A Unique 'Side-on' Bridging Mode for the Formyl (CHO) Ligand in a Binuclear Tantalum Complex; *X*-Ray Structural Study of $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(\mu\text{-}H)(\mu\text{-}CHO)$

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Summary A single-crystal *X*-ray structural analysis of the binuclear species $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(\mu\text{-}H)(\mu\text{-}CHO)$ has been carried out; this molecule contains a 'side-on' bridging formyl group in which interatomic distances are Ta(1)–C(1) 2·085(12), Ta(2)–C(1) 2·119(11), Ta(1)–O 2·094(8), Ta(2)–O 2·089(9), and C–O 1·496(14) Å.

TRANSITION-METAL σ-acyls have been known for more than 20 years and have been fully characterized *via* X-ray diffraction studies.[1,2] In contrast, σ-formyl complexes have proved rather elusive.[3] The first structural study of such a species, $(\eta^5\text{-}C_5H_5)Re(PPh_3)(NO)(CHO)$, was reported in 1979;[4] a structural study of $(\eta^5\text{-}C_5H_5)_2W(=CH\text{-}O\text{-})Zr(H)(\eta^5\text{-}C_5Me_5)_2$, a heterobimetallic complex in which a μ-CHO moiety behaves as an oxycarbene ligand, has also appeared recently.[5]

Schrock *et al.* have recently discovered[6] the reaction sequence shown (equation 1) wherein H_2 and CO are assembled at a ditantalum centre yielding a hydridoformyl derivative. No unambiguous structure could be assigned to this complex, although the possibility of an oxiran skeleton was considered. We now report the results of an X-ray structural analysis on this unusual species.

$$2\,(\eta^5\text{-}C_5Me_4Et)Ta(CH_2CMe_3)_2Cl_2 \xrightarrow[-CMe_4]{+H_2} [(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(H)_2 \xrightarrow{+CO} [(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(H)(CHO) \quad (1)$$

Crystal data: $C_{23}H_{36}Cl_4OTa_2$, $M = 832\cdot3$, triclinic, space group $P\bar{1}$ (C_i^1; No. 2), $a = 11\cdot114(3)$, $b = 14\cdot856(4)$, $c = 8\cdot858(2)$ Å, $\alpha = 82\cdot98(2)$, $\beta = 103\cdot91(2)$, $\gamma = 105\cdot56(2)^\circ$, $U = 1364\cdot9(6)$ Å^3, $D_c = 2\cdot02$ g cm^{-3}, $Z = 2$, $\mu(\text{Mo-}K_\alpha) = 88\cdot4$ cm^{-1}. Diffraction data were collected with a Syntex $P2_1$ automated four-circle diffractometer, using Mo-K_α radiation and a coupled θ(crystal)—2θ(counter) scan technique.[7] The structure was solved by a combination of Patterson and difference-Fourier techniques. All non-hydrogen atoms were located and refined anisotropically. Convergence was reached with R 5·7% for all 3587 independent data with $4\cdot0 < 2\theta < 45\cdot0^\circ$ (no datum rejected). The resulting structure is shown in the Figure and may be formally represented by structure (**1**).†

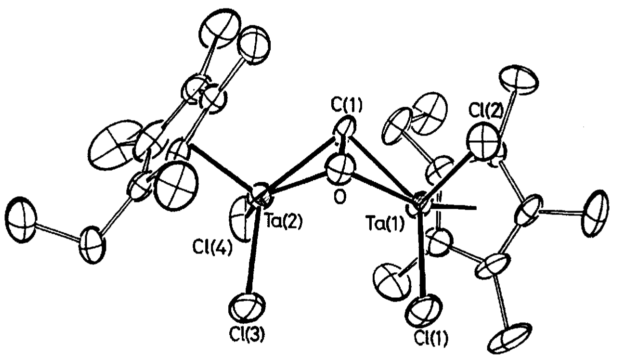
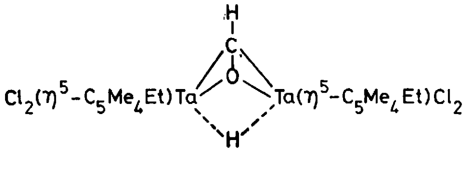


FIGURE. Overall geometry of the $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(\mu\text{-H})(\mu\text{-CHO})$ molecule. ORTEP-II diagram; 30% atomic vibration ellipsoids.

There is no crystallographic symmetry imposed upon the dinuclear molecule. The formyl ligand bridges the two tantalum atoms in a symmetrical 'side-on' manner, with Ta(1)–C(1) = 2·085(12), Ta(2)–C(1) = 2·119(11), Ta(1)–O = 2·094(8), and Ta(2)–O = 2·089(9) Å. The Ta(1)–[C(1)–O]–Ta(2) system has a 'butterfly' geometry with an angle of 71·15° between the Ta(1)–C(1)–O and Ta(2)–C(1)–O planes. The C(1)–O distance of 1·496(14) Å shows this bond to be significantly activated (the C–O single-bond length in alcohols, ethers, or epoxides is *ca.* 1·43 Å).[8] Interestingly, reaction of the present molecule with PMe_3 results in complete cleavage of the C–O linkage, yielding the triply bridged dinuclear species $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(H)(\mu\text{-O})(\mu\text{-CHPMe}_3)$, which has been characterized crystallographically[6,9] and in which the C $\cdots$ O distance is now 2·58(2) Å.



(1)

Neither the formyl hydrogen nor the bridging hydride ligand were found directly from the structural study, but their presence is revealed unambiguously by ^1H and ^{13}C n.m.r. studies.[6]

The bridging hydride ligand is believed to occupy a position spanning an axial site on Ta(2) (*trans* to the $\eta^5\text{-}C_5Me_4Et$ ligand) and an equatorial site on Ta(1) [*trans* to Cl(2)]. The Ta(1) . . . Ta(2) distance of 3·186(1) Å and the overall configuration of the molecule are consistent with this suggestion.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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