Preparation and Crystal Structure of $(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$: A Compound with an Unsupported, Donor–Acceptor Metal–Metal Bond

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The crystal structure of $(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$ [prepared from $Os(CO)_5$ and $GeCl_4$] reveals that the $Os(CO)_5$ unit acts as a donor ligand towards the second osmium atom *via* an unsupported, donor–acceptor Os–Os bond.

Organometallic complexes with eighteen valence electrons are known to exhibit basic properties and form adducts with H^+, BF_3, $AlCl_3$, $HgCl_2$[1] and even with metal ions such as Fe^{2+} (ref. 2) and Ag^+ (ref. 3). Furthermore, donor–acceptor metal–metal bonds where one metal atom donates a pair of electrons to a second have been proposed for a number of compounds in order to account for their stoicheiometries in terms of the 18-electron rule.[4] However, in all these cases the donor–acceptor bond either formed part of an extended metal framework or was supported by bridging ligands. We report here the synthesis, characterization, and crystal structure of the remarkably stable compound $(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$ (**1**) in which the $Os(CO)_5$ moiety acts as a donor ligand to the second osmium centre *via* an unsupported, donor–acceptor Os–Os bond.

Reaction of $Os(CO)_5$[5] in hexane solution with $GeCl_4$ at 60 °C results in the formation of diamagnetic (**1**) in approximately 60% yield after 16 h (the compound is insoluble in hexane and precipitates from the reaction mixture). The i.r. spectrum of (**1**) in CH_2Cl_2 solution showed five bands in the terminal carbonyl region: 2167.5m, 2106.5m, 2082s, 2035.5m, and 2003.5m cm^{-1}. The ^{13}C n.m.r. spectrum of the compound (CD_2Cl_2 solution, -50 °C) consists of four sharp resonances at δ 179.8, 170.3, 170.0, and 157.5 p.p.m. in the approximate ratio of 2:1:4:1, respectively.

Crystal data: $C_8Cl_4GeO_8Os_2$, $M = 818.9$, monoclinic, space group Pn, $a = 10.038(2)$, $b = 21.042(2)$, $c = 13.385(3)$ Å, $\beta = 106.81(2)°$, $U = 2706.37$ Å^3, $Z = 6$, $D_c = 3.014$ g cm^{-3}. *X*-Ray diffraction data were collected on a Picker FACS-I diffractometer using graphite monochromated Mo-K_α radiation. An analytic absorption correction was applied to the data ($\mu = 163.3$ cm^{-1}). Of a total of 2556 unique reflections with $2\theta < 40°$, 2310 with $I > 2.3\sigma(I)$ were used for structure solution and refinement. The structure was solved by heavy-atom methods and block-diagonal refinement of 380 variables (Os, Ge, and Cl with anisotropic temperature factors, C and O isotropic) gave $R = 0.033$, $R_w = 0.036$ (with weights based on counter statistics).†

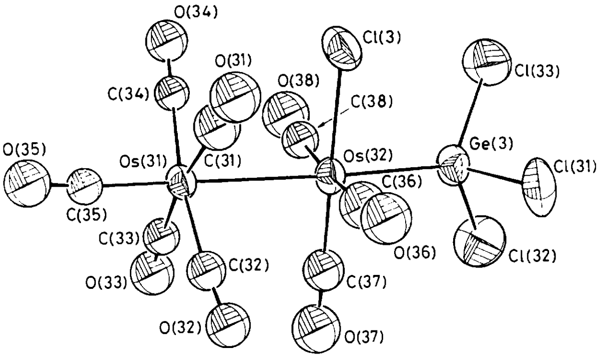

Figure 1. ORTEP diagram of molecule 3 of $(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$ (**1**). Selected distances (Å) for molecules 1, 2, 3: Os–Os 2.931(1), 2.927(2), 2.916(2); Os–Ge 2.430(3), 2.425(3), 2.418(3); Os–Cl 2.448(8), 2.435(7), 2.459(8); and angles (°): Os–Os–Ge 178.54(10), 172.35(9), 177.64(9); Os(*n*2)–Os(*n*1)–C(*n*1—4) range 82.2(8)—87.4(9); Os(*n*1)-Os(*n*2)-C(*n*6—8) range 88.2(11)—95.4(9).

The structure consists of three crystallographically independent $(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$ molecules which are chemically identical. Selected dimensions are given in the caption to Figure 1 which is an ORTEP plot of one molecule. The only crystallographically significant differences that can be observed within the accuracy of this analysis are the Os–Os distance in molecule 3 and the Os–Os–Ge angle in

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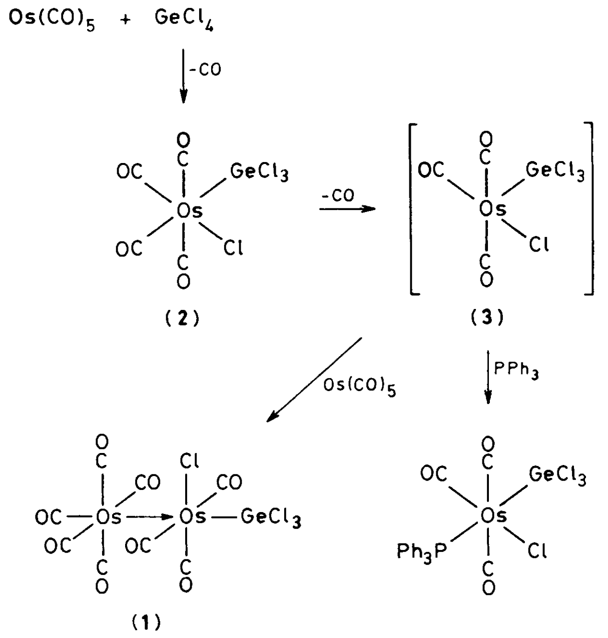
† Atomic co-ordinates are available on request from Professor Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk.-Str. 1, D-5300 Bonn 1, W. Germany. Any request should be accompanied by the full literature citation for this communication.



Scheme 1

molecule 2. As can be seen in Figure 1 the 18-electron moiety $Os(CO)_5$ acts as a donor ligand to the second osmium atom; the co-ordination about each osmium atom is approximately octahedral. The Os–Os distances [range 2.916(2)–2.931(1) Å] are somewhat longer than usual unbridged Os–Os bond lengths; *e.g.* in $Os_3(CO)_{12}$ the mean value is 2.877(13) Å.[6] However, the observed distances for each molecule of (**1**) are similar to that found in $(Cl_3Si)Os_3(CO)_{12}(SiCl_3)$ [Os–Os = 2.912(1) Å][7] and the slight lengthening over normal Os–Os bond lengths may be a reflection of the *trans* influence of the group 4 ligand. The slight inward leaning found for the radial carbonyls on the $Os(CO)_5$ ligand is normal[8] and cannot be construed as a semi-bridging bonding mode[9] as has previously been found in many carbonyl complexes where donor–acceptor metal–metal bonds are present. [The range of values of the Os(*n*2)–Os(*n*1)–C(*n*1—4) angles is 82.2—87.4°.]

Compared to pentacarbonylosmium,[5,10] compound (**1**) is surprisingly stable. It was unchanged after heating in solution at 125 °C for 16 h. It showed no detectable reaction in solution, with either I_2 or PPh_3 at 65 °C after 12 h. Under more forcing conditions (125 °C) reaction did occur with these reagents; the mixture of products obtained in each case have not been identified as yet.

A plausible mechanism for the formation of (**1**) is shown in Scheme 1. The lability of the particular carbonyl in the intermediate (**3**) probably arises because of a combination of the *trans* effect of the $GeCl_3$ ligand and the *cis* effect of the chloro group. (This has been observed previously in similar compounds.)[11] When the reaction was carried out in the presence of the good donor ligand PPh_3 the complex $Os(CO)_3(PPh_3)(GeCl_3)(Cl)$ was isolated to the exclusion of (**1**). We have also confirmed the conversion of (**2**) (prepared by an alternative method) into (**1**) by the reaction with $Os(CO)_5$ under the same conditions.

We are currently exploring the scope of the ability of 18-electron species, such as $Os(CO)_5$, to replace labile carbonyls in organometallic complexes. Sufficient results have already been obtained to indicate that it may be a quite general reaction.

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