be reported, confirms the *trans* arrangement of the two diethylphenylphosphine ligands. The chloro and iodo complexes showed identical features in their ^1H NMR spectra, and had closely similar X-ray powder diffraction patterns to the bromo complex. Hence they probably also have the *trans* configuration.

Upon irradiation the ^1H NMR resonances arising from the *trans* complex disappear and new resonances appear and increase in intensity with the time of irradiation. For the bromo product four new septets at $\delta = 1.80$, 2.50, 2.65 and 2.92 ppm appear, and two new quintets at 0.9 and 1.05 ppm. These are considered to be due to formation in solution of a *cis-meridonal* isomer [32], for which virtual coupling is not possible. Decoupling experiments show that the quintet at 0.9 ppm is related to the septets at 1.80 and 2.92 ppm, and the quintet at 1.05 ppm to the two at 2.50 and 2.92 ppm. One set of resonances is assigned to the E_2PhP ligand coordinated opposite the NO ligand, and the other *trans* to a bromine atom. The methylene septets arise from the overlap of two quintets (quintets due to overlap of two quartets). The methyl quintets are due to the overlap of two triplets, due to the coupling of two phosphorus nuclei. Similar changes occur in the ^1H NMR spectra for the chloro and iodo complexes, and a similar isomerization is proposed. In one experiment, for the iodo complex, after a long radiation time evidence was found in the IR and ^1H NMR spectra for free diethylphenylphosphineoxide. In all cases only the *trans* isomer crystallized from solution.

[Ru(NO)X_3($AsPh_3$)$_2$] (X = Cl, Br)

The sparingly soluble complexes showed little visible change when their chloroform suspensions were irradiated. The IR spectra of the recovered materials however, displayed new peaks; a strong broad peak at 850 cm^{-1} which was attributed to ν(AsO) and a weaker peak at 460 cm^{-1} attributed to ν(RuO). These peaks have been reported before for complexes of the form [Ru(NO)X_3($AsPh_3$)($OAsPh_3$)] [25, 33]. The ^1H NMR spectra of the recovered material showed a reduction in the intensity of the signal arising from the starting material, and an increase in the intensity of a new resonance. Eventually, after prolonged irradiation, the appearance of resonances associated with uncoordinated $OAsPh_3$ became apparent.

[Ru(NO)Cl_3($SbPh_3$)$_2$]

The triphenylstibene complex is readily soluble in chloroform. Whereas there is no obvious change when a solution is irradiated, the IR spectrum of the product has a new absorbance at 555 cm^{-1} assignable to ν(SbO) of a coordinated $OSbPh_3$ ligand. There was no evidence for the starting material or any uncoordinated $OSbPh_3$, in the ^1H NMR spectrum of the product. The spectrum, which was simple, suggested a *trans* isomer of [Ru(NO)Cl_3($OSbPh_3$)$_2$]. Elemental analytical results were consistent with this stoichiometry. *Anal.* Found: C, 44.9; H, 4.8. Calc. for [Ru(NO)Cl_3($OSbPh_3$)$_2$] ($C_{36}H_{30}Cl_3NO_3RuSb_2$): C, 44.3; H, 3.1%.

[Os(NO)X_3(PPh_3)$_2$] (X = Cl, Br)

Upon irradiation the insoluble orange coloured complexes suspended in chloroform appeared to go into solution forming an orange solution for the chloro complex, and a pale pink solution for the bromo complex. The ^1H NMR spectra of the solutions showed resonances attributable to phenyl groups and after some time resonances due to uncoordinated $OPPh_3$. The IR spectra had absorbances attributable to coordinated $OPPh_3$; 1120, 720 and 560 cm^{-1} and eventually an additional absorbance at 1180 cm^{-1} appeared indicative of free $OPPh_3$. Elemental analytical results for the complexes isolated from the solutions, were reasonably consistent with the stoichiometry [Os(NO)X_3(PPh_3)($OPPh_3$)]. *Anal.* Found: C, 47.9; H, 4.3. Calc. for [Os(NO)Cl_3(PPh_3)($OPPh_3$)], ($C_{36}H_{30}Cl_3NO_2P_2Os$): C, 49.9; H, 3.4%. Found: C, 44.0; H, 4.5. Calc. for

$[Os(NO)Br_3(PPh_3)(OPPh_3)]$, ($C_{36}H_{30}Br_3NO_2P_2Ru$): C, 43.2; H, 3.0%

$[Rh(NO)X_2(PPh_3)_2]$ ($X = Cl, Br, I$)

The complexes are sparingly soluble in chloroform, and do not undergo any obvious change during irradiation. Single pure products could not be obtained from the solutions, and the ^1H NMR spectra of the products indicated several phenyl environments, and there was evidence for coordinated and uncoordinated $OPPh_3$ from both the IR and NMR spectra. All of the nitric oxide was lost from the three complexes after exposure times of 1–2 days. The low solubilities of the materials prevented the isolation of pure products.

$[Rh(NO)X_2(AsPh_3)_2]$ ($X = Cl, Br, I$)

Similar results to those described above were also obtained for the triphenylarsine rhodium complexes. The NO was lost from all three complexes after irradiation and a mixture of products obtained. There was evidence from both the IR and ^1H NMR spectra for the formation of uncoordinated $OAsPh_3$, as well as some remaining coordinated to the rhodium.

$[Ir(NO)X_2(PPh_3)_2]$ ($X = Cl, Br, I$)

Irradiation of the iridium complexes produced similar results as those obtained for the rhodium analogues. Nitric oxide was lost from the complexes and spectral evidence was obtained for the production of coordinated and uncoordinated $OPPh_3$.

Preparation of some other complexes

Osmium diethylphenylphosphine complexes

Attempts to make analogous diethylphenylphosphine complexes of osmium were not successful. Instead the complex dichloro(nitrosyl)bis(diethylphenylphosphine)(2-methoxyethanoate)-osmium(II), $[Os(NO)Cl_2(Et_2PhP)_2(CH_3OCH_2CH_2O)]$ was isolated. The complex has been characterized by single crystal X-ray diffraction and reported elsewhere [4].

Osmium organosulfide complexes

Attempts to prepare complexes of the type $[Os(NO)X_3(Et_2S)_2]$, similar to the ruthenium compounds, produced instead red coloured complexes containing both diethylsulfide and diethylsulfoxide, viz. $[Os(NO)X_3(Et_2S)(Et_2SO)]$, X = Cl, Br. The structure of the osmium bromo complex has been reported [4].

$[Rh(NO)X_3(PPh_3)_2]$

Complexes of the stoichiometric type $[Rh(NO)X_3(PPh_3)_2]$ have been reported [6, 34, 35]. Different oxidation states have been proposed for the rhodium in the complexes, viz. Rh(II) [6], Rh(III) [34] and Rh(IV) [35]. The reported position of the symmetrical stretching frequency for the NO group, ν(NO) is given as 1660 [6], 1623–1630 [34] and 1390 [35] cm^{-1}. Two of the preparative methods were re-investigated in the present work, however, neither method led to the reported products. A comparison of the products obtained with authentic dihalogeno complexes, using elemental analysis, IR spectra and X-ray powder diffractometry, indicated that the dihalogeno complexes $[Rh(NO)X_2(PPh_3)_2]$ were produced in each instance. *Anal.* Found: C, 59.8; H, 4.7. Calc. for $[Rh(NO)Cl_2(PPh_3)_2]$, ($C_{36}H_{30}NOP_2Rh$): C, 59.4; H, 4.2%. Found: C, 48.3; H, 4.3. Calc. for $[Rh(NO)Br_2(PPh_3)_2]$, $[C_{36}H_{30}Br_2NOP_2Rh]$: C, 48.2; H, 3.4%.

Rhodium organosulfide complexes

Attempts to prepare complexes of the type $[Rh(NO)X_2(Et_2S)_2]$ were unsuccessful. Preparative methods similar to those used for the ruthenium and osmium complexes [1–4] resulted in the formation of complexes of the type $[RhX_3(Et_2S)_3]$. Nitric oxide was readily lost from the intermediate '$Rh(NO)X_3$' entities during the reactions. In one experiment a crystalline material was obtained whose IR spectrum was similar to that of $[RhCl_3(Et_2S)_3]$, but with extra absorbances at 1120 and 920 cm^{-1}, suggesting the presence of both sulfur and oxygen bonded diethylsulfoxide [36–39]. Crystals were studied using single crystal X-ray diffraction, and although the structure of the product did not refine well it was evident that two independent $[RhCl_3(Et_2S)_2(Et_2SO)]$ moieties occurred in the unit cell. Both units contained the diethylsulfoxide ligand bonded to rhodium through sulfur, but one S–O bond was short, 122.7 pm compared with 170.0 pm. Elemental analytical results are consistent with this stoichiometry. *Anal.* Found: C, 28.8; H, 6.4. Calc. for $[RhCl_3(Et_2S)_2(Er_2SO)]$, ($C_{12}H_{30}Cl_3OS_3Rh$): C, 29.1; H, 6.4%.

Discussion

A number of general features have been revealed from the results of the photochemical reactions investigated in this study. A summary of the results is listed in Table 2.

Oxidizing agent

For triphenylphosphine complexes the oxidizing agent was established as NO from information from mass spectrometric analysis, and based on the oxidation reactions of the free ligand. The mechanism for this process is probably similar to that outlined previously for the organosulfide complexes [3]. The photochemical step activates the complex leading to the loss of a small amount of NO. The free NO then oxidizes one of the sulfide ligands, in this case the phosphine, on the starting material. In the case of triphenylarsine complexes the oxidizing agent may either be dioxygen together with UV radiation or nitric oxide. Mass spectrometric analysis was not available, but oxidation reactions of the free ligand suggested that NO was the more likely oxidant. On the other hand, dioxygen is likely to be the oxidizing agent for the triphenylstibine complexes, since nitrogen oxides did not oxidize uncoordinated triphenylstibine.

Effect of the halogen

The main influence of the halogen appears to be that for the heavier halogens greater amounts of uncoordinated $OPPh_3$ and $OAsPh_3$ are produced. This may suggest a dissociative step in the reaction, especially in view of the decreased reaction rate for $[Ru(NO)Br_3(PPh_3)_2]$ when excess PPh_3 is added to the reaction. The steric influence of the larger halogens could assist in such a step. However, the bromo and iodo complexes are also more soluble than the chloro complexes, and this may also influence the extent of the reactions. The fact that in the isomerization of the iodo complex $[Ru(NO)I_3(Et_2PhP)_2]$ there is evidence for the formation of some uncoordinated $OPEt_2Ph$, which is not the case for the bromo and chloro complexes, suggests that a dissociative step is required for the photochemical oxidation reactions, since all three complexes are soluble. On the other hand, since there is little evidence for the oxidation of Et_2PhP, which is known to oxidize readily with either nitrogen oxides or dioxygen, dissociation may not occur for the isomerization reaction, but it may proceed through a twisting mechanism.

Effect of the transition metal

The predominant observation regarding the transition metals is the similar behaviour of the complexes of the metals from the same periodic group. A little NO is lost from the ruthenium and osmium complexes which is then involved in the oxidation reaction, whereas both the rhodium and iridium complexes lose all their NO readily. This difference in behaviour is most likely associated with the different affinity of NO for the metal pairs. In the ruthenium and osmium complexes the NO is coordinated in the linear manner and in the rhodium and iridium complexes it is coordinated in a bent fashion. There is considerable π-interaction between the metal centre and the nitric oxide in the linear bonding mode, but less so for the bent M–NO system. This could explain the greater lability of the NO group for the rhodium and iridium complexes.

Conclusions

The photochemical reactions of complexes of the form $[M(NO)X_3(YPh_3)_2]$ (M = Ru, Y = P, As; M = Os, Y = P) produce complexes $[M(NO)X_3(YPh_3)(OYPh_3)]$ containing coordinated oxidized ligands. Photoirradiation of $[Ru(NO)Cl_3(SbPh_3)_2]$ produces *trans*-$[Ru(NO)Cl_3(OSbPh_3)_2]$. The likely oxidizing agent for the phosphine and arsine complexes is NO and for the stibine complex dioxygen plus radiation. There is some evidence for uncoordinated oxidized ligands $OYPh_3$ after longer irradiation times especially for the bigger halogen. Addition of excess ligand inhibits the loss of NO and these facts suggest dissociation may be important in the process. The complexes $[Ru(NO)X_3(Et_2PhP)_2]$ are formed as the *trans* isomer, but change to the *mer* isomer in solution upon irradiation. Complexes of the form $[M(NO)X_2(YPh_3)_2]$ (M = Rh, Y = As, P; X = Cl, Br, I; M = Ir, Y = P, X = Cl, Br, I) undergo more complex reactions in which all of the NO is lost from the complexes, and uncoordinated $OYPh_3$ is formed. The ready loss of the NO is probably associated with the weaker coordination of the ligand to the metal in the bent mode. The formation of the previously reported complexes $[Rh(NO)X_3(PPh_3)_2]$ (X = Cl, Br) was investigated and it would appear that the products are dihalide complexes of the form $[Rh(NO)X_2(PPh_3)_2]$.

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