

While the system investigated in this study can operate with quantum yields above unity, its overall performance characteristics are far from ideal. Competitive absorption by photogenerated MV^{2+} , for example, causes a serious inner-filter problem (Figure 2, curve c) and effectively precludes the use of excitation wavelengths above 500 nm. Replacement of MV^{2+} by a quencher that, upon reduction by $*Ru(bpy)_3^{2+}$, undergoes irreversible decomposition to weakly absorbing products²³ might lead to significant improvement in this respect. Such a quencher also would tend to minimize reverse electron transfer between the primary photoredox products (e.g. eq 10) and thereby enhance the yield of $Ru(bpy)_3^{3+}$ that can be scavenged by Q.

Finally, photochemical generation of a strong ground-state oxidant appears to be a viable strategy for initiating radical-

cation-mediated catalytic reactions of organic molecules.²⁴ As such, it provides an alternative to the more common approach involving direct reaction of an organic substrate with a photoexcited electron acceptor (e.g. eq 4). Additional studies of transition-metal-containing photoinitiator systems and their possible incorporation into photosensitive materials²⁵ are being pursued.

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(23) Various cobalt(III) ammine complexes, for example, undergo efficient reduction by $*Ru(bpy)_3^{2+}$ to yield weakly absorbing Co(II) species.⁸

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Thermal and Photolytic Reactions of Nitrosyl-Carbonyl Complexes of Rhodium and Iridium with Triphenylphosphine

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The photolysis of $[Rh(NO)(CO)(PPh_3)_2]$ in the presence of PPh_3 in dichloromethane results in the expulsion of NO rather than CO and the formation of *trans*- $[Rh(CO)Cl(PPh_3)_2]$. The thermal reaction and photoreaction of $[Ir(NO)(CO)Cl(PPh_3)_2]BF_4$ (**1**) with PPh_3 lead to dissociation of NO and the formation of the Ir(II) radical $[Ir(CO)Cl(PPh_3)_3]BF_4$ (**2**). The demonstration of the homolytic cleavage of the Ir-NO bond of **1** provides support for the proposal that the photodissociation of NO instead of CO in the compounds $[M(NO)(CO)(PPh_3)_2]$ (where M is Rh or Ir) proceeds from a charge-transfer state that has a bent M-N-O bond.

Introduction

The substitution of the nitrosyl ligand in complexes by other ligands is not commonly observed. The substitution or expulsion of CO instead of NO in the photolyses of $[Mn(NO)(CO)_4]$,¹ $[Co(NO)(CO)_3]$,²⁻⁵ and $[(C_5H_5)M(NO)(CO)_2]$, where M is Cr, Mo, or W,⁶ in solution and $[Co(NO)(CO)_3]$,⁷ $[Mn(NO)(CO)_4]$,⁸ $[Mn(NO)_3(CO)]$,⁹ and $[Fe(NO)_2(CO)_2]$ ¹⁰ in inert-gas matrices may be attributed to the stronger M-NO bond compared to the M-CO bond due to the stronger π -acceptor property of NO compared to that of CO. The substitution of CO in preference to NO in thermal reactions is also known for complexes such as $[Fe(NO)_2(CO)_2]$,¹¹ $[RFe(NO)(CO)_3]$,¹² $[(C_5H_5)Mn(CO)_2(NO)]^+$,¹³⁻¹⁵ $[Ir(NO)(CO)(PPh_3)_2]$,¹⁶ and other complexes with carbonyl and nitrosyl ligands. In contrast to this usual reactivity pattern, the photolysis of $[Ir(NO)(CO)(PPh_3)_2]$ in the presence of PPh_3 has been recently shown to lead to dissociation of NO rather than CO.¹⁷ To elucidate this apparently anomalous observation, we have investigated the photolytic reactions of PPh_3 with the compounds $[Rh(NO)(CO)(PPh_3)_2]$, $[Rh(NO)(PPh_3)_3]$, and $[Ir(NO)(CO)Cl(PPh_3)_2]BF_4$. The thermal reaction of the last compound with PPh_3 has been found to proceed with cleavage of the Ir-NO bond and formation of a relatively stable iridium(II) radical. Dissociation of NO from metal nitrosyl complexes has been recently proposed to be generally responsible for nitrosyl transfer and dioxygenation reactions.¹⁸

Experimental Section

Literature methods were used to prepare $[Rh(NO)(CO)(PPh_3)_2]$,¹⁹ $[Rh(NO)(PPh_3)_3]$,²⁰ and $[Ir(NO)(CO)Cl(PPh_3)_2]PF_6$.²¹ Photolyses were conducted with a 450-W medium-pressure mercury vapor lamp

jacketed with a Pyrex immersion well. Photolyses at 0 and $-78.5^\circ C$ were conducted by placing the lamp in its Pyrex immersion well and the sample in a tube in a Dewar containing ice water or a dry ice-acetone mixture. Infrared data of samples photolyzed in a liquid 0.5-mm NaCl

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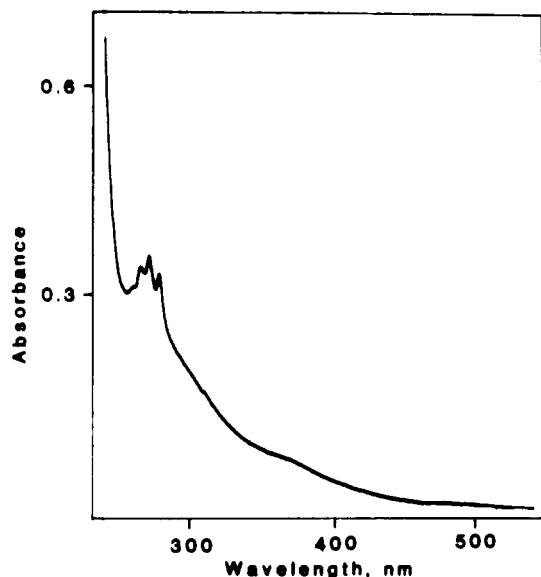


Figure 1. Visible-ultraviolet absorption spectrum of $[\text{Rh}(\text{NO})(\text{CO})(\text{PPh}_3)_2]$ 3.5×10^{-5} M in dichloromethane.

cell were collected with a Perkin-Elmer Model 983 spectrophotometer. The IR spectra of solutions containing PPh_3 and solvent were recorded, held in memory, and subtracted from the spectra of solutions containing the same concentration of PPh_3 and the nitrosyl complex. Phosphorus-31 NMR spectra were recorded with a JEOL FX 90Q spectrometer or IBM AF-200 FT NMR spectrometer. Electron spin resonance spectra of samples were recorded on a Varian E-line Century Series X-band spectrometer equipped with an Air Products Heli-trans low-temperature system at the California Institute of Technology. The X-band EPR spectrum (9.237 GHz) of a polycrystalline sample of $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]\text{BF}_4$ in dichloromethane was recorded at 8.3 ± 1 K. The spectrometer parameters were as follows: modulation frequency 100 kHz, modulation amplitude 8 G, scan time 8 min, time constant 0.128 s, spectrometer gain 6.3×10^4 , and microwave power 0.2 mW. Electron spin resonance spectra at 87 K were recorded on a Varian E-3 X-band EPR spectrometer at the University of Minnesota. The magnetic susceptibility of $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]\text{BF}_4$ was measured with a Johnson Matthey Inc. magnetic susceptibility balance with $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a standard.

A solution containing 200 mg (0.20 mmol) of $[\text{Ir}(\text{NO})(\text{CO})\text{Cl}(\text{PPh}_3)_2]\text{BF}_4$ and 100 mg (0.38 mmol) of PPh_3 in 15 mL of CH_2Cl_2 was allowed to react for 1 h in the dark. The solvent was removed in vacuo, and the solid product **2** remaining was washed thoroughly with Et_2O . IR (cm^{-1} , Nujol): 1998 vs (CO); 1059 vs, b (BF_4). Anal. Calcd for $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]\text{BF}_4 \cdot \text{H}_2\text{O}$, $\text{C}_{55}\text{H}_{47}\text{O}_2\text{P}_3\text{IrClBF}_4$: C, 57.6; H, 4.27. Found: C, 56.8; H, 4.29. Attempts to recrystallize the solid (250 mg) from CH_2Cl_2 , CHCl_3 , EtOH , Et_2O , and other solvents were not successful. The compound decomposes to form $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ and $[\text{Ir}(\text{CO})\text{Cl}_3(\text{PPh}_3)_2]$.

Photolysis of $[\text{Ir}(\text{NO})(\text{CO})\text{Cl}(\text{PPh}_3)_2]\text{BF}_4$ (1**) and PPh_3 at Low Temperatures.** Two solutions each 7.0 mM in **1** and 22 mM in PPh_3 were maintained at -78°C in a dry ice-acetone bath. One solution kept in the dark for 30 min showed no noticeable reaction. The other solution exposed to UV light for 23 min initially gave product **2** with $\nu(\text{CO})$ at 2007 cm^{-1} . After 58 min, the formation of products with absorption at 1973 cm^{-1} due to *trans*- $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ and at 2073 cm^{-1} due to $[\text{Ir}(\text{CO})\text{Cl}_3(\text{PPh}_3)_2]$ ²⁰ was observed. The photolysis of **1** and PPh_3 in CH_2Cl_2 at 0°C similarly gave **2** as the first-formed product followed by formation of $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$. A solution of 100 mg (0.100 mmol) of $[\text{Ir}(\text{NO})(\text{CO})\text{Cl}(\text{PPh}_3)_2]\text{PF}_6$ and 205 mg (0.78 mmol) of PPh_3 in 10 mL of CH_2Cl_2 was photolyzed at 0°C for 2.5 h. A yellow precipitate that was formed was removed by filtration and identified to be $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ (IR $\nu(\text{CO})$ 1950 cm^{-1} in Nujol and TLC (silica gel plates with elution with CHCl_3)) by comparison with a known sample. The solvent was removed in vacuo, and the solid that remained was washed with Et_2O . The IR spectrum of the solid had bands due to $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$, Ph_3PO (1180 and 1120 cm^{-1}), and PF_6^- (838 cm^{-1}). Recrystallization of this solid from chloroform-ethanol gave $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$.

Results and Discussion

Photolysis of $[\text{Rh}(\text{NO})(\text{CO})(\text{PPh}_3)_2]$. The ultraviolet-visible absorption spectrum of $[\text{Rh}(\text{NO})(\text{CO})(\text{PPh}_3)_2]$ in dichloro-

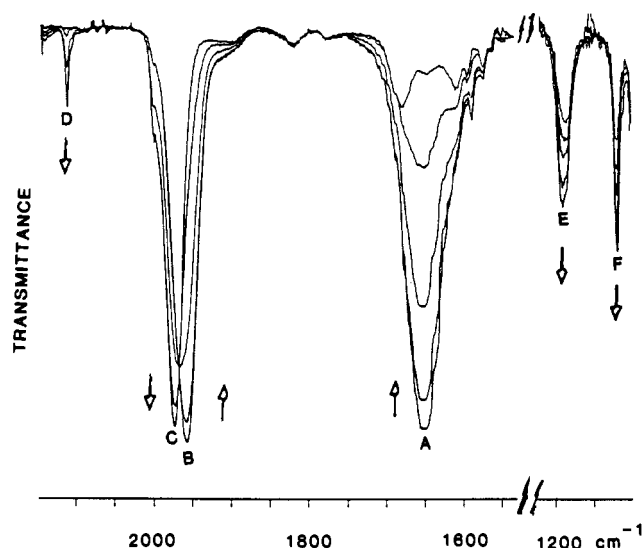
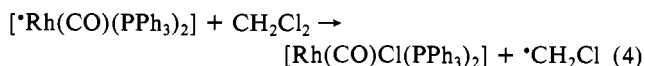
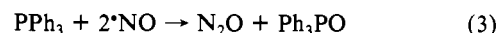
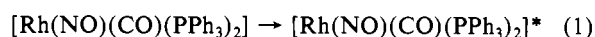


Figure 2. Photolysis of 19.5 mM $[\text{Rh}(\text{NO})(\text{CO})(\text{PPh}_3)_2]$ and 10.2 mM PPh_3 in dichloromethane at 3, 9, 21, and 45 min.

methane is shown in Figure 1. Pyrex-filtered irradiation above 300 nm was conducted on the sample on the shoulder of the strong band. The course of photolysis of $[\text{Rh}(\text{NO})(\text{CO})(\text{PPh}_3)_2]$ in dichloromethane in the presence of PPh_3 is shown by the IR spectra displayed in Figure 2. The disappearance of the nitrosyl-carbonyl complex is shown by the decay of the intensity of the NO stretching band (A) at 1654 cm^{-1} and $\nu(\text{CO})$ (B) at 1959 cm^{-1} . The product that has an absorption band (C) at 1975 cm^{-1} was shown to be *trans*- $[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ by comparison of its IR spectrum with that of a known sample. The growth of an absorption band at 366 nm in the UV spectrum of the photolyzed solution also confirms the formation of $[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$.²² The increasing intensities of bands at 1187 cm^{-1} (E) and 1120 cm^{-1} (F) due to Ph_3PO and at 2223 cm^{-1} (D) due to N_2O were also observed. These frequencies were authenticated with samples of N_2O and Ph_3PO . The presence of Ph_3PO and $[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ in the photolyzed solution was also verified by thin-layer chromatography using silica gel plates eluted with chloroform.

The formation of *trans*- $[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ in the photolysis of $[\text{Rh}(\text{NO})(\text{CO})(\text{PPh}_3)_2]$ as shown in Figure 1 may be explained by the sequence of reactions



The photoreaction proceeds in the same way previously reported for the $[\text{Ir}(\text{NO})(\text{CO})(\text{PPh}_3)_2]$ system,¹⁷ except for one significant difference. An intermediate with absorption in the 1932-cm^{-1} region that was observed for the iridium complex was not observed for the rhodium complex. The low 1932-cm^{-1} frequency observed for the $[\text{Ir}(\text{CO})(\text{PPh}_3)_3]$ intermediate was attributed to increased back-bonding to CO resulting from the ligation of three PPh_3 ligands on Ir. The absence of this intermediate in the rhodium system is attributed to the lower effective nuclear charge of rhodium compared to that of the iridium atom, which leads to higher coordination numbers typically observed for iridium complexes than for rhodium complexes. The scavenging of $\cdot\text{NO}$ by PPh_3 solutions to form N_2O and Ph_3PO was previously shown,¹⁷ and the reactions of organometallic radicals with halocarbon compounds have been recently discussed.²³

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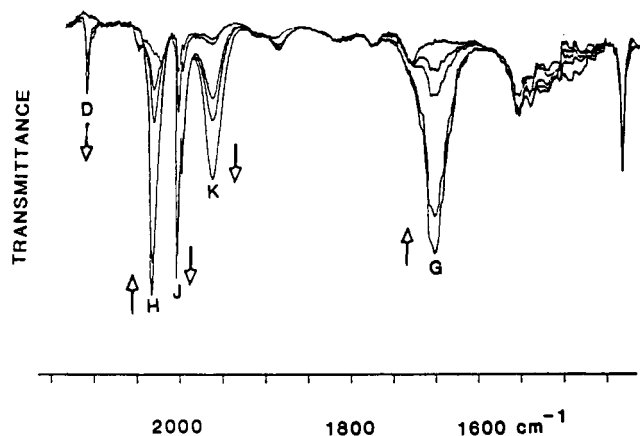


Figure 3. Photolysis of 6.24 mM $[\text{Ir}(\text{NO})(\text{CO})\text{Cl}(\text{PPh}_3)_2]\text{PF}_6$ and 19.5 mM PPh_3 in dichloromethane at 0, 2, 6, 10, and 18 min.

The photolysis of a solution containing 47.8 mg (5.2×10^{-5} mol) of $[\text{Rh}(\text{NO})(\text{PPh}_3)_3]$ in 10 mL of 0.112 M PPh_3 in dichloromethane with Pyrex-filtered irradiation over a period of 45 min resulted in very slow degradation of the $\nu(\text{NO})$ band at 1612 cm^{-1} . In comparison, the same concentration of $[\text{Rh}(\text{NO})(\text{CO})(\text{PPh}_3)_2]$ was completely converted to $[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ in 45 min. Thus, an alternative to reaction 2 in the above mechanism is the initial elimination of CO instead of NO, followed by rapid loss of NO from the 16-electron $[\text{Rh}(\text{NO})(\text{PPh}_3)_2]$ complex. Flash photolytic studies have demonstrated the photoexpulsion of CO from $[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$.²⁴

Reaction of $[\text{Ir}(\text{NO})(\text{CO})\text{Cl}(\text{PPh}_3)_2]\text{PF}_6$ with PPh_3 . Infrared measurements indicated that $[\text{Ir}(\text{NO})(\text{CO})\text{Cl}(\text{PPh}_3)_2]\text{PF}_6$ (**1**) does not readily decompose by thermal or photolytic pathways in the absence of triphenylphosphine. The IR spectra during the photolysis of $[\text{Ir}(\text{NO})(\text{CO})\text{Cl}(\text{PPh}_3)_2]\text{PF}_6$ (**1**) at 25°C in the presence of PPh_3 in dichloromethane are shown in Figure 3. The disappearance of the reactant **1** is shown by the decay of IR absorption bands at 1702 cm^{-1} (NO) (G) and at 2065 cm^{-1} (CO) (H). The products formed in the reaction include the compound **2** with a sharp strong band at 2007 cm^{-1} (J) and a compound with $\nu(\text{CO})$ at 1963 cm^{-1} (K). This latter compound was shown to be *trans*- $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ by comparison with a known sample and also by its isolation from the photolyzed solution. The formation of N_2O is shown by the band at 2223 cm^{-1} (D) and that of Ph_3PO by bands at 1119 and 1190 cm^{-1} . The intensity of the NO stretching frequency at 1702 cm^{-1} (G) decreases during the course of the reaction without growth of any bands in the $1500\text{--}1900\text{-cm}^{-1}$ region, which is characteristic of metal nitrosyl complexes.²⁵ The primary Ir-NO bond cleavage is clearly homolytic, since a heterolytic cleavage yielding NO^+ would lead directly to $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ instead of the observed product **2**. Photolysis of a dichloromethane solution of **1** and PPh_3 at -78°C was found to initially give **2** and subsequently *trans*- $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$.

The reaction of $[\text{Ir}(\text{NO})(\text{CO})\text{Cl}(\text{PPh}_3)_2]\text{BF}_4$ with PPh_3 also proceeds in the dark to give **2** as the initial primary product along with smaller amounts of $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ and $[\text{Ir}_3(\text{CO})\text{Cl}_3(\text{PPh}_3)_2]$. Further definitive evidence of the heterolytic cleavage of the Ir-NO bond was obtained by the observation of an IR band at 1887 cm^{-1} due to $\cdot\text{NO}$ in a dichloromethane solution that was 6.7 mM in $[\text{Ir}(\text{NO})(\text{CO})\text{Cl}(\text{PPh}_3)_2]\text{BF}_4$ and 6.3 mM in PPh_3 . The formation of $\cdot\text{NO}$ was also indicated by the observation of a strong EPR signal in a dichloromethane solution of **1** and PPh_3 at 87 K that disappeared when the solution was purged with nitrogen. Compound **2** in dichloromethane in the presence of PPh_3 decomposed to form *trans*- $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ and $[\text{Ir}(\text{CO})\text{Cl}_3(\text{PPh}_3)_2]$. The photoreaction and the dark reaction were observed to be faster

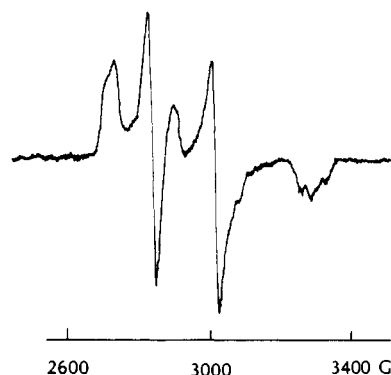
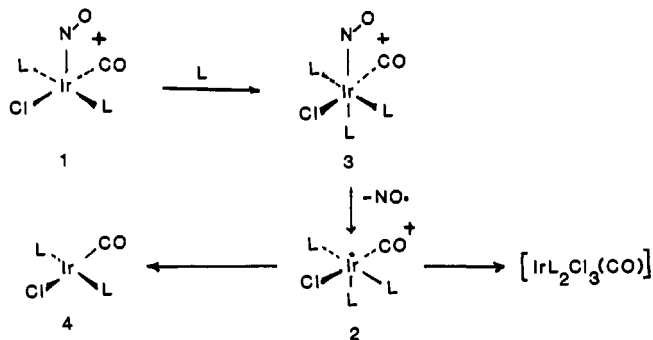


Figure 4. X-Band EPR spectrum (9.344 GHz) of a polycrystalline sample of $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_3]\text{BF}_4$ in dichloromethane at 108 K. The spectrometer parameters were as follows: modulation amplitude 8 G, scan time 8 min, time constant 0.3 s, spectrometer gain 10×10^5 , and microwave power 1.10 mW.

Scheme I



in solutions with higher concentrations of PPh_3 .

Compound **2** can also be formed by reactions of **1** with PPh_3 in solvents such as ethanol, nitromethane, and acetonitrile. Although efforts to isolate compound **2** as a crystalline sample suitable for X-ray diffraction studies have not been successful, the following observations provide insights on its composition and structure. A solid sample of **2** with stoichiometry $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_3]\text{BF}_4$ could be isolated from the reaction mixture, but efforts to recrystallize the sample resulted in its conversion to mixtures of Ir(I) and Ir(III) compounds. A $^{31}\text{P}\{^1\text{H}\}$ NMR study of a solution containing 0.130 g (0.14 mmol) of **1** and 0.129 g (0.49 mmol) of PPh_3 in 2.5 mL of CD_2Cl_2 initially showed resonances at 3.2 ppm for **1** and -4.6 ppm for PPh_3 . Within 2 min a peak at $+26.3$ ppm due to Ph_3PO and a broad peak at -5.2 ppm due to the 18-electron species $[\text{Ir}(\text{NO})(\text{CO})(\text{PPh}_3)_3\text{Cl}]\text{BF}_4$ (**3**) were observed. The spectra taken at 10, 15, and 30 min showed the increasing intensity of the resonance at $+26.3$ ppm due to Ph_3PO and the decreasing intensity of the resonance at -5.2 ppm. After 1 h, when the resonance at -5.2 ppm was nearly completely decayed, only a weak broad band at -3.0 ppm was observed in addition to resonances due to PPh_3 and Ph_3PO . Since there was no growth of a resonance due to an iridium species concomitant with the decay of the -5.2 ppm resonance, the formation of a paramagnetic Ir(II) compound was indicated. The strong absorption band at 2007 cm^{-1} for **2** also supports its designation as an iridium(II) compound because the CO stretching frequencies are in the $2040\text{--}2080\text{-cm}^{-1}$ region for related Ir(III) carbonyl complexes and in the $1930\text{--}1970\text{-cm}^{-1}$ region for Ir(I) carbonyl complexes.²⁶

The low-temperature (87 K) EPR spectrum of a powder sample of **2** (Figure 4) consists of a g_{\perp} signal (a doublet of triplets) at $g_{\perp} = 2.128$ and the high-field portion of a doublet signal centered at $g_{\parallel} = 2.00$. This latter signal shows evidence of additional Ir hyperfine splitting. The low-field portion of g_{\parallel} is obscured by the

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g_{\perp} signal. The data are consistent with a square-pyramidal geometry about Ir(II) with two trans PPh_3 ligands in the square basal plane and the third PPh_3 ligand in the apical position as shown in Scheme I. The unpaired electron then resides in the d_{z^2} orbital. Magnetic susceptibility measurements by the Gouy method on a solid sample of **2** at 26 °C gave a magnetic moment μ of 1.91 μ_B . Stable monomeric iridium(II) complexes are rare,^{27,28} and most complexes of the d^7 Ir(II) ion known are dimeric with metal-metal bonds or metal-ligand-ligand-metal interaction. Electron spin resonance studies of $[\text{IrBr}_3(\text{NO})(\text{PPh}_3)_2]$ and $[\text{Ir}(\text{AsPh}_3)(\text{CNC}_6\text{H}_4\text{Me-}p)(\text{O}_2\text{CR})_2]$ indicate significant delocalization of the unpaired electron on the ligands.^{27,28} The ESR spectrum shown in Figure 4, the first report of the spectrum of a monomeric cationic five-coordinate Ir(II) complex, likewise indicates considerable delocalization of the unpaired electron on the metal and the PPh_3 ligands.

It is noteworthy that the zerovalent radical complexes $[\text{Rh}(\text{PPh}_3)_2(\text{CO})]$ and $[\text{Ir}(\text{PPh}_3)_2(\text{CO})]$ rapidly scavenge chlorine from chlorocarbon solvents, but the iridium(II) radical **2** reacts more slowly with chlorocarbon solvents. The apparent stability of **2** must be attributed to resistance to dimerization by Coulombic repulsions of the cationic monomers, as well as the steric bulk of the three PPh_3 ligands, and the delocalization of the electron on the ligands.

The Ir-NO bond cleavage reaction, which was shown to proceed in the dark, is also enhanced by UV light. Since the reaction is enhanced by higher concentrations of PPh_3 , the formation of the 18-electron complex $[\text{Ir}(\text{NO})(\text{CO})\text{Cl}(\text{PPh}_3)_3]^+$ (**3**) is expected. (See Scheme I where L is PPh_3 .) Evidence for the formation of **3** was also indicated by the ^{31}P NMR data. Expulsion of NO from **3** as detected by IR and ESR spectra gives the paramagnetic compound $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_3]^+$ (**2**). The iridium(II) compound **2** was found to decompose to form the Ir(I) and Ir(III) compounds *trans*- $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ (**4**) and $[\text{Ir}(\text{CO})\text{Cl}_3(\text{PPh}_3)_2]$. The formation of **4** was enhanced by UV irradiation.

The cleavage of the Ir-NO bond instead of the Ir-CO bond of $[\text{Ir}(\text{NO})(\text{CO})\text{Cl}(\text{PPh}_3)_2]^+$ in its thermal reaction with PPh_3

may be attributed to the weak Ir-NO bond in this compound. X-ray diffraction studies established that this compound has a structure with a weak bent Ir-N=O bond²¹ instead of a strong linear Ir=N=O bond as has been reported for $[\text{Ir}(\text{NO})(\text{CO})(\text{PPh}_3)_2]$.²⁹ Molecular orbital considerations of the geometric and electronic structures of complexes with linear $\text{M}=\text{N}=\text{O}$ and with bent $\text{M}-\text{N}=\text{O}$ bonds have been presented, and the correlation diagram that should be applicable for the $[\text{M}(\text{NO})(\text{CO})(\text{PPh}_3)_2]$ complexes should be the diagram for the $[\text{MNO}]^{10}$ unit.²⁵ Since we have demonstrated the heterolytic cleavage of the Ir-N bond in the reaction of PPh_3 with compound **1**, which has a bent Ir-N=O bond, and since the thermal reaction of $[\text{Rh}(\text{NO})(\text{CO})(\text{PPh}_3)_2]$ with PPh_3 proceeds with displacement of CO instead of NO from the strong linear $\text{Rh}=\text{N}=\text{O}$ bond, it is reasonable to propose that the cleavage of the Rh-NO bond in the photolysis of $[\text{Rh}(\text{NO})(\text{CO})(\text{PPh}_3)_2]$ proceeds by photoexcitation from a ground-state structure that has a strong linear $\text{M}=\text{N}=\text{O}$ bond to an excited state that has a weaker bent $\text{M}-\text{N}=\text{O}$ bond. The rhodium to nitrosyl ligand charge-transfer excited state is expected to be lowest in energy as d-d transitions are spin-forbidden for the d^{10} complex, and the Rh to ligand CO and PPh_3 charge-transfer transitions are expected to be at much higher energies. Zink and co-workers were the first to propose the photochemical consequence of a linear to bent geometry change in the photolysis of metal nitrosyl complexes.^{5,30} Yang and Zink also determined the change from linear to bent geometry and the change in oxidation state for $\text{K}_2[\text{Fe}(\text{CN})_5(\text{NO})]$ by excited-state Raman spectroscopic studies.³¹

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fac-mer Equilibrium in Solutions of VCl_3 in Acetonitrile¹

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Both the equivalent conductivity and the proton NMR spectra of solutions of vanadium trichloride in acetonitrile indicate the presence of a second species above 50 °C. The maximum value found for the equivalent conductivity, 6.21 $\text{cm}^2 \text{mol}^{-1} \Omega^{-1}$ at 76 °C, is too low for a 1:1 electrolyte. The two species present are very likely the *fac* and *mer* isomers of $\text{VCl}_3 \cdot 3\text{CH}_3\text{CN}$.

Introduction

Early work²⁻⁴ on the complexes of TiCl_3 and VCl_3 with nitriles suggested the presence in solution of only the neutral $\text{MCl}_3 \cdot 3\text{CH}_3\text{CN}$. Comparison of solution absorption spectra with diffuse reflectance spectra of the solids indicated that for both TiCl_3 and VCl_3 the species in solution were the same as the isolated solids.

Confirmation of this was found in the low values of the equivalent conductivity.³⁻⁵ The infrared spectra have been used in an attempt to distinguish between the *fac* and *mer* isomers.^{4,6}

However, NMR line width data for the $\text{TiCl}_3 \cdot \text{CH}_3\text{CN}$ system show two species present in the temperature range -40 to +80 °C.⁷ One possibility is the *fac-mer* isomer pair. Another is $\text{TiCl}_3 \cdot 3\text{CH}_3\text{CN}$ and $\text{TiCl}_2 \cdot 4\text{CH}_3\text{CN}^+$. The similarity in spectral and electrical behavior between TiCl_3 and VCl_3 suggested that the NMR spectrum of VCl_3 would show a second species at higher

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