A Tantalum Carbyne Complex

Sir:

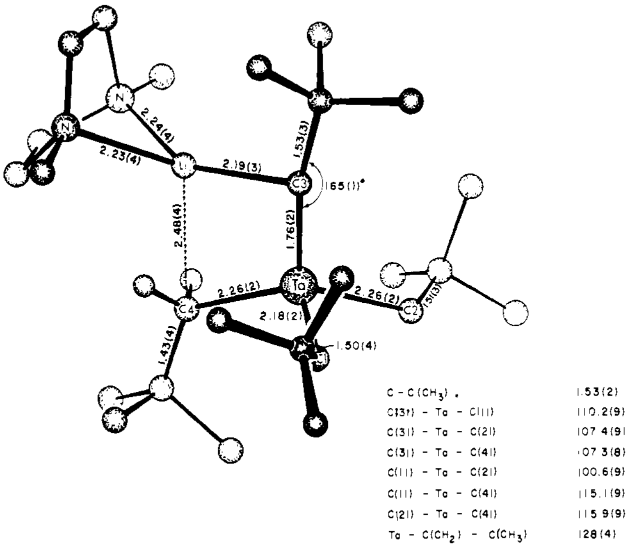
Intramolecular α-hydrogen abstraction in "$Ta[CH_2C(CH_3)_3]_5$" gives neopentane and $Ta[CH_2C(CH_3)_3]_3[CHC(CH_3)_3]$ (**1**), one of the very few carbene complexes not containing a heteroatom like oxygen or nitrogen.[1] Further studies showed that the carbene α-hydrogen in **1** can be removed by butyllithium in the presence of (e.g.) a diamine to give $Ta[CH_2C(CH_3)_3]_3\{C[C(CH_3)_3][Li{\cdot}L]\}$ (**2**; L = *N,N'*-dimethylpiperazine[2] (dmp)), a "lithio-carbene" complex. The crystal structure of **2** shows that it is best formulated as a "carbyne", $\{[(CH_3)_3CCH_2]_3Ta{\equiv}CC(CH_3)_3\}{\cdot}Li$ (dmp).

Crystals of **2** (from pentane) are orthorhombic, the space group is $P2_12_12_1$ (it imposes no point symmetry), and cell dimensions are a = 17.196 (6) b = 17.512 (4), and c = 10.503 (3) Å. The calculated density for four molecules per cell is 1.23 g cm^{-3}. A total of 2478 reflections were measured by counter techniques and corrected for absorption effects. The structure was solved by heavy atom techniques and refined by least-squares methods to $R = 0.071$ $(\Sigma\|F_o| - |F_c\|/\Sigma|F_o|)$ for 2192 reflections with $F_o > \sigma(F_o)$. The working model included all methylene hydrogens.

Coordination about tantalum (Figure 1) is nearly tetrahedral (C-Ta-C = 100.6 (9) to 115.9 (9)°). Repulsion between *tert*-butyl groups opens the neopentyl Ta-C-C angles to ca. 128° (cf. $Cr[CH_2C(CH_3)_2(C_6H_5)]_4$ (ref 3)). Bond distances within the chelated lithium fragment, between neopentyl α-carbons and tantalum, and between α- and β-carbons are normal. The large vibrational and/or librational motion of the methyl groups to some extent limits the precision of all structural parameters.

Two unusual features are the short Ta-C(3) distance (1.76 (2) Å) and the large Ta-C(3)-C angle (165 (1)°). Neither is consistent with interpretation as a lithio-carbene, $Ta{=}C[C(CH_3)_3][Li{\cdot}L]$; Ta=C should be about 2.05 Å and Ta-C-C about 120° (ref 4). Since a Ta-C single bond distance is about 2.25 Å, 1.76 Å is more consistent with a triple bond between Ta and C(3). The large Ta-C(3)-C angle is also consistent with this interpretation. In fact both values compare well with the M≡C bond distances and M≡C—C angles in the only other previously known carbyne complexes,[5] $(CO)_4XMCR$ and $(CO)_3[P(CH_3)_3]XMCR$ (M = Cr, Mo, W; X = halogen) (see Table I). There is therefore little doubt that **2** is more a carbyne than a carbene complex.

A valence bond description of the bonding of "$[Li(dmp)]^+$" to "$[Ta\{CH_2C(CH_3)_3\}_3\{CC(CH_3)_3\}]^-$" is not straightforward. The angles subtended at the Li atom preclude tetrahedral coordination. Though the Li-C(3) distance is normal for a covalent bond, the Li-C(4) distance is long and probably at best a very weak interaction since the bonding requirements of C(4) are already satisfied. A more satisfactory bonding interpretation is based on trigonal Li. The bisector of the N-Li-N angle points directly at the center of the Ta≡C(3) bond, an interaction related to the association of N-chelated Li moieties with electron-rich centers in delocalized carbanion systems.[6] In any case, no description seriously jeopardizes the carbyne interpretation. That the lithium fragment may dissociate to give a true salt in some circumstances is suggested by the fact that the conductance of **2** in THF is about 20% that of $[Li(THF)_4]^+[Ta(C_6H_5)_6]^-$ (ref 7).



$C-C(CH_3)$.	1.53(2)
C(31) - Ta - C(11)	110.2(9)
C(31) - Ta - C(21)	107 4(9)
C(31) - Ta - C(41)	107 3(8)
C(11) - Ta - C(21)	100.6(9)
C(11) - Ta - C(41)	115.1(9)
C(21) - Ta - C(41)	115 9(9)
$Ta-C(CH_2)-C(CH_3)$	128(4)

Figure 1. Molecular structure of $\{[(CH_3)_3CCH_2]_3Ta{\equiv}CC(CH_3)_3\}{\cdot}Li(dmp)$ (dmp = *N,N'*-dimethylpiperazine).

Table I. Bond Distances and Angles in Metal–Carbyne Complexes

No.		M≡C (Å)	M≡C—C (deg)
2	$\{[(CH_3)_3CCH_2]_3Ta{\equiv}CC(CH_3)_3\}{\cdot}Li(dmp)$	1.76 (2)	165 (1)
3	$(CO)_4(I)WC(C_6H_5)$	1.90 (5)	162 (4)
4	$(CO)_4(I)CrC(CH_3)$	1.69 (1)	180 (fixed)
5	$(CO)_3[P(CH_3)_3](Br)CrCCH_3$	1.68 (3)	177 (3)

That **2** is formed by deprotonation of the carbene carbon in **1** should not be overlooked; i.e., **1** which is deuterated 81% at the neopentylidene α-carbon[1] reacts with $LiC_4H_9{\cdot}$dmp in hexane to give **2** and butane-81% d_1. The neopentyl and neopentylidene ligands in **1** are probably stereochemically and sterically essentially identical. Therefore the *neopentylidene* α-hydrogen is *more acidic* than neopentyl α-hydrogens, a fact which may help to explain why $\{M[CH_2Si(CH_3)_3]_2[CSi(CH_3)_3]\}_2$ (**6**, M = Nb or Ta),[8] and not $M[CH_2Si(CH_3)_3]_3[CHSi(CH_3)_3]$ (**7**), has been isolated; the carbene α-hydrogen in **7** should be more acidic than in **1** since its carbon is α to Si.

References and Notes

(1) R. R. Schrock, *J. Am. Chem. Soc.*, **96**, 6796 (1974).
(2) L can also be $(THF)_2$, *N,N,N',N'*-tetramethylethylenediamine, (*p*-dioxane)$_2$, or 1,2-dimethoxyethane.
(3) V. Gramlich and K. Pfefferkorn, *J. Organomet. Chem.*, **61**, 247 (1973).
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(5) E. O. Fischer, G. Kreis, C. G. Kreiter, J. Müller, G. Huttner, and H. Lorenz, *Angew. Chem., Int. Ed. Engl.*, **12**, 564 (1973); G. Huttner, H. Lorenz, and W. Gartzke, *ibid.*, **13**, 609 (1974).
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