Complexes of the Platinum Metals. Part 24.[1] The Role of Dioxygen in the Reactions of Trifluoroacetic Acid with the Rhodium and Iridium Nitrosyls $[M(NO)(PPh_3)_3]$

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The role of dioxygen in the conversion of the nitrosyls $[M(NO)(PPh_3)_3]$ (M = Rh or Ir) to the nitrosyl trifluoroacetates $[M(O_2CCF_3)_2(NO)(PPh_3)_2]$ by trifluoroacetic acid, CF_3CO_2H, under aerobic conditions has been investigated by n.m.r. spectroscopy and gas uptake/evolution measurements. The rhodium reaction has been shown to proceed rapidly to completion in the presence of air with the consumption of a stoicheiometric amount of dioxygen (one mole per mole of complex) but occur only slowly and inefficiently under anaerobic conditions. In contrast, the corresponding iridium reaction occurs quite readily under anaerobic conditions. Mechanisms are proposed for these reactions and a similar dioxygen dependence in the reaction of $[Pt(PPh_3)_4]$ with acetic acid is discussed.

In the preceding paper[1] we reported the synthesis of the complexes $[M(O_2CR)_2(NO)(PPh_3)_2]$ (M = Rh or Ir; R = CF_3, C_2F_5, or C_6F_5) from the nitrosyls $[M(NO)(PPh_3)_3]$ and the appropriate perfluorocarboxylic acids, and described their characterisation by spectroscopic and *X*-ray diffraction methods. We also noted that, whereas the synthesis of the iridium complexes proceeds under anaerobic conditions, the corresponding rhodium-based reactions give the required products in significant yield only in the presence of dioxygen. The present paper describes studies on the mechanisms of these and some related reactions, in particular the role of dioxygen in the rhodium reaction and in a comparable platinum(0) system.

Experimental

Complexes mentioned in this paper were prepared by methods described or referenced in the preceding paper.[1] Anaerobic solutions were prepared and manipulated under dinitrogen using serum caps, double-ended needles, and gas-tight syringes. Spectroscopic measurements were performed as described in the preceding paper.[1] The apparatus and techniques used to make gas uptake measurements have been described elsewhere.[2]

Results

Red solutions of $[Rh(NO)(PPh_3)_3]$ in benzene or toluene are stable for indefinite periods under anaerobic conditions and show a well resolved $^{31}P-\{^1H\}$ n.m.r. doublet pattern [δ 47.66 p.p.m.] $^1J(RhP) = 175$ Hz, which remains unchanged over a period of several weeks. As previously reported[3] there is no evidence of dissociated triphenylphosphine in these solutions. On admission of dioxygen at 1 atm (*ca.* 10^5 Pa) to a toluene solution of $[Rh(NO)(PPh_3)_3]$ there is visible evidence of rapid decomposition. The solution turns dark brown and gas uptake measurements indicate that two molecules of dioxygen are consumed per mole of complex (Figure 1). The sole phosphorus-containing product is triphenylphosphine oxide (monitored by $^{31}P-\{^1H\}$ n.m.r.). No tractable rhodium-containing product could be isolated and no evidence for the liberation of nitric oxide was observed. In the presence of an ample supply of dioxygen the initial rhodium complex catalyses the oxidation of free triphenylphosphine to triphenylphosphine oxide.

Addition of trifluoroacetic acid (*ca.* 4 moles per mole of complex) to a benzene solution of $[Rh(NO)(PPh_3)_3]$ under anaerobic conditions produces no discernible change. However, examination of the red solution by $^{31}P-\{^1H\}$ n.m.r. revealed, in addition to resonances arising from the precursor $[Rh(NO)(PPh_3)_3]$ [δ 47.66 p.p.m., $^1J(RhP) = 175$ Hz] and free triphenylphosphine, three new signals, attributable to rhodium-bearing species, which grew in intensity as the concentration of acid was increased (Figure 2). One of the new resonances [δ 20.0 p.p.m., $^1J(RhP) = 116.2$ Hz] was readily assigned to the final product $[Rh(O_2CCF_3)_2(NO)(PPh_3)_2]$. The remaining two resonance patterns presumably arise from intermediates formed by acid (CF_3CO_2H) attack on $[Rh(NO)(PPh_3)_3]$. The first of these consists of a doublet of triplets [δ 50.6 p.p.m., $^1J(RhP) = 184$, $^2J(PP') = 40.5$ Hz] and a doublet of doublets [δ 32.5 p.p.m., $^1J(RhP) = 147$, $^2J(PP') = 40.5$ Hz] indicative of three triphenylphosphine ligands arranged in *mer* configuration. The chemical shift values and the magnitudes of the couplings $^1J(RhP)$ and $^2J(PP')$ strongly suggest that the complex in question contains square-planar rhodium(I) rather than octahedral rhodium(III).[4] Consequently we formulate this species as $[Rh(NHO)(PPh_3)_3][O_2CCF_3]$ rather than *mer*-$[RhH(O_2CCF_3)(NO)(PPh_3)_3]$ or other possible rhodium(III) intermediates. The presence of $[Rh(NHO)(PPh_3)_3][O_2CCF_3]$ in equilibrium with $[Rh(NO)(PPh_3)_3]$ seems entirely feasible since reversible protonation of nitrosyl ligands is known to occur in several platinum group nitrosyl complexes including $[Os(NO)_2(PPh_3)_2]$ and $[Ir(NO)(PPh_3)_3]$.[5] The final resonance pattern, a doublet [δ 25.26 p.p.m., $^1J(RhP) = 116$ Hz] has parameters very similar to those reported for $[RhCl_2(NO)(PPh_3)_2]$ [δ 24.8 p.p.m., $^1J(RhP) = 104$ Hz] and

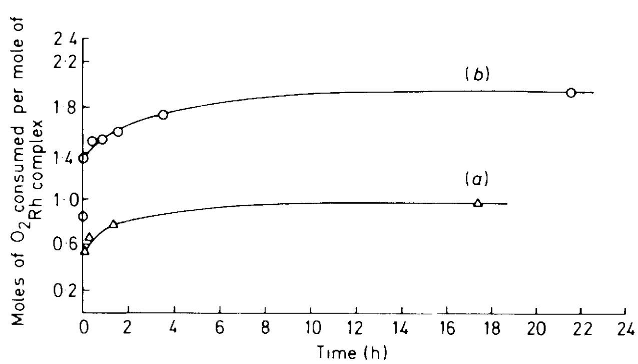


Figure 1. Dioxygen uptake by $[Rh(NO)(PPh_3)_3]$ in benzene solution in the presence (*a*) and absence (*b*) of CF_3CO_2H

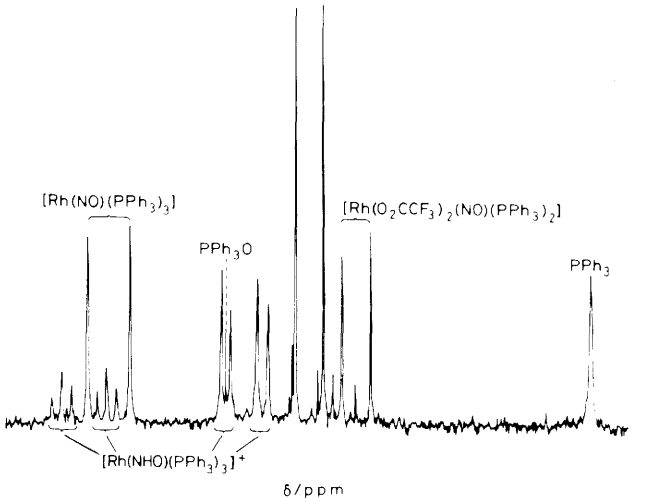


Figure 2. ^{31}P-{^{1}H} N.m.r. spectrum of [Rh(NO)(PPh$_3$)$_3$]/CF$_3$CO$_2$H solution in benzene under anaerobic conditions

[Rh(O$_2$CCF$_3$)$_2$(NO)(PPh$_3$)$_2$]. Narrow-band proton-decoupling experiments establish that the species involved is not a hydride complex. It has not proved possible to make a positive identification of this complex but we believe it to be either *trans*-[Rh(NHO)(O$_2$CCF$_3$)(PPh$_3$)$_2$] or a rhodium(III) product, [Rh(NHOH)(O$_2$CCF$_3$)$_2$(PPh$_3$)$_2$] or [Rh(NH$_2$OH)-(O$_2$CCF$_3$)$_3$(PPh$_3$)$_2$], formed therefrom by further addition of acid. Given that the magnitude of the coupling ^1J(RhP) is more appropriate to *trans*-PPh$_3$ ligands bound to Rh^{III} than Rh^{I}, a rhodium(III) product appears to be most likely. Protonation of [Rh(NO)(PPh$_3$)$_3$] by HCl has been shown previously to afford similar rhodium(III) products, notably [RhCl$_3$(NH$_2$OH)(PPh$_3$)$_2$].[6] Gas evolution measurements performed on anaerobic [Rh(NO)(PPh$_3$)$_3$]/CF$_3$CO$_2$H solutions ([Rh] = 1.6 × 10^{-2} mol dm^{-3}, [CF$_3$CO$_2$H] = 6.0 × 10^{-2} mol dm^{-3}, 10 cm^3 toluene at 30 °C) revealed the liberation of a gas which was identified by g.c. (12-ft Porapak Q column, 30 °C, carrier gas helium, retention time 1.33 relative to CO$_2$ as standard [1.00]) as nitrous oxide. The amount of N$_2$O liberated (0.058 mole per mole of rhodium) corresponds to *ca.* 12% reaction. No evolution of dihydrogen could be detected. Subsequent admission of dioxygen resulted in uptake equal to *ca.* 88% of that expected for a freshly prepared [Rh(NO)(PPh$_3$)$_3$]/CF$_3$CO$_2$H solution (see below).

Admission of dioxygen to *freshly prepared* acetone or benzene solutions of [Rh(NO)(PPh$_3$)$_3$]/CF$_3$CO$_2$H leads to the onset of a rapid reaction; after *ca.* 20 min the red colour is discharged and a clear emerald green solution remains. From this solution the complex [Rh(O$_2$CCF$_3$)$_2$(NO)(PPh$_3$)$_2$] can be isolated in good yield. However, introduction of dioxygen to an 'aged' anaerobic [Rh(NO)(PPh$_3$)$_3$]/CF$_3$CO$_2$H solution affords a much reduced yield of the green product. Gas uptake measurements performed using freshly prepared [Rh(NO)-(PPh$_3$)$_3$]/CF$_3$CO$_2$H solutions in toluene at 5 °C establish that formation of [Rh(O$_2$CCF$_3$)$_2$(NO)(PPh$_3$)$_2$] is accompanied by consumption of one mole of dioxygen per mole of rhodium complex (Figure 1). Formation of [Rh(O$_2$CCF$_3$)$_2$(NO)(PPh$_3$)$_2$] in the presence of dioxygen is not suppressed by the addition of excess triphenylphosphine (*ca.* 5 mole per mole of complex). Introduction of less than the stoicheiometric amount of dioxygen leads to partial conversion. Monitoring of the reaction by ^{31}P-{^{1}H} n.m.r. reveals rapid growth of resonances attributable to the product [Rh(O$_2$CCF$_3$)$_2$(NO)(PPh$_3$)$_2$] and triphenylphosphine oxide at the expense of those arising from the precursor [Rh(NO)(PPh$_3$)$_3$], the various intermediates noted above, and free triphenylphosphine. Addition of oxidising agents (H$_2$O$_2$, PhCO$_2$OH) in place of dioxygen does not lead to formation of the green product [Rh(O$_2$CCF$_3$)$_2$-(NO)(PPh$_3$)$_2$]. Likewise, attempts to alter the rate or course of the reaction by introduction of free radical sources or inhibitors were unsuccessful.

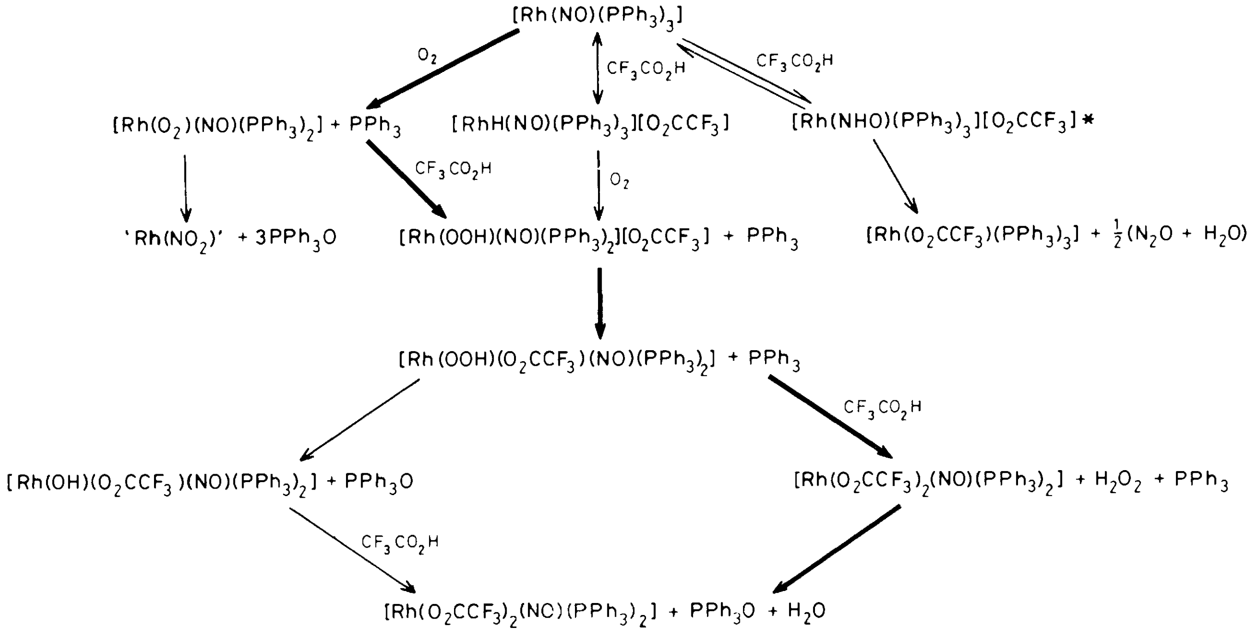
The corresponding reaction of [Ir(NO)(PPh$_3$)$_3$] with trifluoroacetic acid proceeds readily in boiling acetone under aerobic or anaerobic conditions to afford the brown complex [Ir(O$_2$CCF$_3$)$_2$(NO)(PPh$_3$)$_2$] in good yield. A gas evolution experiment performed using a 4.9 × 10^{-3} mol dm^{-3} solution of [Ir(NO)(PPh$_3$)$_3$] with 1.2 × 10^{-2} mol dm^{-3} acid in toluene under argon at 5 °C confirmed the evolution of dihydrogen over a period of 30 min corresponding to *ca.* 30% conversion of [Ir(NO)(PPh$_3$)$_3$] to [Ir(O$_2$CCF$_3$)$_2$(NO)(PPh$_3$)$_2$]; no further gas evolution occurred over longer periods. Proton n.m.r. spectra of solutions having [Ir(NO)(PPh$_3$)$_3$]:CF$_3$CO$_2$H of 1:1 in C$_6$D$_6$ at higher concentrations reveal the essentially quantitative initial formation of [IrH(NO)(PPh$_3$)$_3$][O$_2$CCF$_3$] [δ − 8.1 p.p.m. (q), ^2J(PH) = 20.0 Hz]. Treatment of the 'final' mixture having [Ir(NO)(PPh$_3$)$_3$]:[Ir(O$_2$CCF$_3$)$_2$(NO)(PPh$_3$)$_2$] of 70:30 in the acidic toluene with O$_2$ at 5 °C resulted in a total absorption of 1.0 mole of O$_2$ per mole of [Ir(NO)(PPh$_3$)$_3$] (over *ca.* 4 h). Finally, 5.0 × 10^{-3} mol dm^{-3} solutions of [Ir(NO)(PPh$_3$)$_3$] in toluene at 5 °C absorb dioxygen very slowly {0.20 moles per mole of [Ir(NO)(PPh$_3$)$_3$] over a period of 20 h}; at 25 °C over the same period, the uptake levels off at *ca.* 2.0 moles of O$_2$ per mole of Ir.

In collaboration with Dr. G. W. Parshall we have previously noted that the reaction of [Pt(PPh$_3$)$_4$] with acetic acid in benzene proceeds to form the expected product *cis*-[Pt(O$_2$CCH$_3$)$_2$(PPh$_3$)$_2$] only in the presence of dioxygen.[7] We have not done any further experimental work on this system but we discuss our observations, and their relevance to the present study, in the light of results from another laboratory.[8,9]

Discussion

The Rhodium System.—The sensitivity of [Rh(NO)(PPh$_3$)$_3$] solutions to dioxygen is well known; the effect of even minute traces of dioxygen has been dramatically illustrated by the anomalously low molecular weight values recorded for such solutions by osmometric methods.[10] Determination of dissociation constants by ^{31}P-{^{1}H} n.m.r.[3] and electronic spectroscopic[11] measurements establishes that, under truly anaerobic conditions, the degree of dissociation is in fact very small. Dioxygen also appears to play a part in the catalytic activity of [Rh(NO)(PPh$_3$)$_3$]; thus isomerisation of olefins is reported to occur only after admission of traces of dioxygen to the system.[6] However, the dioxygen dependence of the [Rh(NO)(PPh$_3$)$_3$]/CF$_3$CO$_2$H system was not anticipated, since previous workers have reported that oxidative addition of numerous substrates, including hydrogen chloride to [Rh(NO)(PPh$_3$)$_3$], occurs readily under apparently anaerobic conditions.[6] In an attempt to explain the dioxygen dependence of the [Rh(NO)(PPh$_3$)$_3$]/CF$_3$CO$_2$H system, we examined a wide range of possible mechanisms. The participation of free radicals was considered unlikely and was ruled out by the failure of radical sources or radical inhibitors to affect the course of the reaction. The stoicheiometric nature of the dioxygen uptake decisively eliminates mechanisms involving catalysis or promotion by *traces* of dioxygen. Likewise, the failure of other oxidising agents to fill the role of dioxygen clearly implies that we are dealing with a rhodium dioxygenation rather than a simple oxidation.

More plausible pathways involving protonation and/or dioxygenation of the rhodium complex are outlined in the reaction diagram (Scheme 1). The preferred mechanism is defined by the heavier arrows. Because of the well known



Scheme 1. * Plus further protonation products (see text)

lability of rhodium(I) complexes we have been unable to isolate the postulated intermediates. However, several have been detected and characterised in solution by $^{31}P-\{^1H\}$ n.m.r. Furthermore, the conclusions reached are supported in part by work on the related platinum and palladium systems $[M(PPh_3)_4]/RCO_2H/O_2$ for which a similar mechanism has been advanced, and verified by isolation of the proposed hydroperoxy intermediates.[8,9] In marked contrast to the corresponding iridium complex (see below), the rhodium nitrosyl complex $[Rh(NO)(PPh_3)_3]$ in anaerobic solution appears to be protonated by CF_3CO_2H primarily at the nitrosyl ligand rather than at the metal centre. Thus the dominant protonated species in these systems is $[Rh(NHO)(PPh_3)_3]^+$ rather than $[RhH(NO)(PPh_3)_3]^+$. Co-ordinated NHO ligands are known to decompose with release of N_2O[12] and the detection of this gas in the present reaction strongly implies that decomposition of the $[Rh(NHO)(PPh_3)_3]^+$ cation occurs. Loss of nitrosyl ligands in this way offers a plausible explanation for the failure of the green complex $[Rh(O_2CCF_3)_2(NO)(PPh_3)_2]$ to form in significant amounts under these circumstances. The small amounts of this product detected in solution by $^{31}P-\{^1H\}$ n.m.r. are presumably formed either by an anaerobic route in which the traces of $[RhH(NO)(PPh_3)_3]^+$ generated in the initial protonation react with further acid, or by reactions involving adventitious traces of dioxygen. If the acidified $[Rh(NO)(PPh_3)_3]$ solutions are allowed to stand for more than 2—3 minutes, much of the $[Rh(NHO)(PPh_3)_3][O_2CCF_3]$ formed undergoes further irreversible reaction and subsequent admission of dioxygen affords a much reduced yield of $[Rh(O_2CCF_3)_2(NO)(PPh_3)_2]$.

The rapid reaction of $[Rh(NO)(PPh_3)_3]$ with dioxygen in solution presumably involves formation of a transient dioxygen complex. We tentatively formulate this species as $[Rh(O_2)(NO)(PPh_3)_2]$ but cannot exclude alternative binuclear structures analogous to that established for $[RhCl(O_2)(PPh_3)_2]_2$.[13] In the absence of acid this dioxygen complex is rapidly and irreversibly consumed, together with a second molecule of dioxygen, to form triphenylphosphine oxide and an intractable rhodium-containing product. In view of the $[Rh(NO)(PPh_3)_3]:O_2 = 1:2$ stoicheiometry of the dioxygen uptake we formulate the rhodium residue as 'Rh(NO$_2$)', and the overall reaction as in (1). All the phosphine present is converted

$$[Rh(NO)(PPh_3)_3] + 2\,O_2 \longrightarrow \text{'}Rh(NO_2)\text{'} + 3\,PPh_3O \quad (1)$$

to phosphine oxide. We found no evidence for the evolution of nitrogen oxides during this process but have not exhaustively tested for the same.

We suggest that in the presence of trifluoroacetic acid the dioxygen complex is intercepted and protonated to yield a hydroperoxy intermediate $[Rh(OOH)(O_2CCF_3)(NO)(PPh_3)_2]$. Alternatively 'insertion' of dioxygen into the Rh–H bond of $[RhH(NO)(PPh_3)_3]^+$ with concomitant movement of the equilibrium $[Rh(NHO)(PPh_3)_3]^+ \rightleftharpoons [RhH(NO)(PPh_3)_3]^+$ to the right could yield the same intermediate. Formation of hydroperoxy ligands by protonation of co-ordinated dioxygen[8,9,14] and by 'insertion' of dioxygen into M–H bonds[15–19] has previously been reported for platinum metal complexes akin to those discussed here. Two routes for the further reaction of co-ordinated hydroperoxy ligands could lead to formation of the observed products. The first of these involves reduction of bound –OOH groups by triphenylphosphine to yield triphenylphosphine oxide and a hydroxy species, $[Rh(OH)(O_2CCF_3)(NO)(PPh_3)_2]$, which can subsequently react with a further molecule of acid to form the required product. This pathway parallels one previously proposed for platinum(II) hydroperoxy complexes $[Pt(OOH)(solvent)(PR_3)_2]^+$.[17] The second route involves direct reaction of $[Rh(OOH)(O_2CCF_3)(NO)(PPh_3)_2]$ with a further molecule of acid to generate the required product and a molecule of H_2O_2. The latter then oxidises a molecule of liberated triphenylphosphine to triphenylphosphine oxide in a separate step. Although there is no conclusive evidence available on this point we tentatively suggest that, by analogy with the $[Pt(O_2)(PPh_3)_2]/RCO_2H$ system[8,9] which affords H_2O_2 in high yield, the second route is likely to be the operative one in the present reaction. However, since the rhodium system involves liberation of free triphenylphosphine, the H_2O_2, if formed, would be consumed rapidly *in situ* and could not therefore be readily detected.

The Iridium System.—In sharp contrast to its rhodium analogue, the iridium complex $[Ir(NO)(PPh_3)_3]$ reacts only slowly with dioxygen in toluene solution at 5 °C: gas uptake measurements indicate that *ca.* 0.20 mole is consumed per mole of iridium over a period of *ca.* 20 h, although the 2:1 stoicheiometry was noted at 25 °C indicative of a reaction akin to (1). Furthermore, the reaction between $[Ir(NO)(PPh_3)_3]$ and CF_3CO_2H is essentially independent of dioxygen. Proton n.m.r. spectra of anaerobic $[Ir(NO)(PPh_3)_3]/CF_3CO_2H$ solutions in C_6D_6 reveal that the major protonation product is the known cation $[IrH(NO)(PPh_3)_3]^+$ [δ −8.1 p.p.m. (q), $^2J(PH) = 20.0$ Hz][20] and gas evolution measurements on these solutions confirm liberation of dihydrogen in significant amounts even at 5 °C. It therefore appears that the conversion of $[Ir(NO)(PPh_3)_3]$ to $[Ir(O_2CCF_3)_2(NO)(PPh_3)_2]$ proceeds readily under anaerobic conditions by a series of protonation and H_2 elimination steps (Scheme 2) analogous to those proposed for the corresponding reactions of the nitrosyls $[M(NO)(PPh_3)_3]$ (M = Rh or Ir) with HCl.[6,20] The enhanced rate and 1:1 stoicheiometry of dioxygen uptake observed for $[Ir(NO)(PPh_3)_3]$ in the presence of trifluoroacetic acid suggest that under aerobic conditions a competing reaction (Scheme 3), analogous to that described for rhodium, may also be operative for the iridium system. An earlier report[21] that $[IrH(NO)(PPh_3)_3]^+$ reacts with dioxygen to afford $[Ir(OH)(NO)(PPh_3)_2]^+$ and PPh_3O lends some support to this suggestion.

$$[Ir(NO)(PPh_3)_3] \xrightarrow{CF_3CO_2H} [IrH(NO)(PPh_3)_3][O_2CCF_3]$$

$$[IrH(NO)(PPh_3)_3][O_2CCF_3] \longrightarrow [IrH(O_2CCF_3)(NO)(PPh_3)_2] + PPh_3$$

$$[IrH(O_2CCF_3)(NO)(PPh_3)_2] \xrightarrow{CF_3CO_2H} [Ir(O_2CCF_3)_2(NO)(PPh_3)_2] + H_2$$

Scheme 2.

$$[Ir(NO)(PPh_3)_3] \xrightarrow{CF_3CO_2H} [IrH(NO)(PPh_3)_3][O_2CCF_3]$$

$$[IrH(NO)(PPh_3)_3][O_2CCF_3] \xrightarrow{O_2} [Ir(OOH)(O_2CCF_3)(NO)(PPh_3)_2] + PPh_3$$

$$[Ir(OOH)(O_2CCF_3)(NO)(PPh_3)_2] + PPh_3 \longrightarrow [Ir(OH)(O_2CCF_3)(NO)(PPh_3)_2] + PPh_3O$$

$$[Ir(OH)(O_2CCF_3)(NO)(PPh_3)_2] \xrightarrow{CF_3CO_2H} [Ir(O_2CCF_3)_2(NO)(PPh_3)_2] + H_2O$$

Scheme 3.

The Platinum System.—Independent reports[8,9] that the palladium and platinum complexes $[M(O_2)(PPh_3)_2]$ react with carboxylic acids, RCO_2H, to form *cis*-$[M(OOH)(O_2CR)(PPh_3)_2]$ and thence *cis*-$[M(O_2CR)_2(PPh_3)_2] + H_2O_2$ cast new light on our earlier observation[7] that $[Pt(PPh_3)_4]$ reacts with CH_3CO_2H to form *cis*-$[Pt(O_2CCH_3)_2(PPh_3)_2]$ only in the presence of air. It now seems probable that the aerobic nature of the reaction reflects the intermediate formation of $[Pt(O_2)(PPh_3)_2]$. Conversely the failure of the reaction to proceed under anaerobic conditions must indicate that a simple protonation mechanism, which is known to afford the species $[PtH(PPh_3)_3]^+$ with mineral acids,[22] does not proceed further with carboxylic acids except possibly under more forcing conditions.

Conclusions

It appears that the differences in the reaction patterns of the rhodium and iridium nitrosyls toward CF_3CO_2H can be traced to the initial protonation step. The rhodium complex protonates primarily at the nitrosyl ligand under anaerobic conditions to yield an unstable NHO species which subsequently reacts irreversibly to afford N_2O thus preventing formation of the anticipated nitrosyl $[Rh(O_2CCF_3)_2(NO)(PPh_3)_2]$. The introduction of dioxygen leads to formation of a hydroperoxy complex, by protonation of bound O_2 or by insertion of O_2 into the Rh–H bond and initiates a rapid conversion to $[Rh(O_2CCF_3)_2(NO)(PPh_3)_2]$. In contrast, the iridium complex, having a more basic metal centre, forms a hydride species $[IrH(NO)(PPh_3)_3]^+$ on protonation. This cation, or, if air is present, the hydroxy cation $[Ir(OH)(NO)(PPh_3)_2]^+$ formed therefrom by dioxygen attack, reacts readily with more acid to afford $[Ir(O_2CCF_3)_2(NO)(PPh_3)_2]$.

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