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Preliminary communication

NEW NITROSYL(PERFLUOROCARBOXYLATO) COMPLEXES OF THE PLATINUM METALS

ALAN DOBSON and STEPHEN D. ROBINSON*
Department of Chemistry, King's College, Strand, London, WC2R 2LS (Great Britain)

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Summary

Perfluorocarboxylic acids (R_FCOOH) ($R_F = CF_3, C_2F_5$ and (for Rh) C_6F_5) react with the species $[M(NO)_2(PPh_3)_2]$ (M = Ru, Os) and $[M'(NO)(PPh_3)_3]$ (M' = Rh, Ir) to yield new nitrosyl complexes $[Ru(OCOR_F)_3(NO)(PPh_3)_2]$, $[OsH(OCOR_F)_2(NO)(PPh_3)_2]$, $[Os(OCOR_F)(NO)_2(PPh_3)_2][OCOR_F]$, $[Ir(OCOR_F)(NO)(PPh_3)_2][OCOR_F]$ and $[Rh(OCOR_F)_2(NO)(PPh_3)_2]$.

The increasing significance of nitrosyl and carboxylate ligands in homogeneous catalysis has prompted an investigation of complexes containing these groups bound within the same coordination sphere. To the small number of known examples we now add five new series of complexes possessing this interesting ligand combination.

Perfluorocarboxylic acids (R_FCOOH)** react with $[Ru(NO)_2(PPh_3)_2]$ in boiling toluene or 2-methoxyethanol to yield the air-stable, orange-brown species $[Ru(OCOR_F)_3(NO)(PPh_3)_2]$ (ν(NO) ca. 1905 cm^{-1}) which are formulated as Ru^{II}/NO^+ derivatives analogous to the known trihalides $[RuX_3(NO)(PPh_3)_2]$ (ν(NO) ca. 1875 cm^{-1}) [1]. However, the nature of the products obtained from $[Os(NO)_2(PPh_3)_2]$ is solvent dependent; reactions in boiling 2-methoxyethanol afford the hydrides $[OsH(OCOR_F)_2(NO)(PPh_3)_2]$ (ν(OsH) ca. 2170, ν(NO) ca. 1820 cm^{-1}; τ(OsH) ca. 16.0. ^2J(PH) ca. 14.0 Hz) whereas those performed in boiling toluene solution yield salts $[Os(OCOR_F)(NO)_2(PPh_3)_2][OCOR_F]$ (ν(NO) ca. 1820 and 1610*** cm^{-1}) analogous to the known species $[Os(OH)(NO)_2(PPh_3)_2][X]$ (X = BF_4, PF_6; ν(NO) ca. 1842 and 1632 cm^{-1}) [2]. Prolonged vigorous treatment of the hydrides $[OsH(OCOR_F)_2(NO)(PPh_3)_2]$ with excess acid, R_FCOOH, failed to yield osmium analogues of the ruthenium products $[Ru(OCOR_F)_3(NO)(PPh_3)_2]$.

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*To whom correspondence should be addressed.

**$R_F = CF_3$, C_2F_5 and (for Rh) C_6F_5.

***Masked by ν(OCO) vibration.

The iridium nitrosyl, $[Ir(NO)(PPh_3)_3]$, on treatment with perfluorocarboxylic acids in boiling acetone, affords products of stoichiometry $[Ir(OCOR_F)_2(NO)(PPh_3)_2]$ (ν(NO) ca. 1800). These are formulated as salts $[Ir(OCOR_F)(NO)(PPh_3)_2][OCOR_F]$ analogous to the known species $[IrX(NO)(PPh_3)_2][Y]$ (X=OH,Cl,I,OEt; Y = ClO_4, BF_4, PF_6; ν(NO) ca. 1840-1900 cm^{-1}) [3] rather than analogues of the non-ionic dihalides $[IrX_2(NO)(PPh_3)_2]$ (ν(NO) ca. 1550 cm^{-1}) [4]. Whereas the above reactions all occur equally well under aerobic or anaerobic conditions, the presence of dioxygen is essential to the reaction of $[Rh(NO)(PPh_3)_3]$ with perfluorocarboxylic acids in acetone, and the products are green non-ionic species $[Rh(OCOR_F)_2(NO)(PPh_3)_2]$ (ν(NO) ca. 1665 cm^{-1}) analogous to the known dihalides $[RhX_2(NO)(PPh_3)_2]$ (ν(NO) ca. 1630 cm^{-1}) [4].

Formation of the salts $[Ir(OCOR_F)(NO)(PPh_3)_2][OCOR_F]$ and $[Os(OCOR_F)(NO)_2(PPh_3)_2][OCOR_F]$ presumably involves successive protonations at the metal centre followed by elimination of dihydrogen and coordination of a perfluorocarboxylate anion. In contrast, mechanisms involving protonation of a nitrosyl ligand, either directly or by transfer from the metal, afford the best rationalisation for the formation of the complexes $[Ru(OCOR_F)_3(NO)(PPh_3)_2]$ and $[OsH(OCOR_F)_2(NO)(PPh_3)_2]$. Similar mechanisms have previously been advanced to account for the reactions of $[Ir(NO)(PPh_3)_3]$ and $[Os(NO)_2(PPh_3)_2]$ with hydrochloric acid [5,6]. The dioxygen dependence of the rhodium/perfluorocarboxylic acid systems, which is unexpected in view of the numerous related "oxidative addition" reactions undergone by $[Rh(NO)(PPh_3)_3]$ under apparently anaerobic conditions [7], is under investigation. Attempts to characterise intermediates and to establish detailed mechanisms for these reactions are in progress.

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