# Quantitative Formation of Coordinated Hydroxamate (2–) Ligands by Attack of Perfluorocarboxylic Acids on $[\overline{Os(NO)_2}(PPh_3)_2]$; the X-Ray Crystal Structure of $[\overline{Os\{ON:C(O}\overline{)}CF_3\}(O_2CCF_3)(NO)(PPh_3)_2]$

BARRY HAYMORE, JOHN C. HUFFMAN

*Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Ind 47405, U.S.A.*

ALAN DOBSON and STEPHEN D. ROBINSON

*Department of Chemistry, King's College, Strand, London WC2R 2LS, U.K.*

Received June 30, 1982

Current interest in the reactions of coordinated nitric oxide ligands, in particular those leading to formation of nitrogen–carbon bonds [1], prompts this report of a novel reaction involving quantitative formation of trifluoroacetohydroxamate(2–) ligands, $CF_3C(O){:}NO$, by attack of trifluoroacetic acid on $[Os(NO)_2(PPh_3)_2]$. Treatment of $[Os(NO)_2(PPh_3)_2]$ with a ten-fold molar excess of trifluoroacetic acid in boiling toluene over a period of 30 min. affords an essentially quantitative yield (95–99% by $^{31}P$ NMR) of an air-stable, orange complex which crystallises from methanol/toluene in 87–92% yield. The infrared spectrum of the product shows bands attributable to monodentate carboxylate ligands (1689 and 1401 $cm^{-1}$) and triphenylphosphine together with strong bands at 1818 and 1609 $cm^{-1}$. NMR data are $^{31}P\{^1H\}$ −7.4(d) and −13.6(d) ppm, $^2J(PP') = 11.9$ Hz; $^{19}F$, 94.3(s) and 87.7(s) ppm*. Pentafluoropropionic acid affords an analogous product with similar yield and spectroscopic properties. Since chemical and spectroscopic evidence alone did not permit identification of these products an X-ray diffractive study was undertaken. The structure of the trifluoroacetic acid derivative was determined at −160 °C using a well-formed bright orange solvated crystal (dimensions 0.12 × 0.13 × 0.13 mm) grown from methylene chloride/methanol.

*Crystal data*: $C_{40}H_{30}F_6N_2O_5OsP_2 \cdot CH_2Cl_2$. F Wt = 984.81 + 84.94 triclinic, space group $P\bar{1}$, $a = 12.709(3)$, $b = 22.694(8)$, $c = 9.662(3)$ Å, $\alpha = 118.282(3)$, $\beta = 113.593(3)$, $\gamma = 59.659(4)°$, $U = 2070.1$ Å$^3$, $D_{calc} = 1.720$ g cm$^{-3}$, $Z = 2$, $\mu$(Mo-K$_\alpha$) = 33.7 cm$^{-1}$.

Data was collected using a Picker goniostat. The structure was solved by a combination of direct methods and Fourier techniques. Hydrogen atoms were included as fixed atom contributors (dC–H = 0.95 Å, $B_{iso} = 4.0$ Å$^2$), phenyl carbons were assigned isotropic thermal parameters and all other atoms anisotropic thermal parameters in the full-matrix refinement. Final residuals are $R(F) = 0.051$ and $Rw(F) = 0.049$ for 4730 independent reflections with $I > 2.33\sigma(I)$.

The crystal contains molecules of the neutral six coordinate osmium(II) complex $[\overline{Os\{ON:C(O}\overline{)}CF_3\}(O_2CCF_3)(NO)(PPh_3)_2]$ and dichloro-methane solvent in a 1/1 ratio. The most noteworthy features of the complex (Fig. 1) are the chelating O,O′-trifluoroacetohydroxamate(2–) ligand and the strained *cis* disposition of the two bulky triphenylphosphine ligands ($\angle P_1$–Os–$P_2$ = 106.51(8)°]. The hydroxamate ligand is unequivocally bound through both oxygen atoms and the carbon–nitrogen ($C_2$–$N_2$) distance (1.277(11) Å) is very close to that expected for a carbon–nitrogen double bond. The other bond angles and distances (Fig. 1) are similar to those found in related structures [2, 3]. In the light of this structure the infrared bands at 1818 and 1609 $cm^{-1}$ can be attributed to $\nu$(NO) and $\nu$(C=N) respectively.

To account for the formation of the hydroxamate ligand we postulate a reaction mechanism involving

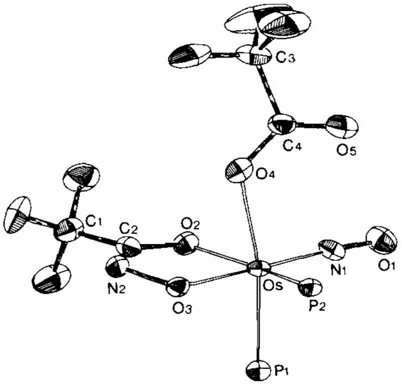

Fig. 1. A perspective drawing of $\overline{Os\{ON:C(O}\overline{)}CF_3\}(O_2CCF_3)$-(NO)$(PPh_3)_2$ showing the atom labelling scheme. The solvent molecule and six phenyl groups have been omitted for clarity. Some important bond distances (Å) and angles (deg.) are: Os–$P_1$ = 2.378(2), Os–$P_2$ = 2.397(2), Os–$N_1$ = 1.739(7), Os–$O_2$ = 2.069(6), Os–$O_3$ = 1.973(6), Os–$O_4$ = 2.116(6), $N_1$–$O_1$ = 1.207(10), $C_2$–$O_2$ = 1.310(10), $C_2$–$N_2$ = 1.277(11), $N_2$–$O_3$ = 1.421(9), $C_1$–$C_2$ = 1.511(13), $P_1$–Os–$P_2$ = 106.51(8), $O_2$–Os–$O_3$ = 78.2(2), $N_2$–$C_2$–$O_2$ = 127.0(8), Os–$O_3$–$N_2$ = 115.7(5), Os–$O_2$–$C_2$ = 109.0(5), $O_3$–$N_2$–$C_2$ = 109.3(7).

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*NMR spectra were taken in $CH_2Cl_2$ or $CD_2Cl_2$ at 25 °C and are referenced to external 85% $H_3PO_4$ ($^{31}P$) and internal $C_6F_6$ ($^{19}F$). More positive chemical shifts indicate lower field. Descriptions of spectra ignore long range fluorine–phosphorus couplings $^5J(PF) = 1.0$ to 1.5 Hz seen when the phosphine ligand is *trans* to a fluorine containing group.

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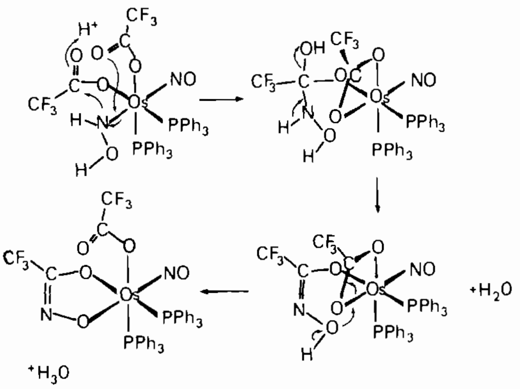

successive protonations at a nitrosyl ligand to yield $[Os(O_2CCF_3)_2(NHOH)(NO)(PPh_3)_2]$ followed by an intramolecular condensation between the NHOH ligand and the carbonyl group of a $O_2CCF_3$ ligand (Scheme). Sampling of the gases over the reaction mixture established the liberation of water during the reaction and the absence of dihydrogen. Narrow band $\{^1H\}$ decoupled $(C_6H_5)$ $^{31}P$ NMR spectra of the reaction mixture failed to detect any evidence of osmium hydrido intermediates (no P–H couplings). The protonation steps leading to formation of $[Os(O_2CCF_3)_2(NHOH)(NO)(PPh_3)_2]$ parallel the known formation of $[OsCl_2(NHOH)(NO)(PPh_3)_2]$ from $[Os(NO)_2(PPh_3)_2]$ and HCl [4]. Experimental evidence supporting the presence of $[Os(O_2CCF_3)_2(NHOH)(NO)(PPh_3)_2]$ as an intermediate is provided by $^{31}P$ NMR spectra of $[Os(NO)_2(PPh_3)_2]$/ $CF_3COOH$ solutions in cold toluene which display a strong singlet signal ($\delta = -10.5$ ppm) very close to that observed for $[OsCl_2(NHOH)(NO)(PPh_3)_2]$ ($\delta = -8.7$ ppm). Treatment of the corresponding ruthenium complex $[Ru(NO)_2(PPh_3)_2]$ with trifluoroacetic acid in boiling toluene afforded $[Ru(O_2CCF_3)_3(NO)(PPh_3)_2]$ in good yield together with isolable quantities of $[NH_3OH][O_2CCF_3]$. No evidence of a ruthenium hydroxamate product was found. Presumably in the ruthenium system further protonation leading to formation and liberation of $NH_2OH$ takes precedent over the intramolecular condensation step. Further chemical studies on the chemistry of these systems are in progress.

## Acknowledgement

We thank the Marshall M. Wrubel Computing Center at Indiana University for computing time.

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