Synthesis and *X*-Ray Crystal Structure of the Trimetallic Neopentylidyne Complex $[\{Cl_2(MeOCH_2CH_2OMe)Ta(\mu\text{-}CCMe_3)\}_2Zn(\mu\text{-}Cl)_2]$

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α-Hydrogen abstraction from the neopentylidene complex $[Cl_3(MeOCH_2CH_2OMe)Ta(CHCMe_3)]$ by $(Me_3CCH_2)_2Zn$ results in the bridging neopentylidyne complexes $[\{Cl_2(MeOCH_2CH_2OMe)Ta(\mu\text{-}CCMe_3)\}_2Zn(\mu\text{-}Cl)_2]$ and $[\{Cl_2(MeOCH_2CH_2OMe)Ta(\mu\text{-}CCMe_3)\}Zn(CH_2CMe_3)Cl]$; the crystal structure of the first complex reveals the co-ordination of two $Ta{\equiv}CCMe_3$ fragments to one $ZnCl_2$ molecule.

As part of our search for labile d^0 tantalum alkylidyne complexes and their possible use in the conversion of alkynes, we have now prepared a series of bridging neopentylidyne complexes *via* α-hydrogen abstraction from the neopentylidene group in $[Cl_3(dme)Ta(CHCMe_3)]$ (**1**) (dme = 1,2-dimethoxyethane) by $(Me_3CCH_2)_2Zn$ and Me_3CCH_2Li (Scheme 1).

Complex (**1**) was prepared from $Ta(CH_2CMe_3)_2Cl_3$ in dme in the presence of one equivalent of tetrahydrofuran to induce the α-hydrogen abstraction,[1] since direct preparation in dme proved not to be possible.

Upon reaction of (**1**) with half a molar equivalent of $(Me_3CCH_2)_2Zn$ in diethyl ether, neopentane was evolved, and the trimetallic pink-red complex $[\{Cl_2(dme)Ta(\mu\text{-}CCMe_3)\}_2Zn(\mu\text{-}Cl)_2]$ (**2**) precipitated from solution. When the reaction was performed with one equivalent of $(Me_3CCH_2)_2Zn$ in benzene the soluble red bimetallic complex $[\{Cl_2(dme)Ta(\mu\text{-}CCMe_3)\}Zn(CH_2CMe_3)Cl]$ (**3**) was slowly formed. In accordance with the above two reactions, (**3**) proved to be unstable in diethyl ether: it disproportionated to $(Me_3CCH_2)_2Zn$ and (**2**) through precipitation of (**2**). The instantaneous reaction of (**1**) with one equivalent of Me_3CCH_2Li produced the bright-red bimetallic complex $[(Me_3CCH_2)_3Ta(\mu\text{-}CCMe_3)][Li(dme)]$ (**4**), which has been reported before.[2] Quantitative conversion of (**1**) into (**4**) was obtained upon use of four equivalents of $MeCCH_2Li$. No intermediates were observed in the ^1H n.m.r. spectrum upon use of one equivalent of Me_3CCH_2Li. So, in the above reactions α-hydrogen abstraction from the neopentylidene group in (**1**) is accompanied by a varying degree of alkylation, depending on the nature of the solvent and the alkylating agent. The com-

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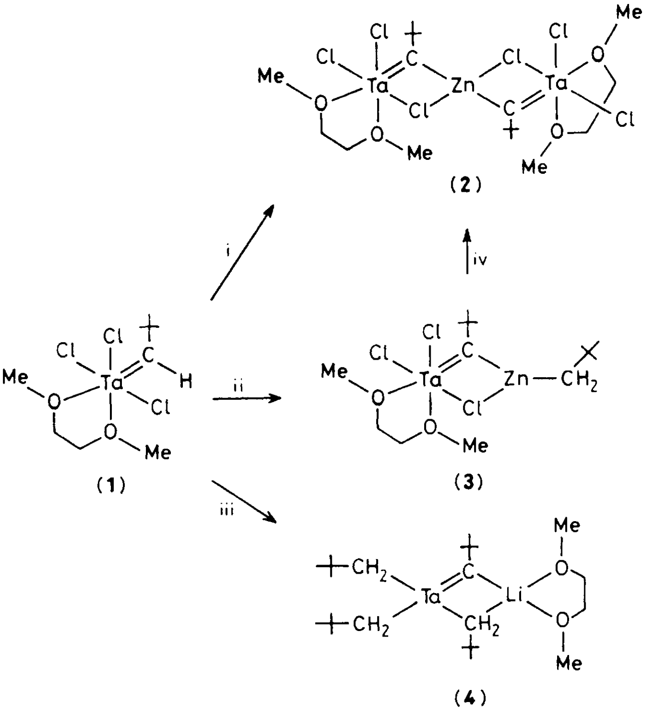

Scheme 1. i, 0.5 mol/mol $(Me_3CCH_2)_2Zn$ in diethyl ether, 4 h; ii, 1 mol/mol $(Me_3CCH_2)_2Zn$ in benzene, 2 h; iii, 4 mol/mol Me_3CCH_2Li in benzene, instantaneous; iv, diethyl ether, instantaneous.

plexes (1), (2), (3), and (4) have been identified by ^1H and ^{13}C n.m.r. spectroscopy.‡

The structure of (2) was determined by a single crystal *X*-ray diffraction study of the complex (Figure 1).§

Crystal data: $C_{18}H_{38}Cl_6Ta_2Zn$, $M = 964.19$, orthorhombic, space group *Pbca*, $a = 9.519(2)$, $b = 14.026(3)$, $c = 44.645(9)$ Å, $U = 5960.7$ Å^3, $Z = 8$, $D_c = 2.15$ g cm^{-3}, $F(000) = 3648$, $\mu(\text{Cu-}K_\alpha) = 196.4$ cm^{-1}, $\lambda = 1.54184$ Å. At convergence $R = 0.063$ ($R_w = 0.081$) for 2799 unique observed reflections [$I > 3.0\,\sigma(I)$] measured in the range $5.6 \leqslant 2\theta \leqslant 150°$ at 164 K on an Enraf-Nonius CAD4 diffractometer.

The molecule has virtual C_2 symmetry although there is no crystallographic symmetry imposed. Complex (2) represents the first trimetallic example of stabilization of a transition metal alkylidyne unit by a non-transition metal Lewis acid.

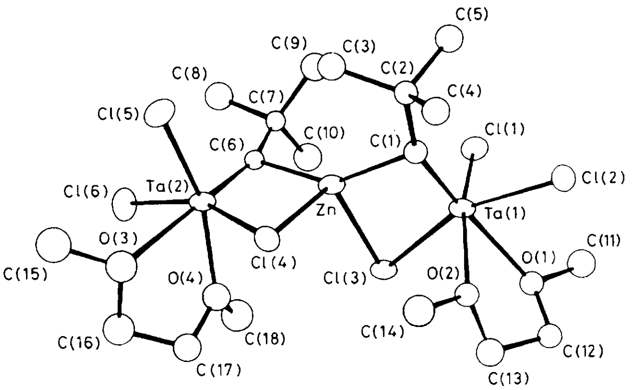

Figure 1. Molecular structure of $[\{Cl_2(MeOCH_2CH_2OMe)Ta(\mu\text{-}CCMe_3)\}_2Zn(\mu\text{-}Cl_2)]$ (2). Selected dimensions not presented in the text (Å and °). Distances: Ta(1)–O(1) 2.461(13), Ta(1)–O(2) 2.165(12), Ta(2)–O(3) 2.412(3), Ta(2)–O(4) 2.175(14). Angles: Ta(1)–C(1)–C(2) 156(1), Ta(2)–C(6)–C(7) 159(1), Ta(1)–C(1)–Zn 90.8(7), Ta(2)–C(6)–Zn 91.1(7), Zn–C(1)–C(2) 113(1), Zn–C(6)–C(7) 110(1), C(1)–Zn–C(6) 147.0(6), Cl(3)–Zn–Cl(4) 105.0(2).

Two binuclear complexes of similar geometry have been characterized before by *X*-ray diffraction: the (neopentylidyne)tantalum (d^0) complex $[(Me_3CCH_2)_3Ta(\mu\text{-}CCMe_3)][Li(dmp)]$ (5) (dmp = *N,N'*-dimethylpiperazidine)[2] and the (neopentylidyne)tungsten (d^2) complex $[\{Cl(Me_3P)_3W(\mu\text{-}CH)\}AlMe_2R]$ (R = Cl, Me) (6).[3]

$$[(Me_3CCH_2)_3Ta(\mu\text{-}CCMe_3)][Li(dmp)]$$
(5)

$$[\{Cl(Me_3P)_3W(\mu\text{-}CH)\}AlMe_2R]$$
(6) R = Cl, Me

$$[Ta(CHCMe_3)(PMe_3)_2(\mu\text{-}Cl)Cl_2]_2$$
(7)

The observed geometry of the Ta–C(CMe$_3$)–Zn fragment (Figure 1) is very similar to that observed for the Ta–C(CMe$_3$)–Li fragment in (5), the W–C(H)–Al fragment in (6), and the Ta–C(CMe$_3$)–H fragment in the (neopentylidene)tantalum(d^0) complex $[Ta(CHCMe_3)(PMe_3)_2(\mu\text{-}Cl)Cl_2]_2$ (7).[4] Comparison of the Ta–C bond lengths in (2) [Ta(1)–C(1) 1.86(2) and Ta(2)–C(6) 1.79(2) Å] with that in (7) [1.898(2) Å] suggests that the Ta–C bonds in (2) are intermediate between a double and triple bond. The long C–Zn distances in (2) [C(1)–Zn 2.10(2) and C(6)–Zn 2.13(2) Å], which exceed those reported for C(sp^3)–Zn in tetrahedral zinc(II) complexes (1.94—2.03 Å),[5] reflect a weak C–Zn interaction, analogous to the weak C–Li, C–Al, and C–H interactions in (5), (6), and (7). The Ta–Zn distances in (2) [Ta(1)–Zn 2.825(3) and Ta(2)–Zn 2.804(3) Å] do not exclude a weak Ta–Zn interaction. Comparison of the bridging Ta–Cl and Zn–Cl distances in (2) [Ta(1)–Cl(3) 2.451(4) and Ta(2)–Cl(4) 2.454(4); Zn–Cl(3) 2.535(5) and Zn–Cl(4) 2.496(6) Å] with the terminal Ta–Cl distances in (2) [Ta(1)–Cl(1) 2.375(4), Ta(1)–Cl(2) 2.390(4), Ta(2)–Cl(5) 2.366(5), and Ta(2)–Cl(6) 2.390(4) Å] and terminal Zn–Cl distances reported before (2.15—2.26 Å),[5a,6] suggests that bridging chlorines are bonded more tightly to Ta than to Zn.

The bonding in (2) can be described in two ways, (A) and (B). The mesomer (A) represents a tantalum alkylidyne species stabilized by a double Lewis acid–base interaction. The mesomer (B) formally represents a tantalum (zinca-alkylidene) species with one Lewis acid–base interaction, in which the zinca-alkylidene moiety resembles the distorted neopentylidene group in (7). Preliminary study of the reaction of

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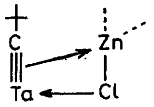
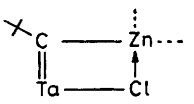
‡ Characteristic n.m.r. data of (1), (2), (3), and (4) (δ in p.p.m. relative to Me_4Si, *J* in Hz) (resonances for dme, typical for asymmetric co-ordination mode, have been omitted). (1) ^1H n.m.r. (CD_2Cl_2): 3.17 (s, 1H, C*H*CMe$_3$) and 1.13 (s, 9H, CHC*Me*$_3$); ^{13}C n.m.r. (CD_2Cl_2): 252.8 (d, *C*HCMe$_3$), 46.2 (s, CH*C*Me$_3$), and 33.2 p.p.m. (q, CHC*Me*$_3$). (2) ^1H n.m.r. (CD_2Cl_2): 1.34 (s, 18H, CC*Me*$_3$); ^{13}C n.m.r. (CD_2Cl_2): 279.5 (s, *C*CMe$_3$), 50.4 (s, C*C*Me$_3$), and 35.8 p.p.m. [q, CC*Me*$_3$, *J*(CH) 120]. (3) ^1H n.m.r. (CD_2Cl_2) [structural assignment based on the analogy of the n.m.r. data with data for (2)]; 1.25 (s, 9H, CC*Me*$_3$), 1.08 (s, 9H, CH$_2$C*Me*$_3$), and 0.9—0.8 (br. s, 2H, C*H*$_2$CMe$_3$), ^{13}C n.m.r. (C_6D_6): 277.7 (s, *C*CMe$_3$), 49.9 (s, C*C*Me$_3$), 35.4 (q, CC*Me*$_3$), 31.6 (q, CH$_2$C*Me*$_3$), and 27.8 p.p.m. (t, *C*H$_2$CMe$_3$). (4) ^1H n.m.r. (C_6D_6): 1.61 (s, 9H, CC*Me*$_3$), 1.46 (s, 27H, CH$_2$C*Me*$_3$), and 0.66 (br. s, 6H, C*H*$_2$CMe$_3$).

§ The single crystal *X*-ray study of (2) was carried out by the Molecular Structure Corporation, 3304 Longmire Drive, College Station, Texas 77840, U.S.A. Atomic co-ordinates 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.



(A)



(B)

(**2**) with alkynes underlines the importance of the resonance structure (A): dme and $ZnCl_2$ are displaced from (**2**) and the neopentylidyne species $Cl_2Ta{\equiv}CCMe_3$ contained in (**2**) are each converted by two molecules of alkyne (R–C≡C–R) into the η^5-cyclopentadienyl species (η^5-$C_5R_4CMe_3$)$TaCl_2$.[7] So in this (unexpected) reaction (**2**) clearly behaves as a $ZnCl_2$-stabilised neopentylidyne complex.

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