References and Notes

(1) Part 3: E. L. Muetterties, M. C. Rakowski, F. J. Hirsekorn, W. D. Larson, V. J. Basus, and F. A. L. Anet, *J. Am. Chem. Soc.*, **97**, 1266 (1975).
(2) E. L. Muetterties and F. J. Hirsekorn, *J. Am. Chem. Soc.*, **96**, 4063 (1974).
(3) F. J. Hirsekorn, M. C. Rakowski, and E. L. Muetterties, *J. Am. Chem. Soc.*, **97**, 237 (1975).
(4) V. A. Avilov, Y. G. Borod'ko, V. P. Panov, M. L. Khidekel, and P. S. Chekrii, *Kinet. Catal. (Engl. Transl.)*, **9**, 582 (1968).
(5) O. N. Efimov, O. N. Eremenko, A. G. Ovcharenko, M. L. Khidekel, and P. S. Chekrii, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 778 (1969).
(6) O. N. Efimov, M. L. Khidekel, V. A. Avilov, P. S. Chekrii, O. N. Eremenko, and A. G. Ovcharenko, *J. Gen. Chem. USSR (Engl. Transl.)*, **38**, 2581 (1968).
(7) S. J. Lapporte, *Ann. N.Y. Acad. Sci.*, **158**, 510 (1969).
(8) S. J. Lapporte and W. Schuett, *J. Org. Chem.*, **28**, 1947 (1963).
(9) I. Wender, R. Levine, and M. Orchin, *J. Am. Chem. Soc.*, **72**, 4375 (1950).
(10) H. Feder and J. Halpern, *J. Am. Chem. Soc.*, **97**, 7186, (1975).
(11) E. L. Muetterties and F. J. Hirsekorn, *J. Am. Chem. Soc.*, **96**, 7920 (1974).
(12) M. C. Rakowski and E. L. Muetterties, submitted for publication.
(13) J. Atwood and E. L. Muetterties, to be submitted for publication.
(14) A. B. Richmond, *J. Chromatogr. Sc.*, **7**, 321 (1969).
(15) D. Seyferth and M. A. Weiner, *Org. Synth.*, **41**, 30 (1961).
(16) H. F. Klein and H. H. Karsch, *Inorg. Chem.*, **14**, 473 (1975).

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Photoinduced Oxidation of Coordinated Ligands in *trans*-[RhCl(CO)(PPh₃)₂]. Generation of a Decarbonylation Agent

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Ultraviolet irradiation of air-saturated solutions of *trans*-[RhCl(CO)(PPh₃)₂] results in oxidation of CO to CO_2 and PPh₃ to Ph_3PO and formation of an oligomeric complex formulated as $[RhCl(O_2)(Ph_3PO)_{0.67}]_x$. The 254 and 366 nm disappearance quantum yields for *trans*-[RhCl(CO)(PPh₃)₂] are 0.02, and quantum yields of other *trans*-[RhCl(CO)L₂] (L = PMePh₂, PMe₂Ph, PEtPh₂, PEt₂Ph, PEt₃) complexes vary from 0.01 to 0.05. The rhodium containing photoproduct from the photolysis of *trans*-[RhClCO(PPh₃)₂] can be converted into [RhCl(PPh₃)₃] by treatment with excess PPh₃ in refluxing ethanol, and the photoproduct with excess PPh₃ will decarbonylate benzaldehyde and phenylacetyl chloride to give *trans*-[RhCl(CO)(PPh₃)₂], benzene, and benzyl chloride, respectively.

Introduction

It is now well-established[1-3] that [RhCl(PPh₃)₃] is a useful reagent for affecting the decarbonylation of aldehydes and acyl and aroyl halides, presumably by acting through three-coordinate [RhCl(PPh₃)₂] (eq 1-2).[4] The reactions are stoi-

$$RCHO + [RhCl(PPh_3)_2] \rightarrow RH + \textit{trans}\text{-}[RhCl(CO)(PPh_3)_2] \quad (1)$$

$$RCOCl + [RhCl(PPh_3)_2] \rightarrow RCl + \textit{trans}\text{-}[RhCl(CO)(PPh_3)_2] \quad (2)$$

chiometric with 1 mol of rhodium complex required for each mole of carbonyl compound consumed. The reactions cannot be made catalytic at a useful temperature because *trans*-[RhCl(CO)(PPh₃)₂] does not lose carbon monoxide and the active reagent cannot be regenerated thermally.[5,6] Since a large number of transition metal carbonyl complexes are known to dissociate CO upon irradiation,[7] it was our initial expectation that [RhCl(PPh₃)₂] or its dimer could be formed from *trans*-[RhCl(CO)(PPh₃)₂] through photoinduced loss of carbon monoxide. The decarbonylation cycle would then be complete and the reaction could be made catalytic by continuous photolysis. We have examined the photochemical properties of *trans*-[RhCl(CO)(PPh₃)₂] and have observed, however, that simple photoelimination of CO does not occur, but rather that CO and PPh₃ are oxidized to CO_2 and Ph_3PO upon irradiation of the complex in the presence of oxygen. The details of this photochemical study are reported herein, and methods are presented for the easy and convenient conversion of the rhodium containing photoproduct into [RhCl(PPh₃)₃] and for recycling rhodium in the decarbonylation scheme.

Experimental Section

Triethylphosphine and triphenylphosphine were obtained from the Aldrich Chemical Co., and PPh₃ was recrystallized from EtOH before use. PMePh₂, PMe₂Ph, PEtPh₂, and PEt₂Ph were synthesized from PPh₂Cl and PPhCl₂ and the appropriate Grignard reagent following an adaptation of the published procedure.[8] The *trans*-[RhCl(CO)L₂] complexes were prepared according to the literature.[9-11]

Irradiation Procedures. The irradiations were conducted using either a low-pressure Hg arc lamp (254 nm) or a 450-W Hanovia medium-pressure Hg arc lamp equipped with Corning 0-52 and 7-37 glass filters (366 nm). The disappearance quantum yields were measured at 254 and 366 nm using ferrioxalate actinometry and a conventional merry-go-round apparatus by following the decrease in intensity of the principal absorption band near 365 nm of oxygen-saturated CH_2Cl_2 solutions of each of the complexes. Photolyses were conducted in standard 1.0 cm path length quartz uv spectrophotometer cuvettes, in 1.0 mm NaCl infrared solution cells, or in 300 ml Pyrex flasks for isolation of the photoproducts. Uv–visible and infrared spectral changes occurring during the photolyses were obtained for all the *trans*-[RhCl(CO)L₂] complexes and were virtually identical. Measurement of the stoichiometry of the reaction and characterization of the photoproduct were only performed for *trans*-[RhCl(CO)(PPh₃)₂], detailed below.

Photolysis of *trans*-[RhCl(CO)(PPh₃)₂]. Irradiation of oxygen-saturated toluene or CH_2Cl_2 solutions of *trans*-[RhCl(CO)(PPh₃)₂] induces a rapid color change from yellow to orange-red. Irradiated toluene solutions deposit a tan precipitate which after washing with EtOH and Et₂O analyzes approximately for $[RhCl(O_2)(Ph_3PO)_{0.67}]_x$. Calcd: C, 40.47; H, 2.81; Rh, 28.92; Cl, 9.96; P, 5.84; O, by difference, 12.01. Found: C, 37.23; H, 3.24; Rh, 28.52; Cl, 9.91; P, 5.47; O, by difference, 15.63. A solution of 0.5054 g (0.73 mmol) of *trans*-[RhCl(CO)(PPh₃)₂] irradiated to completion in toluene yielded 0.2549 g (0.92 mmol) of uncoordinated Ph_3PO isolated by evaporation of the irradiated solution followed by repeated washing of the resultant tan solid with EtOH and finally sublimation of Ph_3PO. Oxygen uptake measurements were performed by irradiating 20–25 ml of 6.24×10^{-3} M and 1.06×10^{-2} M CH_2Cl_2 solutions of *trans*-[RhCl(CO)(PPh₃)₂], and the amount of O_2 absorbed was measured with a 10 ml micro gas buret. The entire system was maintained at a constant temperature of 23 °C, and values of 1.70, 1.60, and 1.48 mol of oxygen ab-
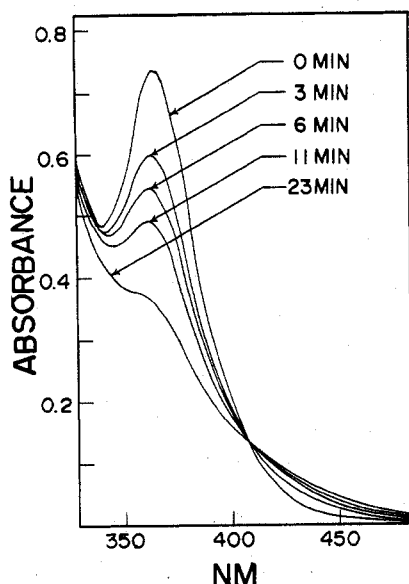
Figure 1. Electronic absorption spectral changes during 366 nm irradiation of a 2.0 × 10⁻⁴ M air-saturated CH₂Cl₂ solution of *trans*-[RhCl(CO)(PPh₃)₂].

sorbed/mol of complex were obtained. Isopiestic molecular weight measurements of CH₂Cl₂ solutions of the photoproduct gave values of 1.8×10^3 and 3.7×10^3 g/mol.

Conversion of *trans*-[RhCl(CO)(PPh₃)₂] into [RhCl(PPh₃)₃]. An oxygen-saturated toluene solution of *trans*-[RhCl(CO)(PPh₃)₂] (0.3726 g; 0.54 mmol) was irradiated with 366 nm until the electronic absorption spectral changes indicated that the reaction was complete. Toluene was removed by evaporation and 2.1180 g of PPh₃ in 25 ml of EtOH was added to the resultant solid. This suspension was refluxed for 2 h under N₂, during which time red crystals of [RhCl(PPh₃)₃] (0.3030 g; 0.33 mmol) were deposited. This was the highest yield (61%) obtained in several runs, although the yield can most likely be increased by performing the experiment on a larger scale since some loss of complex occurs during workup.

Decarbonylation Experiments. A toluene solution of *trans*-[RhCl(CO)(PPh₃)₂] (0.5969 g) was irradiated with 366 nm until the electronic absorption spectral changes indicated that the reaction was complete. Benzaldehyde (5.4 g) and PPh₃ (2.33 g) were added and the solution was refluxed for 1 h during which time the color changed from orange-red to yellow. Addition of EtOH to the solution precipitated *trans*-[RhCl(CO)(PPh₃)₂] (0.4976 g) with an 83% recovery. The formation of benzene was verified by VPC analysis in this and similar experiments in which the irradiations were conducted in CH₂Cl₂ solutions and in which the decarbonylations were accomplished in neat benzaldehyde with added PPh₃. Decarbonylation of phenylacetyl chloride was accomplished in a similar manner yielding *trans*-[RhCl(CO)(PPh₃)₂] and benzyl chloride.

Spectral Measurements. Electronic absorption spectra were measured using a Cary 17 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 621 spectrophotometer and mass spectra were obtained with an AEI-MS-902 mass spectrometer.

Results

No net photochemical reaction is observed when *trans*-[RhCl(CO)(PPh₃)₂] is irradiated with 254 or 366 nm in oxygen-free solutions. However, 366 nm photolysis of an oxygen-saturated 2.0 × 10⁻⁴ M CH₂Cl₂ solution of *trans*-[RhCl(CO)(PPh₃)₂] results in the electronic absorption spectral changes shown in Figure 1. As the irradiation proceeds a smooth decrease in the 364 nm band is observed, and an isosbestic point is initially maintained at 408 nm. Identical spectral changes obtained on photolysis of benzene and toluene solutions of the complex. In CH₂Cl₂ solution, in the infrared spectral region, *trans*-[RhCl(CO)(PPh₃)₂] displays a single carbonyl stretch at 1974 cm⁻¹, and irradiation leads to a decrease in intensity of this band and the simultaneous appearance of a new band at 2337 cm⁻¹. Tri-

**Table I.** Quantum Yields of Disappearance of *trans*-[RhCl(CO)L₂] Complexes[a]

L	Φ_{254} nm	Φ_{366} nm
PPh₃	0.02	0.02
PPh₂Me	0.01	0.01
PPh₂Et	0.03	0.03
PPhMe₂	0.01	0.02
PPhEt₂	0.01	0.03
PEt₃	0.04	0.05

[a] Oxygen-saturated 10⁻³ M CH₂Cl₂ solutions; error limits ±10%.

phenylphosphine bands at 990 and 1095 cm⁻¹ also decrease in intensity, with new bands appearing at 1188, 1165, and 1117 cm⁻¹. These latter bands are characteristic of triphenylphosphine oxide,[12] and the 2337 cm⁻¹ band is attributable to CO₂, as evidenced by the spectrum of CO₂ in CH₂Cl₂. Similar infrared spectral changes are observed in toluene, and the formation of CO₂ has been substantiated by mass spectral analysis of the gases above an irradiated toluene solution. The photoreaction can be completely inhibited by excess PPh₃. No reaction, for example, was observed after 1 h of 366 nm irradiation of a CH₂Cl₂ solution of *trans*-[RhCl(CO)(PPh₃)₂] containing a fivefold molar excess of PPh₃, whereas a similar solution without excess PPh₃ undergoes complete photolysis in less than 1 h.

Solutions of *trans*-[RhCl(CO)(PPh₃)₂] change color from yellow to orange-red when irradiated, and addition of diethyl ether to concentrated irradiated solutions results in the precipitation of an amorphous red-brown powder. This powder may be purified by reprecipitation from CH₂Cl₂/Et₂O solutions, but a crystalline sample has never been obtained. The electronic absorption spectrum of this species in CH₂Cl₂ solution is identical with that of an irradiated *trans*-[RhCl-(CO)(PPh₃)₂] solution, and the infrared spectrum (KBr disk) shows bands at 1188, 1160, and 1117 cm⁻¹ attributable to Ph₃PO. Bands assignable to a carbonyl stretch, to entrapped solvent, or to Rh–O₂ vibrations (850–900 cm⁻¹) were not observed. Elemental analysis of the tan precipitate suggests the empirical formula RhClC₁₂H₁₀O₂.₆₇. Isopiestic molecular weight measurements in CH₂Cl₂ solutions of the precipitate from two different photolyses gave values of 1800 and 3700 g/mol, and we tentatively formulate the compound as the oligomer [RhCl(O₂)(Ph₃PO)₀.₆₇]ₓ. Our isolation of 1.25 mol of uncoordinated Ph₃PO from an irradiated CH₂Cl₂ solution and the uptake of 2.59 ± 0.11 mol of O₂/mol of *trans*-[RhCl(CO)(PPh₃)₂] irradiated are consistent with this formulation and suggest the overall stoichiometry expressed in eq 3. Rhodium containing products with similar properties
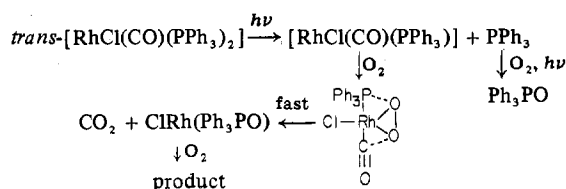
$$\textit{trans-}[RhCl(CO)(PPh_3)_2] + 2.5O_2 \xrightarrow{h\nu} [RhCl(O_2)(Ph_3PO)_{0.67}]_x$$
$$+ 1.33Ph_3PO + CO_2 \qquad (3)$$
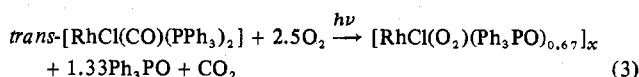
and formulations have also been isolated from the air oxidation of [RhCl(PPh₃)₃] solutions.[13,14]

Several other *trans*-[RhCl(CO)L₂] complexes with different tertiary phosphines are also photosensitive in the presence of oxygen, and their electronic and infrared spectral changes upon irradiation suggest that photoreaction pathways similar to that for *trans*-[RhCl(CO)(PPh₃)₂] obtain. The quantum yields for disappearance of the *trans*-[RhCl(CO)L₂] complexes are summarized in Table I, and they do not vary significantly with either the nature of the phosphine or the wavelength of irradiation. No attempts were made to isolate the photoproducts from any of the complexes except for L = PPh₃.

Although the identity of the photoproduct is not firmly established, we have discovered that it can be converted to [RhCl(PPh₃)₃] by treatment of refluxing ethanol solutions containing the product with excess PPh₃. In a typical experiment, a sample of *trans*-[RhCl(CO)(PPh₃)₂] was irra-

Scheme I

$$trans\text{-}[RhCl(CO)(PPh_3)_2] \xrightarrow{h\nu} [RhCl(CO)(PPh_3)] + PPh_3$$

$$\downarrow O_2 \qquad\qquad \downarrow O_2, h\nu$$

$$CO_2 + ClRh(Ph_3PO) \xleftarrow{\text{fast}} \begin{array}{c} Ph_3P\cdots O \\ Cl-Rh \\ C\cdots O \\ \| \\ O \end{array} \qquad Ph_3PO$$

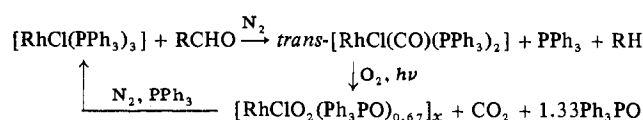$$\downarrow O_2$$

$$\text{product}$$

diated in toluene until the electronic absorption spectrum indicated that the reaction was complete. Removal of toluene, addition of PPh₃ in ethanol, and refluxing under N₂ for 2 h gave a 61% yield of crystalline [RhCl(PPh₃)₃]. The generation of [RhCl(PPh₃)₃] suggested that a similar reaction could be employed to decarbonylate aldehydes and acyl halides. Indeed, treatment of a toluene solution of the photoproduct with excess PPh₃ and benzaldehyde at reflux under dry N₂ for 1 h yielded benzene and 83% regeneration of *trans*-[RhCl(CO)(PPh₃)₂]. An analogous procedure was employed for the decarbonylation of phenylacetyl chloride by an irradiated solution of the complex and yielded benzyl chloride and *trans*-[RhCl-(CO)(PPh₃)₂]. Presumably, the reaction proceeds through formation of the known decarbonylation agent, [RhCl(PPh₃)₂].

Although there is no noticeable decomposition of *trans*-[RhCl(CO)(PPh₃)₂] when toluene solutions are refluxed under an oxygen atmosphere, oxidation can be induced by gentle heating in the presence of a radical initiator. Aerated solutions of *trans*-[RhCl(CO)(PPh₃)₂] containing azobisisobutyronitrile, for example, turn orange-red when heated to 60 °C and display electronic absorption spectral changes similar to those obtained upon irradiation. Further, a product similar to ours has been isolated from *trans*-[RhCl(CO)(PPh₃)₂] catalyzed olefin oxidations,[14] a reaction believed to proceed through decomposition of autoxidation generated peroxides by *trans*-[RhCl(CO)(PPh₃)₂].[15] We have observed, however, that radical inhibitors (2,6-di-*tert*-butyl-4-methylphenol and duroquinone) do not at all inhibit the *photoinduced* oxidation, suggesting that a different reaction mechanism is involved.

Discussion

The results reported herein clearly indicate that CO and PPh₃ are oxidized to CO₂ and Ph₃PO when *trans*-[RhCl-(CO)(PPh₃)₂] is irradiated in the presence of oxygen. The exact nature of the rhodium containing photoproduct is still unknown, and the complex will be extremely difficult to characterize further due to its amorphous and apparently oligomeric nature. Any mechanism proposed to account for the observed photochemistry of *trans*-[RhCl(CO)(PPh₃)₂] must be consistent with the inhibition of the reaction by excess PPh₃ and the oxidation of CO to CO₂. The formation of CO₂ suggests that simple photoelimination of CO does not occur, and this conclusion is substantiated by our failure to observe any photoassisted decarbonylation when *trans*-[RhCl(CO)-(PPh₃)₂] is irradiated in degassed solutions containing *n*-heptanal. Unlike its iridium analogue, an oxygen adduct of *trans*-[RhCl(CO)(PPh₃)₂] has never been isolated, and the electronic absorption spectrum of the complex does not vary from degassed to oxygen-saturated solutions. Hence, an oxygen complex is not likely formed to a significant extent, and the 0.02 quantum yield rules out any mechanism based on the photolysis of an oxygen adduct. Inhibition of the reaction by excess PPh₃ strongly suggests that dissociation of PPh₃ occurs in the primary photochemical step. We thus propose the mechanism outlined in Scheme I in which irradiation of the complex leads to elimination of PPh₃ and formation of three coordinate [RhCl(CO)(PPh₃)]. This 14 valence electron complex would be expected to form an oxygen adduct which could subsequently decompose through an intermediate similar to that proposed for the catalytic oxidation
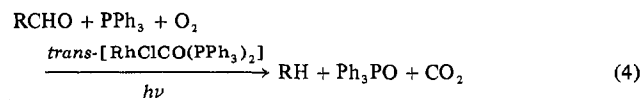
Scheme II

$$[RhCl(PPh_3)_3] + RCHO \xrightarrow{N_2} trans\text{-}[RhCl(CO)(PPh_3)_2] + PPh_3 + RH$$

$$\uparrow \qquad\qquad\qquad \downarrow O_2, h\nu$$

$$\underline{\quad N_2, PPh_3 \quad} \quad [RhClO_2(Ph_3PO)_{0.67}]_x + CO_2 + 1.33Ph_3PO$$

of PPh₃ by [Pt(O₂)(PPh₃)₂].[16] The initially dissociated PPh₃ will photolyze to Ph₃PO under these conditions since tertiary phosphines are known to yield the corresponding oxide upon irradiation.[17]

The least energetic bands in the electronic absorption spectrum of *trans*-[RhCl(CO)(PPh₃)₂] have been assigned[18] as $d_{z^2} \rightarrow b_1\pi$ metal-to-ligand charge transfer (MLCT) transitions. The $b_1\pi$ molecular orbital populated in these excited states is a combination of phosphorus d orbitals, a CO π^* orbital, and the rhodium $5p_z$ orbital. If our proposed photochemical mechanism is correct, then ligand dissociation results either from such a MLCT excited state or from a nonspectroscopically observed ligand field excited state. The latter alternative appears more likely since luminescence spectra of the structurally similar complexes, [Rh-(Ph₂PCH₂CH₂PPh₂)₂]⁺ and [Rh(Ph₂PCHCHPPh₂)₂]⁺, suggest that the lowest excited states may possess a small admixture of one or more ligand field states[19] and since it is difficult to rationalize photosubstitution from a $(d_{z^2})^1(b_1\pi)^1$ state. Further, the photosubstitution reactions of a series of [Ru(NH₃)₅L]²⁺ complexes upon irradiation into MLCT bands has been recently shown to occur from nonspectroscopically observable excited states that are most likely ligand field in character.[20]

Although the original goal of this research (i.e., photolabilization of CO and generation of [RhCl(PPh₃)₂]) was not realized, our results do show that the Rh complexes in the decarbonylation reaction can be easily and efficiently recycled for use in batchwise preparations by regenerating the active decarbonylation agent through photolysis of *trans*-[RhCl-(CO)(PPh₃)₂]. The sensitivity of [RhCl(PPh₃)₃] toward oxygen, yielding Ph₃PO and Rh–Ph₃PO complexes, and the necessity of using oxygen to photochemically remove CO from *trans*-[RhCl(CO)(PPh₃)₂] require separate and distinct steps in the decarbonylation cycle (Scheme II), and the reaction cannot be made truly photocatalytic. The overall stoichiometry of a decarbonylation reaction would then be as written in eq 4.

$$RCHO + PPh_3 + O_2$$

$$\xrightarrow[h\nu]{trans\text{-}[RhClCO(PPh_3)_2]} RH + Ph_3PO + CO_2 \qquad (4)$$

References and Notes

(1) K. Ohno and J. Tsuji, *J. Am. Chem. Soc.*, **90**, 99 (1968).
(2) A. Emery, A. C. Oehlschlager, and A. M. Unrau, *Tetrahedron Lett.*, **50**, 4401 (1970).
(3) J. Blum, E. Oppenheimer, and E. D. Bergmann, *J. Am. Chem. Soc.*, **89**, 2338 (1967).
(4) Although eq 1 and 2 show RH and RCl as the decarbonylation products, in some cases products arise from loss of H₂ or HCl in addition to CO.[1]
(5) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).
(6) The decarbonylation reaction can be made catalytic for high boiling (>200 °C) aldehydes and acyl halides by refluxing a solution of pure substrate with the catalyst. It is postulated[1] that carbonyl loss occurs from the intermediate acyl complex rather than from *trans*-[RhCl(CO)(PPh₃)₂].

(7) M. S. Wrighton, *Chem. Rev.*, **74**, 401 (1974).
(8) M. A. Mathur, W. H. Myers, H. H. Sisler, and G. E. Ryschkewitsch, *Inorg. Synth.*, **15**, 128 (1975).
(9) D. Evans, J. A. Osborn, and G. Wilkinson, *Inorg. Synth.*, **11**, 99 (1971).
(10) L. Vallarino, *J. Chem. Soc.*, 2287 (1957).
(11) G. M. Intille, *Inorg. Chem.*, **11**, 695 (1972).
(12) G. B. Deacon and J. H. S. Green, *Spectrochim. Acta, Part A*, **24**, 845 (1968).
(13) K. Takao, M. Wayaku, Y. Fujiwara, T. Imanaka, and S. Teranishi, *Bull. Chem. Soc. Jpn.*, **43**, 3898 (1970).
(14) G. W. Dudley, G. Read, and P. J. C Walker, *J. Chem. Soc., Dalton Trans.*, 1926 (1974).

(15) (a) J. P. Collman, M. Kubota, and J. W. Hosking, *J. Am. Chem. Soc.*, **89**, 4809 (1967); (b) J. E. Lyons and J. O. Turner, *J. Org. Chem.*, **37**, 2881 (1972).
(16) J. P. Birk, J. Halpern, and A. L. Pickard, *J. Am. Chem. Soc.*, **90**, 4491 (1968).
(17) G. L. Geoffroy, D. A. Denton, and C. W. Eigenbrot, Jr., *Inorg. Chem.*, **15**, 2310 (1976).
(18) R. Brady, B. R. Flynn, G. L. Geoffroy, H. B. Gray, J. Peone, Jr., and L. Vaska, *Inorg. Chem.*, **15**, 1485 (1976).
(19) G. L. Geoffroy, M. S. Wrighton, G. S. Hammond, and H. B. Gray, *J. Am. Chem. Soc.*, **96**, 3105 (1974).
(20) G. Malouf and P. C. Ford, *J. Am. Chem. Soc.*, **96**, 601 (1974).

Synthesis and Reactivity of Cationic Pentacoordinate Nitrosyl Complexes

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The syntheses of two new series of cationic pentacoordinate nitrosyl complexes of iridium and rhodium are described. Their physical properties and spectroscopic data are reported. The bonding modes of the nitrosyl ligand and the geometries around the metal are discussed in comparison with x-ray structures of known compounds and molecular orbital theories. The possibility that the nitrosyl ligand acts as an electron pair sink and pump by interconversion of the bonding modes is considered.

Introduction

There has been a great deal of interest in the synthesis,[1] structure,[2] bonding,[3] and reactivity[3] of pentacoordinate nitrosyl complexes. It is well known that nitric oxide coordinates to transition metal complexes in a linear or bent manner. From a structural point of view the linear arrangement has been viewed in terms of NO^+ and the bent arrangement in terms of NO^-. For the pentacoordinate species the predominant geometries are the square pyramid with a strongly bent apical nitrosyl and a triagonal bipyramid with a linear equatorial nitrosyl. Recently evidence has been reported for the existence of conformational equilibria between the two pentacoordinate forms of metal nitrosyls, whereby the coordination geometry about the metal changes as the metal and the nitrosyl undergo a formal redox reaction.[4] Further studies of these conformational equilibria are being carried out in our laboratories.[5] In this paper we report the synthesis and the characterization of some pentacoordinate cationic nitrosyl complexes of rhodium and iridium and their reactions with neutral ligands. The novel compounds obtained are consistent with (i) present theories of the stability and the geometries of the pentacoordinate nitrosyl complexes[3] and (ii) the capacity of the nitrosyl ligand to act as an electron sink or pump.[4-6]

Experimental Section

All the reactions and subsequent operations were performed in an atmosphere of nitrogen which had been purified by passing it down a column of R 3-11 BASF deoxygenating catalyst and then drying over molecular sieves. All solvents were deoxygenated prior to use and the transfers were carried out with the flexible needle technique or the syringe technique. Acetonitrile was purified as described by Coetzee et al.;[7] absolute ethanol was dried over 3 Å molecular sieves; reagent grade diethyl ether and hexane were purified by distillation from Na. All other chemicals and ligands used were readily available reagent grade chemicals and were used throughout. $RhCl_3 \cdot 3H_2O$ and $Na_2IrCl_6 \cdot 6H_2O$ were purchased from Johnson and Matthey Ltd. Infrared spectra were recorded with a Perkin-Elmer 180 (4000–180 cm^{-1}). The solid samples were run as KBr or CsI pellets. Conductivity measurements were carried out with a Jones 0.1-cm cell and a LKB 5300B Conductolyzer conductivity bridge. Proton NMR spectra were obtained using a Varian Associates XL-100 spectrometer with tetramethylsilane as internal standard. ^{31}P NMR spectra were recorded in 10-mm tubes using the Fourier transform technique at 40.5 MHz, employing a Varian XL-100 spectrometer. All spectra employed

white-noise proton decoupling. ^{31}P chemical shifts are with respect to external 85% H_3PO_4, downfield shifts being negative. NMR samples were prepared by deoxygenating the solids and the solvents with argon separately and using the needle technique for mixing. The elemental analyses were determined by the Microanalysis Laboratory of the Istituto di Farmacia dell'Università di Pisa, Pisa, Italy.

The starting complexes $IrI_2(NO)(P(C_6H_5)_3)_2$ (**1a**) and $RhI_2(NO)(P(C_6H_5)_3)_2$ (**1b**) were prepared as described in the literature.[8,9]

Preparation of $(M(NO)(CH_3CN)_2(P(C_6H_5)_3)_2)(PF_6)_2$ (2a, M = Ir; 2b, M = Rh). To a suspension of 0.7 mmol of the appropriate iodide complex in 20 ml of acetonitrile was added 1.4 mmol of silver hexafluorophosphate in 10 ml of acetonitrile and the mixture was magnetically stirred at room temperature for 15 min. The silver iodide precipitate was removed by filtration in a Schlenk tube. The green solution was concentrated to a small volume under reduced pressure. Slow addition of a 20-ml syringe of ethanol led to the precipitation of the nitrile complexes 2 as green crystals. The precipitate was filtered, washed with ethanol and ether, and dried under vacuum: yield 70% 2a, 85% 2b. Anal. Calcd for (2a) $C_{40}H_{36}F_{12}IrN_3OP_4$: C, 42.94; H, 3.24; N, 3.75. Found: C, 43.01; H, 3.26; N, 3.70. Calcd for (2b) $C_{40}H_{36}F_{12}N_3OP_4Rh$: C, 46.66; H, 3.52; N, 4.08. Found: C, 46.80; H, 3.48; N, 4.10.

Preparation of $(Ir(NO)(N-N)(P(C_6H_5)_3)_2)(PF_6)_2$ (3a, N-N = 2,2′-Bipyridine; 4a, N-N = 1,10-Phenantroline). (i) To a suspension of 0.1 mmol of 2a in 5 ml of ethanol was added the stoichiometric amount of the bidentate ligand in 2 ml of ethanol. The mixture was stirred under reflux for 10 min. After cooling the light brown precipitate was filtered, washed with ethanol and hexane, and dried under vacuum. The crude products were recrystallized from methylene chloride–ethanol to give light brown microcrystals (quantitative yield).

(ii) The same complexes can be obtained in low yields from 1a in ethanol by reaction with a stoichiometric amount of ligand in ethanol and fourfold excess of ammonium hexafluorophosphate in ethanol. The mixture was stirred at room temperature for 7 days. The light brown precipitate was filtered, washed with ethanol and hexane, and dried under vacuum.

(iii) The same complexes can be obtained in quantitative yield from 5 by reaction with a stoichiometric amount of ligand in ethanol solution in the presence of perchloric acid. Anal. Calcd for (3a) $C_{46}H_{38}F_{12}IrN_3OP_4$: C, 46.31; H, 3.20; N, 3.52. Found: C, 45.80; H, 3.26; N, 3.51. Calcd for (4a) $C_{48}H_{38}F_{12}IrN_3OP_4$: C, 47.50; H, 3.12; N, 3.45. Found: C, 48.00; H, 3.10; N, 3.49.

Preparation of $(Rh(NO)(N-N)(P(C_6H_5)_3)_2)(PF_6)_2$ (3b, N-N = 2,2′-Bipyridine; 4b, N-N = 1,10-Phenantroline). (i) These compounds were prepared from 2b using the analogous procedure described above for the iridium analogues except that the reactions were carried out