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The Crystal and Molecular Structure of Bis(trifluoroacetato)nitrosylbis(triphenylphosphine)rhodium and its Iridium Analogue

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The coordination arrangements adopted by pentacoordinated mononitrosyl complexes of the group VIII metals have been rationalised in terms of two closely related basic structures – tetragonal pyramidal and trigonal bipyramidal – with apical angular and equatorial linear nitrosyl groups respectively [1]. Theoretical studies have led to the correlation of these coordination arrangements with the electronic configuration of the central metal atom and the nature of the ancillary ligands [2, 3]. However, the numerous X-ray diffraction studies reported for complexes of this type have revealed subtle variations of these ideal structures and have served to maintain interest in the field. We now report two new diffraction studies which provide further evidence of the rich structural diversity found in these systems.

The products of stoichiometry $M(O_2CCF_3)_2(NO)(PPh_3)_2$ (M = Rh or Ir) previously prepared in our laboratory by treatment of the corresponding nitrosyls $M(NO)(PPh_3)_3$ with trifluoroacetic acid in acetone solution [4] were apparently simple analogues of the well-known dichlorides $MCl_2(NO)(PPh_3)_2$. However they display chemical and spectroscopic anomalies which appeared to merit further investigation. In particular the rhodium complex forms only in the presence of dioxygen and the iridium complex has a nitrosyl stretching frequency (1800 cm^{-1}) substantially removed from that of its dichloro analogue (1550 cm^{-1}). X-ray diffraction studies undertaken to help resolve these anomalies have revealed structures significantly different from those previously established for the pair of isomorphous dichloronitrosyl complexes $MCl_2(NO)(PPh_3)_2$ [5, 6].

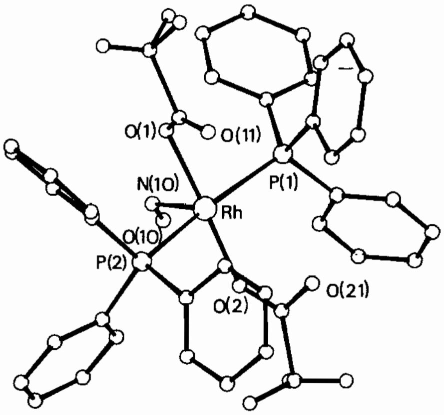

Fig. 1. The molecular structure of $Rh(O_2CCF_3)_2(NO)(PPh_3)_2$. Selected geometry parameters are: Rh–N(1) 1.93(2); Rh–O(1) 2.10(2); Rh–O(2) 2.03(2); Rh····O(11) 2.72(2); Rh····O(21) 3.16(2); Rh–P(1) 2.389(8); Rh–P(2) 2.374(9); N(10)–O(10) 1.12(3) Å; N(10)–Rh–O(1) 82(1); N(10)–Rh–O(2) 98(9); N(10)–Rh–P(1) 95(1); N(10)–Rh–P(2) 101(1); O(1)–Rh–O(2) 178(1); P(1)–Rh–P(2) 163.7(1); Rh–N(10)–O(10) 122(1)°.

Experimental

The complexes were synthesized according to the literature procedure [4] and formed bright green (M = Rh) or orange brown crystals (M = Ir) from acetone/light petroleum.

Crystal Data

$Rh(O_2CCF_3)_2(NO)(PPh_3)_2$. *M* = 883.52 amu, monoclinic, *a* = 12.593(2), *b* = 15.466(3), *c* = 20.479(3) Å, *β* = 100.03(2)°, *U* = 3928 Å^3, space group *Cc*, *Z* = 4, D_{calc} = 1.49 g cm^{-3}, *F*(000) = 1784, $\mu(M_o - K_\alpha)$ = 5.14 cm^{-1}, *R* = 0.085 for 2918/3611 observed data measured on a diffractometer.

$Ir(O_2CCF_3)_2(NO)(PPh_3)_2 \cdot (CH_3)_2CO$. *F.M.* = 1030.90 amu, orthorhombic, *a* = 19.171(2), *b* = 22.684(3), *c* = 20.169(3) Å, *U* = 8771 Å^3, space group *Pbcn*, *Z* = 8, D_{calc} 1.563 g cm^{-3}, *F*(000) = 3824, $\mu(M_o - K_\alpha)$ = 30.39 cm^{-1}, *R* = 0.082 for 3791/7704 data.

Results and Discussion

The rhodium complex, $Rh(O_2CCF_3)_2(NO)(PPh_3)_2$ has a tetragonal pyramidal structure (Fig. 1) with an apical angular nitrosyl ligand (∠Rh–N–O = 122.2(16)°] not dissimilar in form and molecular dimensions to that found for the corresponding

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dichloride $RhCl_2(NO)(PPh_3)_2$ [5]. However, it differs from the latter complex in one important aspect. Whereas in most tetragonal pyramidal nitrosyl complexes, including $RhCl_2(NO)(PPh_3)_2$, the N–O vector is coplanar with one of the basal metal ligand vectors, in the present complex the N–O vector is coplanar with the bisector of the Rh–O and Rh–P vectors. A rather similar situation has previously been reported for the tetragonal pyramidal complex *cis*-$RhBr_2(NO)\{P(OPh)_3\}_2$ where the N–O vector is directed between the Rh–P vectors and hence towards the most crowded part of the molecule [7].

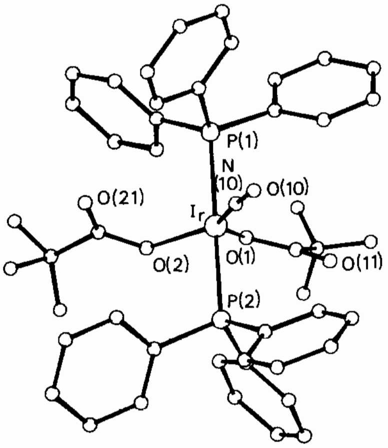

Fig. 2. The molecular structure of $Ir(O_2CCF_3)_2(NO)(PPh_3)_2$. Selected geometry parameters are: Ir–N(10) 1.59(3); Ir–O(1) 2.14(2); Ir–O(2) 2.11(2); Ir····O(11) 3.15(2); Ir····O(21) 3.23(2); Ir–P(1) 2.378(5); Ir–P(2) 2.372(5); N(10)–O(10) 1.28(4) Å; N(10)–Ir–O(1) 142(1); N(10)–Ir–O(2) 144(1); N(10)–Ir–P(1) 89(1); N(10)–Ir–P(2) 93(1); O(1)–Ir–O(2) 74.6(6); P(1)–Ir–P(2) 177.9(3); Ir–N(10)–O(10) 178(2)°.

In order to explore the possible reasons for the adoption of this particular conformation, we have analysed the steric interactions in the $Rh(O_2CCF_3)_2(NO)(PPh_3)_2$ molecule using our recently developed potential energy program EENY2 [8, 9]. The main results, which will be described in detail in the full publication on this work, are that the molecular conformation lies in a well-defined P.E. minimum with respect to rotation of ligands about the metal–ligand bonds, and that the oxygen of the bent NO group is involved in small but significant attractive interactions with components of all the other ligands present. Rotation of the NO group about the Rh–N bond in any direction either removes these attractive interactions or introduces repulsions. It seems clear, therefore, that the orientation found may well arise because steric interactions override any alternative electronically preferred orientation.

In contrast the iridium complex $Ir(O_2CCF_3)_2(NO)(PPh_3)_2$ has a structure very different from those found for the corresponding dichloride, $IrCl_2(NO)(PPh_3)_2$ [6], and for the rhodium complexes discussed above. The coordination geometry about the metal atom is essentially trigonal bipyramidal with axial triphenylphosphine ligands and an equatorial linear nitrosyl group (Fig. 2). The nitrosyl ligand apparently has an unusually long N–O bond [1.28(4) Å] and an unusually short Ir–N bond [1.59(3) Å], although in view of difficulties encountered in the refinement of this structure these values may be unreliable. However, the most interesting feature of the structure is the very acute angle [74.6(6)°] subtended at the iridium by the coordinated oxygen atoms of the two monodentate carboxylate ligands. A very similar trigonal bipyramidal structure with axial triphenylphosphine ligands and an equatorial linear nitrosyl group has recently been reported by Tiripicchio *et al.* [10] for the di-cation $[Ir(o\text{-phen})(NO)(PPh_3)_2]^{2+}$. In this complex the angle subtended at the iridium by the two nitrogen atoms of the *o*-phenanthroline ligand is also very acute (75.8°). The presence of this small angle was attributed to geometric constraints arising from a combination of long Ir–N (*o*-phen) distances – induced by the high *trans* influence of the linear nitrosyl ligand – and the narrow bite of the *o*-phenanthroline chelate ligand. However, in the present complex, which displays an even smaller subtended angle at the iridium, similar factors are clearly not operative since only non-chelate ligands are involved.

In an attempt to throw fresh light on this problem we have examined the $Ir(O_2CCF_3)_2(NO)(PPh_3)_2$ structure using the potential energy programme EENY2. In this case the equatorial O–Ir–O angle was allowed to vary in the energy minimisation process but no force field was assigned to this variation. Again the experimentally determined structure is close to the steric energy minimum, with torsion angles for the orientations of the ligands about the Ir–ligand bonds changing by less than ±10° in the minimisation process. In addition, the O–Ir–O angle actually reduced to 64° at which point the O(1)···O(2) interaction was exactly zero. Although a full calculation would have to include an allowance for a change in energy due to changes in this angle, the results do suggest that the value found experimentally may well arise from steric interactions in the molecule, particularly those involving the non-metal-bonded carboxylate oxygens.

Studies on related systems designed to throw further light on the factors governing the structures adopted by $MX_2(NO)(PR_3)_2$ complexes are in progress.

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