

Tuning of Tantalum Alkylidene Reactivity with a Terdentate Aryl Amine Ligand: Synthesis, Structure and Reactivity of $[TaCl_2\{C_6H_3(CH_2NMe_2)_{2-2,6}\}(CHBu^t)]$

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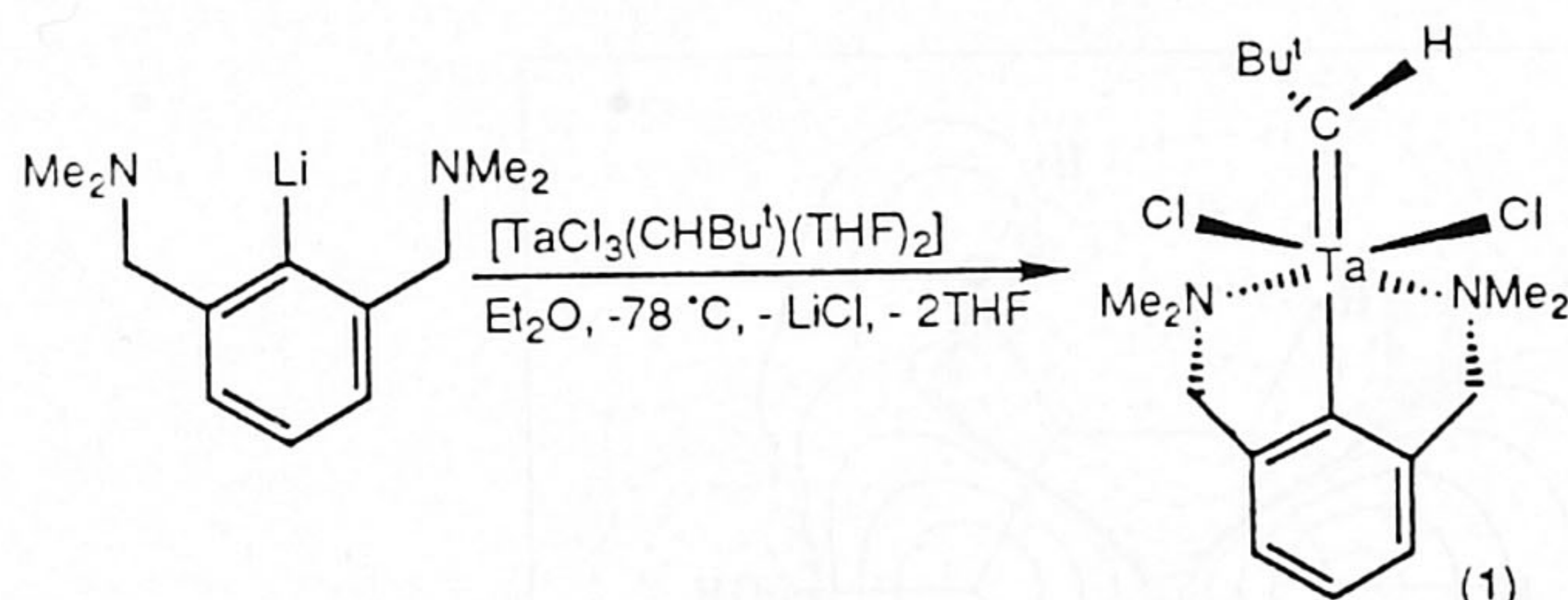
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Abstract. The terdentate aryldiamine ligand in the aryltantalum(V) alkylidene complex $[TaCl_2\{C_6H_3(CH_2NMe_2)_{2-2,6}\}(CHBu^t)]$ (1) controls alkylidene reactivity in a range of metal-mediated Wittig reactions. An X-ray diffraction study of (1) shows that the hexacoordinate tantalum centre has a very irregular ligand array in which the aryldiamine ligand adopts a new *facial* N,C,N coordination mode.

Recently, we initiated a study to ascertain whether the reactivity of a tantalum alkylidene function can be controlled by chelating ligands with appropriate electronic and steric characteristics. This research may provide new leads in the design of catalysts for olefin metathesis. Here, we wish to report the synthesis and reactivity of a tantalum alkylidene complex with the potentially terdentate, monoanionic 2,6-bis[(dimethylamino)methyl]phenyl ligand, *i.e.* $[C_6H_3(CH_2NMe_2)_{2-2,6}]^-$.



Scheme 1

The reaction of $[Li\{C_6H_3(CH_2NMe_2)_{2-2,6}\}]_2^1$ with one equivalent of $[TaCl_3(CHBu^t)(THF)_2]^2$ (THF = tetrahydrofuran) at $-78^\circ C$ in Et_2O gave a purple suspension from which $[TaCl_2\{C_6H_3(CH_2NMe_2)_{2-2,6}\}(CHBu^t)]$ (1) was isolated after work-up as a purple powder in 90% yield (Scheme 1). Complex (1) is thermally stable at room temperature and the solid can even be safely handled for short periods in air. The 1H and ^{13}C NMR data of (1)³ are characteristic and consistent with the presence of a neopentylidene functionality and terdentate N,C,N

coordination of the $\{C_6H_3(CH_2NMe_2)_{2-2,6}\}^-$ ligand.

To confirm these deductions and to elucidate the stereochemistry of the ligand distribution around tantalum, a single-crystal X-ray analysis of (1) was carried out. Suitable crystals of (1) were grown from a benzene solution into which pentane vapour was allowed to diffuse slowly. The structure determination shows (1) to be a mononuclear, hexacoordinated tantalum species $[TaCl_2\{C_6H_3(CH_2NMe_2)_{2-2,6}\}(CHBu^t)]$ with a very irregular ligand array (Figure 1).⁴ The best least-squares coordination plane is described by Ta, Cl(1), Cl(2), N(1) and N(2) with two mutually *cis* chlorine atoms [$\angle Cl(1)-Ta-Cl(2) = 79.51(4)^\circ$] and two pseudo *cis*-positioned nitrogen donor atoms [$\angle N(1)-Ta-N(2) = 118.63(14)^\circ$]. Coordinated to tantalum on opposite sides of this plane are the *ipso* carbon atom of the aryldiamine [C(4)] and the α carbon atom [C(13)] of the neopentylidene grouping [$\angle C(4)-Ta-C(13) = 139.01(15)^\circ$]. A fascinating aspect of the structure of (1) is that the $\{C_6H_3(CH_2NMe_2)_{2-2,6}\}^-$ ligand has adopted a previously unreported *facial* N,C,N bonding mode to the metal centre. This contrasts with the situation in octahedral organometallic complexes of the late transition metals where this ligand adopts *meridional* coordination with N-M-N angles of typically $161-163^\circ$.⁵ It also is interesting to note that the terdentate N,C,N ligand in (1) now covers a similar set of coordination sites, and donates the same number of bonding electrons, as a η^5 -bonded cyclopentadienyl system.

Table I Reactions of $[TaCl_2\{C_6H_3(CH_2NMe_2)_{2-2,6}\}(CHBu^t)]$ with $R^1R^2C=O$ and $R^1R^2C=NR$ substrates^a

Substrate	Reaction time ^b	Organic product ^c	Inorganic product ^d
PhC(H)=O	<60 s	PhC(H)=C(H)Bu ^t 45% <i>cis</i> , 55% <i>trans</i>	$[TaCl_2(O-\mu)(ncn)]_2^e$
Me ₂ C=O	~1 h	Me ₂ C=C(H)Bu ^t	$[TaCl_2(O-\mu)(ncn)]_2^e$
PhC(H)=NMe	24 h	PhC(H)=C(H)Bu ^t 70% <i>cis</i> , 30% <i>trans</i>	$[TaCl_2(NMe)(ncn)]$
PhC(H)=NSiMe ₃	~15 d (<i>t</i> _{1/2})	PhC(H)=C(H)Bu ^t 70% <i>cis</i> , 30% <i>trans</i>	$[TaCl_2(NSiMe_3)(ncn)]$

^a Reactions were run in sealed NMR tubes using CDCl₃ as solvent with the given substrate in excess. ^b Time for >95% conversion of one equivalent of substrate per equivalent of complex (1). ^c Isomer ratios from integration of ¹H NMR (200.13 MHz) signals. ^d (ncn) = {C₆H₃(CH₂NMe₂)_{2-2,6}}. ^e Degree of association from an X-ray structural analysis.

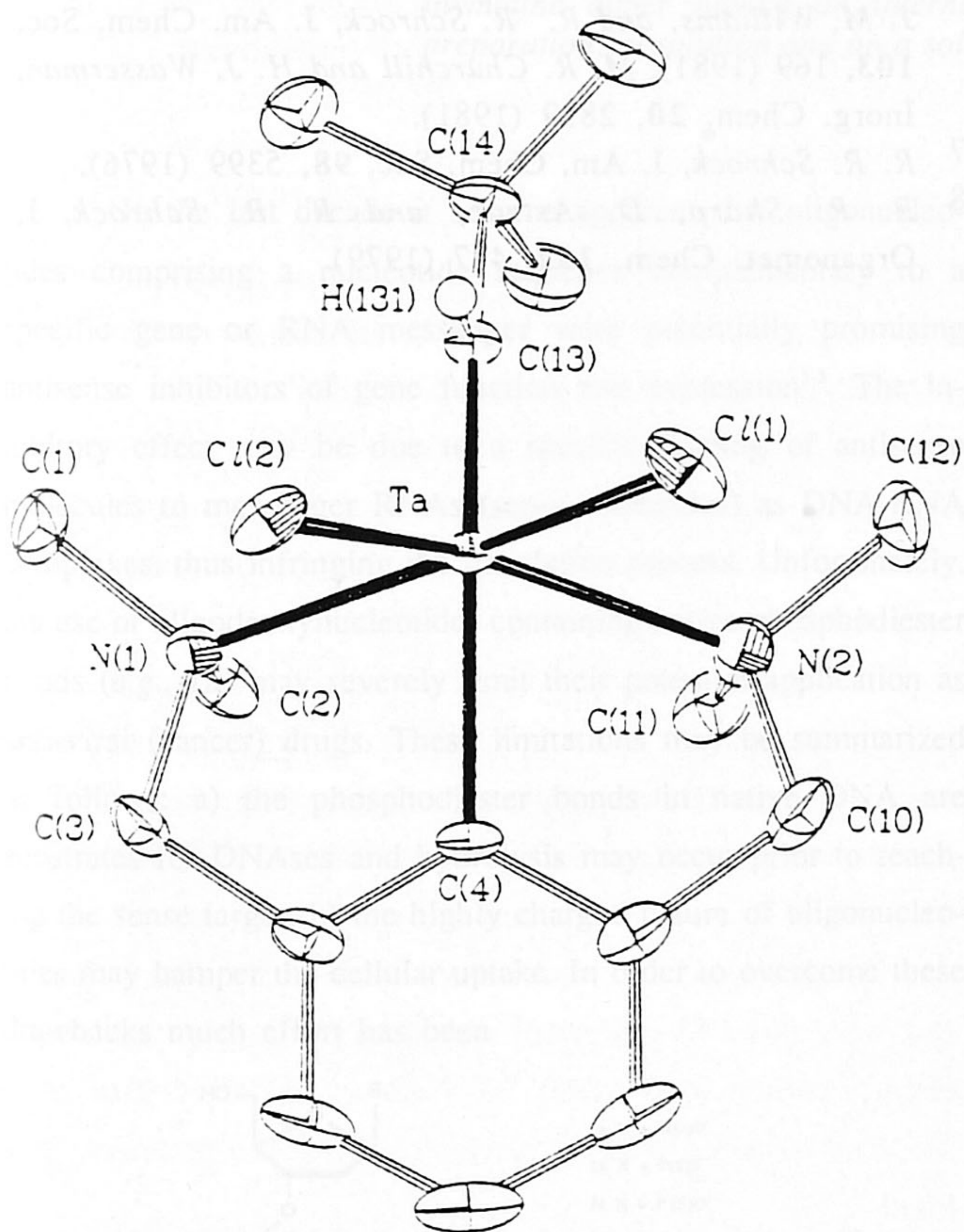


Fig. 1. X-ray structure of $[TaCl_2\{C_6H_3(CH_2NMe_2)_{2-2,6}\}(CHBu^t)]$ (1); ORTEP drawing with 50% probability ellipsoids. Selected bond lengths (Å) and angles (°) subtended at tantalum are: Ta-C(4), 2.154(4); Ta-N(1), 2.345(4); Ta-N(2), 2.373(4); Ta-C(13), 1.938(4); Ta-Cl(1), 2.4247(11); Ta-Cl(2), 2.4313(11). C(4)-Ta-C(13), 139.01(15); Cl(1)-Ta-Cl(2), 79.51(4); Cl(2)-Ta-N(1) 78.94(10), N(1)-Ta-N(2), 118.63(14); N(2)-Ta-Cl(1), 79.35(12).

The structural data for the neopentylidene grouping of (1) are in the same range as those found for other tantalum

neopentylidene complexes.⁶ These include the characteristically large Ta-C_α-C_β angle of 170.6(3)°, the small Ta-C_α-H_α angle of 71(3)° and a short Ta=C_α bond length of 1.938(4) Å (cf. the Ta-C(4) single bond length of 2.154(4) Å).

Table I lists some representative reactions of (1) in CDCl₃ with an excess of various substrates containing a C=O or C=N- function. In these clean, homogeneous reactions one equivalent of an aldehyde, ketone or imine, R¹R²C=Y, is converted to one equivalent of R¹R²C=C(H)Bu^t per equivalent of complex (1). This organic product can be seen as the result of a metal-mediated Wittig reaction. Due to the steric and electronic constraints of the aryldiamine ligand the reaction rate of (1) is significantly lower than that of the simpler neopentylidene complex $[Ta(CH_2Bu^t)_3(CHBu^t)]$.⁷ An interesting finding from our experiments is that the aryldiamine ligand is still *ipso*-C-bonded to tantalum in the inorganic product: the ¹³C NMR spectra of the product mixtures show a characteristic low field resonance for the *ipso* carbon atom at *ca.* 200 ppm.⁸ When these Wittig reactions were performed on a 1 mmol scale the isolated yields of the inorganic products were virtually quantitative. Preliminary results indicate that the reaction of (1) with olefins is generally very slow.

The present results show the accessibility of tantalum alkylidene compounds with intramolecularly coordinated N-donor ligand sites and the versatility of the terdentate aryldiamine ligand with respect to its bonding to transition metal centres. Moreover, in a range of alkylidene centered reactions, the aryldiamine ligand is chemically inert and exhibits potential for controlling the reactivity of alkylidene functionalities.

Acknowledgement

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- 3 Relevant NMR data for (1) (1H and ^{13}C NMR δ relative to $SiMe_4$). 1H NMR ($CDCl_3$, 298K, 200.13 MHz) δ 1.21 [C(H)C(CH $_3$) $_3$, s], 2.61 [C(H)Bu t , s], 2.84 and 3.43 [N(CH $_3$) $_2$, both s], 4.26 and 4.72 [CH $_2$ N, both d, $^2J(HH) = 13.6$ Hz], 7.15 (ArH, m). ^{13}C NMR ($CDCl_3$, 298 K, 50.32 MHz) δ 34.2 [C(CH $_3$) $_3$], 46.5 [C(CH $_3$) $_3$], 49.3 and 59.3 [N(CH $_3$) $_2$], 73.1 (CH $_2$ N), 195.4 (Ar ipso C), 253.5 [C(H)Bu t , $^1J(^{13}C-^1H) = 78$ Hz]. $C_{17}H_{29}Cl_2N_2Ta$: calcd. C, 39.78; H, 5.69; N, 5.46; found: C, 39.35; H, 5.49; N, 4.95.
- 4 Crystal data for (1): $[TaCl_2\{C_6H_3(CH_2NMe_2)_2-2,6\}(CHBu^t)]$, $C_{17}H_{29}Cl_2N_2Ta$, $M = 513.28$, monoclinic space group Cc, $a = 12.983(1)$, $b = 12.384(1)$, $c = 11.969(1)$ Å, $\beta = 95.43(1)^\circ$, $V = 1915.8(3)$ Å 3 , $Z = 4$, $D_c = 1.779$ g cm $^{-3}$, $\mu(MoK\alpha) = 59.5$ cm $^{-1}$. An irregularly shaped crystal (ca. 0.5 x 0.3 x 0.3 mm) of (1), mounted on a glass fibre, was used for data collection on an Enraf-Nonius CAD-4F diffractometer at 100 K with Zr-filtered MoK α radiation ($\theta_{max} = 27.5^\circ$). The structure was solved with direct methods followed by peak optimization (SHELXS-86). H-atoms were introduced at calculated positions (C-H = 0.98 Å), except for H(131) which was located from a difference Fourier map and refined. Absorption correction was applied (Gaussian integration). Full-matrix least-squares refinement on F (SHELX-76) converged at a final R value of 0.014, $wR = 0.015$, $w^{-1} = \sigma^2(F)$ for 2246 unique reflections with $I \geq 2.5 \sigma(I)$. Atomic coordinates, bond lengths, bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
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