COMMUNICATION

THE PREPARATION AND CRYSTAL STRUCTURE OF BIS(BIS(DIPHENYLPHOSPHINO)ETHANE)CARBONYLFORMYLOSMIUM(II) HEXAFLUOROANTIMONATEDICHLOROMETHANE (1/1)

GARRY SMITH and **DAVID J. COLE-HAMILTON***
Donnan Laboratories, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, England

and

MARK THORNTON-PETT and **MICHAEL B. HURSTHOUSE**
Chemistry Department, Queen Mary College, Mile End Road, London E1 4NS, England

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Abstract—Reaction of *trans*$[Os(CO)_2(dppe)_2]^{2+}$ with $[KHB(OPr^i)_3]$ gives the formyl complex *trans*-$[Os(CHO)(CO)(dppe)_2][SbF_6]$ which is thermally very stable; the crystal structure shows it to have *trans* stereochemistry and a long Os–C bond.

We have recently reported[1] the successful isolation of cationic formyl complexes of ruthenium from the action of monohydridic reducing agents on $[Ru(CO)_2(P\text{–}P)_2]^{2+}$ ($P\text{–}P = Ph_2P(CH_2)_nPPh_2$, $n = 1$, dppm; $n = 2$, dppe). Although these formyl complexes are sufficiently inert for isolation and characterisation, they decompose with half-lives of < 15 min in solution at room temperature.[2] We now report the isolation of an analogous osmium complex which is substantially more inert

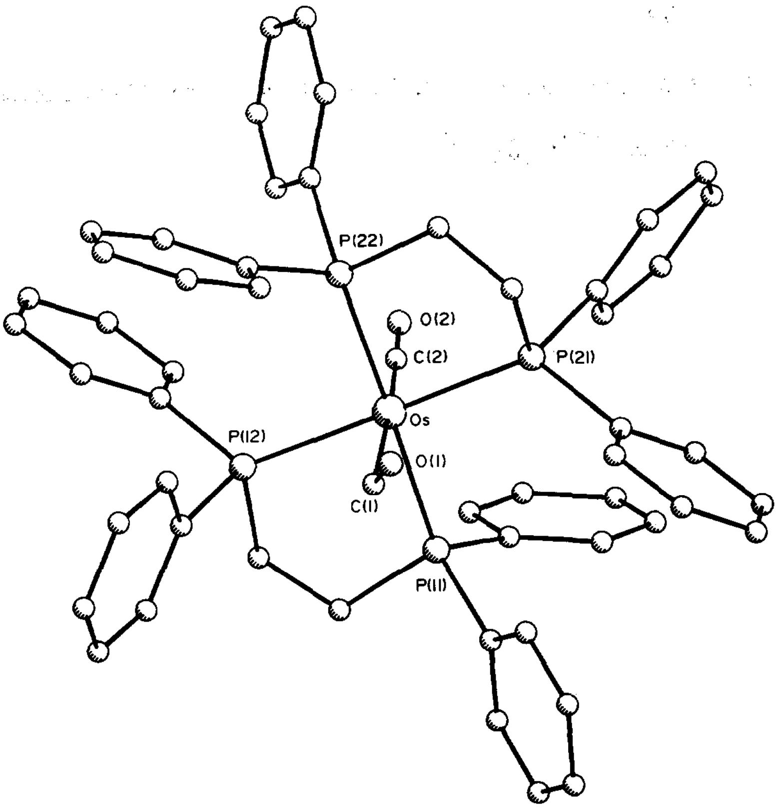

Fig. 1. Solid state structure and atomic numbering scheme for the cation of *trans*-$[Os(CHO)(CO)(dppe)_2][SbF_6]\cdot CH_2Cl_2$. C(1)–O(1), 1.181(11); Os–C(1), 2.155(28); Os–$\hat{C}$(1)–O(1),130.7(27); C(2)–O(2), 1.096(35); Os–C(2), 1.983(32); Os–$\hat{C}$(2)–O(2), 173.0(28); C(1)–$\hat{Os}$–C(2), 172.1(11). Angles in °, lengths in Å.

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*Author to whom correspondence should be addressed.

Treatment of *trans*[$Os(CO)_2(dppe)_2$][SbF_6]$_2$, prepared from [$OsCl_2(dppe)_2$], CO and excess Ag[SbF_6], with excess [$KHB(OPr^i)_3$] leads to the formation of *trans*-[Os(CHO)(CO)$(dppe)_2$][SbF_6] which has been fully characterised spectroscopically.† The complex is very much more thermally stable than its ruthenium analogue. For example, only 60% conversion to *trans*-[$OsCl(CO)(dppe)_2]^+$ is observed on refluxing *trans*-[Os(CHO)(CO)$(dppe)_2$][SbF_6] in $CHCl_3$ under N_2 atmosphere for 5 days, the remaining 40% being mostly unchanged formyl.

In view of the scarcity of information on the structures of transition metal formyls[3–5] in general and cationic formyls in particular, *trans*-[Os(CHO)(CO)$(dppe)_2$][SbF_6]·CH_2Cl_2 was studied by X-ray diffraction methods.‡ The structure of the cation (Fig. 1) shows the presence of mutually *trans* carbonyl and formyl groups, the two being easily distinguished by an Os–$\hat{C}$–O of 130.7° for the formyl ligand, similar to those reported for anionic (134°)[3] or neutral (130, 128°)[4,5] metal formyl complexes.

The formyl C=O bond length (1.181 Å) is somewhat shorter than those observed for [Et_4N][Fe(CHO)$(CO)_3$ $(3,5\text{-}Me_2C_6H_3O)_3P$] (1.195 Å)[3] and [Re($C_5H_5$)(CHO)(NO)($PPh_3$)] (1.225 Å)[4] but longer than that of [Rh-(CHO)(octaethylporphyrin)] (1.175 Å)[5] which is unusual in many ways, including its preparation[6] by insertion of CO into a rhodium hydrogen bond.

Metal formyl complexes are normally believed to have contributions to their structures from the two resonance forms shown in Fig. 2. We assume that the observed short C=O bond length arises from a lesser contribution from form II on account of the positive charge already present on the metal.

Consistent with this, the Os–C bond length (2.155 Å) is comparable with those observed for Os–C single bonds (2.15 Å)[7] but much longer than Os=C as found in [$Os(PPh_3)_2(CO)_2(CC_6H_5Me)$] (1.90 Å).[8] This contrasts with the M–C bond length of, e.g. [Re(C_5H_5)(CHO)(NO)(PPh_3)] which is closer to the value found for Re=C in carbene complexes.[4,9]

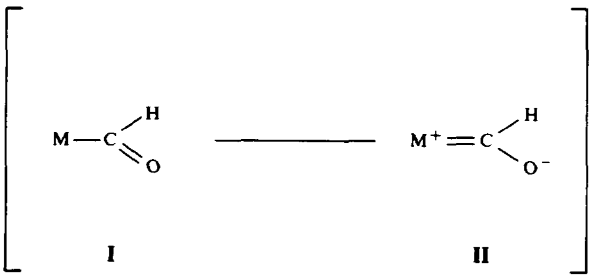

Fig. 2. Possible resonance forms for metal formyl complexes.

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†IR max. cm^{-1}: 2558w($\nu_{C\text{–}H}$), 1965vs and 1960vs($\nu_{C\equiv O}$) {$\nu_{C\equiv O}$ = 1970, CH_2Cl_2 soln}, 1558vs($\nu_{C=O}$); NMR: ^1H; δ14.45qu, J_{PH} = 4.9 Hz, (C*H*O); 5.32s(C*H*$_2Cl_2$); ^{31}P δ17.85s.

‡Crystal data: $Os(CHO)(CO)(Ph_2PCH_2CH_2PPh_2)_2$·$SbF_6$·$CH_2Cl_2$, F.wt = 1363.9, orthorhombic, a = 22.361(4), b = 20.209(2), c = 11.940(2) Å, $V = 5369$ Å^3, space group $Pn2_1a$ (alternative setting of $Pna2_1$, No. 33), $Z = 4$, $D_c = 1.65\ g\,cm^{-3}$, $\mu(Mo\text{–}K_\alpha) = 29.64\ cm^{-1}$, $R = 0.059$ for 2301 observed [$I > 1.5\sigma(I)$] reflections (3861 unique) measured on a diffractometer. The atomic coordinates, thermal parameters and bond lengths and angles have been deposited as supplementary data with the Editor, from whom copies are available on request. Atomic co-ordinates have also been deposited with the Cambridge Crystallographic Data centre.