

## Intramolecular Amine Coordination *versus* NMe C-H Activation: The Stereoselective Synthesis of a Tantalum(V)azacyclopropane Complex

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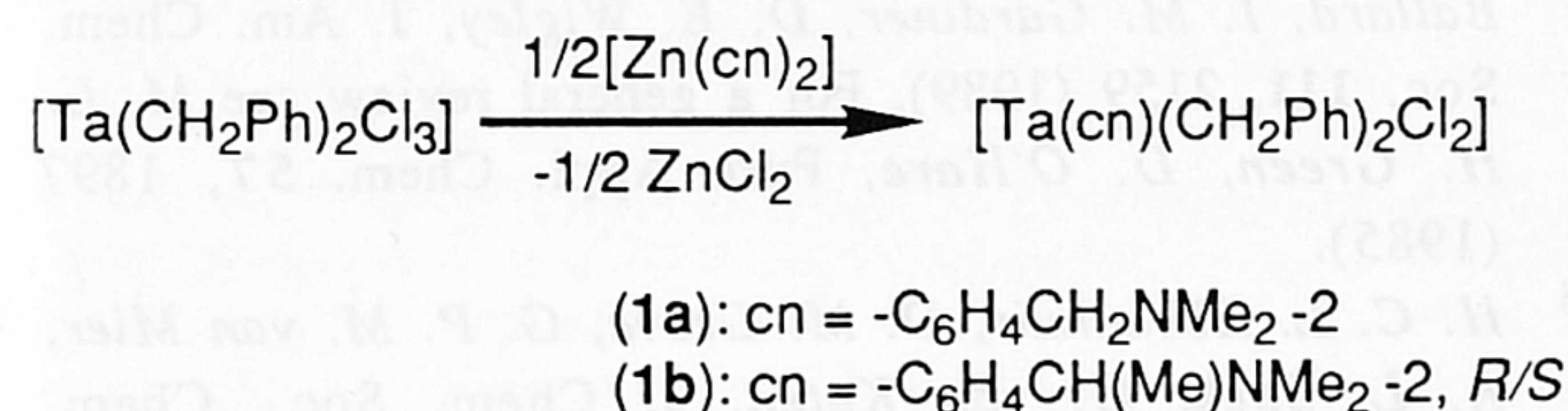
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**Abstract.** A stereoselective C-H activation reaction of a NMe group of  $[\text{Ta}\{\text{C}_6\text{H}_4\text{CH}(\text{Me})\text{NMe}_2\text{-2}\}(\text{CH}_2\text{Ph})_2\text{Cl}_2]$  (**1b**) affords toluene and a species which was isolated as the new pentagonal bipyramidal Ta(V) tetrahydrofuran (THF) adduct  $[\text{Ta}\{\text{C}_6\text{H}_4(\text{CH}(\text{Me})\text{N}(\text{Me})\text{CH}_2\text{-2})\}(\text{CH}_2\text{Ph})\text{Cl}_2(\text{THF})]$  (**2**). The chirality of the arylamine leads to a single structurally characterized diastereoisomer in which intramolecular coordination of the modified amine group produces a triangular Ta-CH<sub>2</sub>-N unit.

Olefin metathesis and C-H activation reactions have been extensively investigated in organotantalum chemistry.<sup>1,2</sup> We have started a study to ascertain whether these processes and their stereochemistry might be controlled by chelate bonded organic groups that have selected electronic characteristics and specifically designed steric constraints. As a first step towards this goal, we recently synthesized and characterized a novel class of organotantalum(V) compounds  $[\text{Ta}\{\text{C}_6\text{H}_4\text{CH}(\text{R})\text{NMe}_2\text{-2}\}(\text{CH}_2\text{Ph})_2\text{Cl}_2]$  (**1**) (Scheme 1).

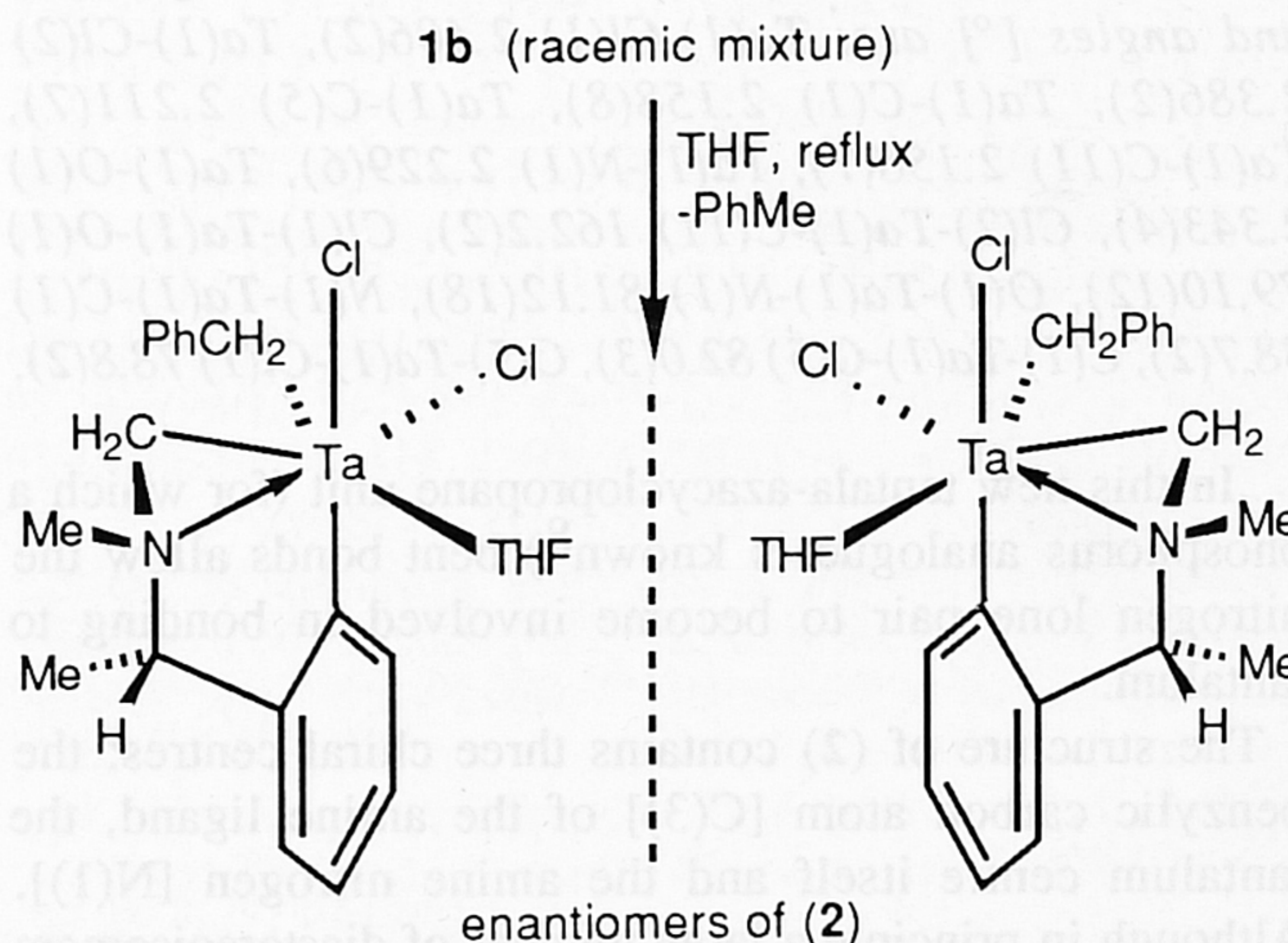


Scheme 1

These species contain, in addition to benzyl and chlorine ligands, an arylamine system that forms a five membered Ta-C-C-N chelate ring.<sup>3</sup> We now report a stereoselective C-H activation reaction of complex (**1b**).

At 58 °C in tetrahydrofuran (THF) complex (**1b**) is converted within 1 hour, with concomitant formation of toluene, to a new complex that was isolated after work-up as the red microcrystalline THF adduct (**2**)<sup>4</sup> in 60% yield (Scheme 2). Complex (**2**) can be handled for short periods in air but is moisture sensitive. The <sup>1</sup>H NMR data of (**2**) are characteristic<sup>5</sup> and are consistent with the presence of

one diastereoisomer (and its enantiomer) with a new NCH<sub>2</sub> unit; *i.e.* C-H activation has taken place within one of the NMe groups of (**1b**).



Scheme 2

To confirm this conclusion and to elucidate the stereochemistry of the ligand distribution around tantalum an X-ray structural analysis of (**2**) was carried out. Suitable crystals of (**2**) were obtained by slow cooling of a diethyl ether solution down to -30 °C. The determined structure (Figure 1)<sup>6</sup> shows (**2**) to be a mononuclear tantalum(V) species  $[\text{Ta}\{\text{C}_6\text{H}_4(\text{CH}(\text{Me})\text{N}(\text{Me})\text{CH}_2\text{-2})\}(\text{CH}_2\text{Ph})\text{Cl}_2(\text{THF})]$  that has a distorted pentagonal bipyramidal



geometry in which a chlorine atom [Cl(2)] and the ring carbon atom [C(11)] of the aryl amine occupy the apical positions. Coordinated to tantalum in the pentagonal plane are: a chlorine atom [Cl(1)], THF [O(1)-bonded], a benzyl group [C(5)-bonded] and both the nitrogen [N(1)] and the carbon [C(1)] of the NCH<sub>2</sub> functionality of the C<sub>6</sub>H<sub>4</sub>(CH(Me)N(Me)CH<sub>2</sub>)-2 ligand. The intramolecular coordination of the NCH<sub>2</sub> group, that generates a triangular Ta-C-N unit [ $\angle$  C(1)-Ta-N(1) = 38.7(2)°], can be best described as a Ta-CH<sub>2</sub>  $\sigma$  bond [Ta-C(1) = 2.158(8) Å] combined with a donative N→Ta interaction [Ta-N(1) = 2.229(6) Å] and a N-CH<sub>2</sub> single bond [N(1)-C(1) = 1.455(9) Å]. Structural data of a recently published yttrium complex<sup>7</sup> with a bridging C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>N(Me)(CH<sub>2</sub>- $\mu$ )-2 functionality seem to make this description more general.

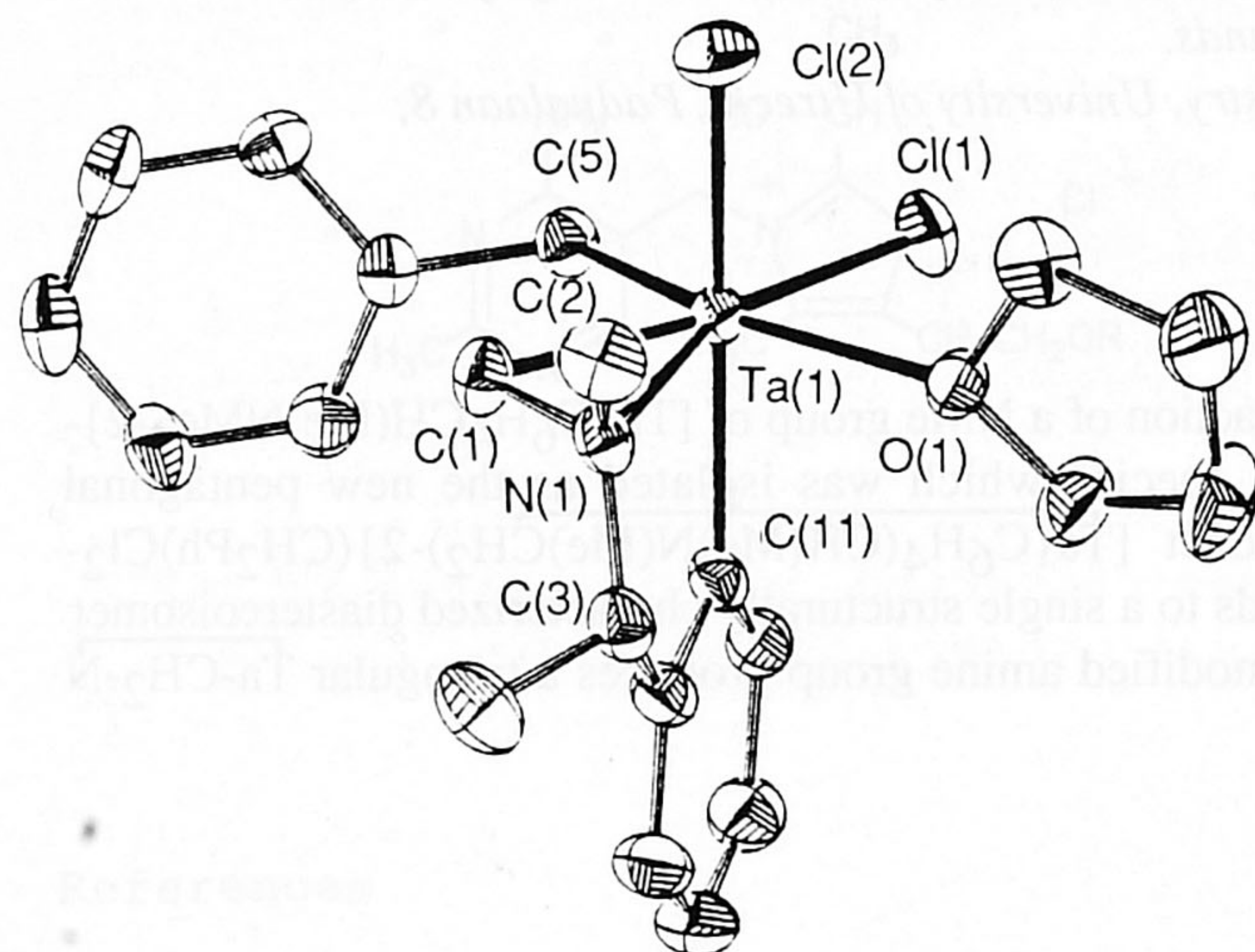


Fig. 1. ORTEP plot of one of the enantiomers of (2) with *S* configuration at the benzylic C atom of the arylamine function (30% probability thermal ellipsoids); hydrogen atoms omitted for clarity. Some selected bond lengths [Å] and angles [°] are: Ta(1)-Cl(1) 2.406(2), Ta(1)-Cl(2) 2.386(2), Ta(1)-C(1) 2.158(8), Ta(1)-C(5) 2.211(7), Ta(1)-C(11) 2.158(7), Ta(1)-N(1) 2.229(6), Ta(1)-O(1) 2.343(4), Cl(2)-Ta(1)-C(11) 162.2(2), Cl(1)-Ta(1)-O(1) 79.10(12), O(1)-Ta(1)-N(1) 81.12(18), N(1)-Ta(1)-C(1) 38.7(2), C(1)-Ta(1)-C(5) 82.0(3), C(5)-Ta(1)-Cl(1) 78.8(2).

In this new tantalum-azacyclopropane unit (for which a phosphorus analogue is known<sup>8</sup>) bent bonds allow the nitrogen lone pair to become involved in bonding to tantalum.

The structure of (2) contains three chiral centres: the benzylic carbon atom [C(3)] of the amine ligand, the tantalum centre itself and the amine nitrogen [N(1)]. Although in principle a large number of diastereoisomers are possible for a compound of formula [Ta{C<sub>6</sub>H<sub>4</sub>(CH(Me)N(Me)CH<sub>2</sub>)-2}(CH<sub>2</sub>Ph)Cl<sub>2</sub>(THF)], the structurally characterized diastereoisomer is obtained in good yield (*vide infra*). Therefore, the overall formation of (2) from (1b) seems to be not only chemoselective but also stereoselective.

The course of the reaction can be followed by <sup>1</sup>H NMR (200.13 MHz, C<sub>6</sub>D<sub>6</sub> : THF-*d*<sub>8</sub> = 4:1). In the case of (1b) the temperature dependency of the <sup>1</sup>H NMR patterns indicate that above *ca.* 330 K the N-Ta dissociation /

association process becomes fast on the NMR time scale. In this <sup>1</sup>H NMR experiment complex (2) is formed from the C-H activation reaction in about 80% yield together with traces of some other diastereoisomers after 30 minutes at 60 °C; *i.e.* the observed reaction has high stereoselectivity. For (1a) formation of toluene begins at higher temperature (*ca.* 373 K) and under these conditions the complex resulting from the C-H activation reaction is seen (<sup>1</sup>H NMR) as a thermally unstable intermediate.<sup>9</sup>

The lower thermal stability of (1b) compared to that of (1a) is probably a direct result of the greater steric interference in the former between one of the NMe groups and the Me substituent at the benzylic position of the amine ligand. When the amine unit is coordinated to tantalum this interference is pronounced and presumably weakens the Ta-N bond. The relief of steric strain may thus be the driving force behind the C-H activation process.

We are currently studying the mechanism of the C-H activation reaction in (1) and similar compounds and, in particular, are interested in discovering whether alkylidene intermediates are involved in this process.

#### Acknowledgement

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- Experimental: All experiments were carried out in an atmosphere of dry nitrogen using standard Schlenk techniques and carefully dried and deoxygenated solvents. (1b): To a magnetically stirred suspension of [Ta(CH<sub>2</sub>Ph)<sub>2</sub>Cl<sub>3</sub>] (3.62 g, 7.71 mmol) in Et<sub>2</sub>O (50 ml) at -78 °C was added over 1 min. a solution of [Zn{C<sub>6</sub>H<sub>4</sub>CH(Me)NMe<sub>2</sub>-2(*R/S*)<sub>2</sub>}] (1.40 g, 3.87 mmol) in cooled Et<sub>2</sub>O (30 ml, -78 °C). After warming the initially orange suspension to 0 °C, a dark red solution resulted from which the solvent was removed *in vacuo*. Extraction of the residue with cold benzene (2 x 20 ml) and subsequent removal of the solvent from



the extract *in vacuo* gave 3.3 g of red (**1b**) (5.9 mmol, 76%). (**2**): A solution of (**1b**) (1.63 g, 2.80 mmol) in THF (20 ml) was heated at 58 °C for 75 minutes. The resulting red solution was allowed to cool down to room temperature and was layered with *ca.* 50 ml of Et<sub>2</sub>O. After standing at -30 °C for several days, microcrystalline, crude product (**2**) was isolated by decantation. Repeated washing with pentane to remove excess THF and drying *in vacuo* yielded 0.95 g of pure red (**2**) (1.69 mmol, 60%). C<sub>21</sub>H<sub>28</sub>Cl<sub>2</sub>NOTa: calcd. C, 44.86; H, 5.02; N, 2.49; found C, 44.73; H, 4.84; N, 2.39.

<sup>5</sup> <sup>1</sup>H NMR data (200.13 MHz, C<sub>6</sub>D<sub>6</sub>), for (**2**) at 294 K: δ 1.10 [d, *J* = 6.5 Hz, C<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)], 1.24 (m, THF), 1.93 and 2.48 (d, *J* = 9.7 Hz, N-CH<sub>2</sub>-Ta), 2.79 (s, NCH<sub>3</sub>), 3.46 and 4.96 (d, *J* = 12.9 Hz, CH<sub>2</sub>Ph), 3.61 (m, THF), 4.08 [q, *J* = 6.5 Hz, C<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)], 6.57 to 7.23 (m, ArH), 8.42 [d, *J* = 7.6 Hz, *o*-H of C<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)].

<sup>6</sup> Crystal data for (**2**): [Ta{C<sub>6</sub>H<sub>4</sub>CH(Me)N(Me)CH<sub>2</sub>-2}-(CH<sub>2</sub>Ph)Cl<sub>2</sub>(THF)] C<sub>21</sub>H<sub>28</sub>Cl<sub>2</sub>NOTa, *M* = 562.32, triclinic space group *P*1, *a* = 9.218(1), *b* = 9.974(1), *c* = 25.930(1) Å, α = 85.75(1), β = 85.70(2), γ = 64.97(1)°, *V* = 2151.7(4) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.73 g cm<sup>-3</sup>, μ(MoK<sub>α</sub>) = 53.1 cm<sup>-1</sup>. A block-shaped crystal (0.26 x 0.43 x

0.87 mm), mounted in a Lindemann glass capillary, was used for data collection on an Enraf-Nonius CAD-4F diffractometer with Zr-filtered MoK<sub>α</sub> radiation (θ<sub>max</sub> = 27.5°). The heavy atoms were located with routine Patterson techniques (SHELXS-86) and the remaining non-H atoms were found in subsequent difference Fourier maps. H-atoms were introduced at calculated positions. THF was refined with a disorder model. An empirical absorption and extinction correction were applied (DIFABS). Full-matrix least-squares refinement converged at a final *R* value: 0.035 *wR* = 0.041; *w*<sup>-1</sup> = σ<sup>2</sup>(*F*) for 7175 unique reflections with *I* ≥ 2.5 σ(*I*). Atomic co-ordinates, bond lengths, bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

<sup>7</sup> M. Booij, N. H. Kiers, A. Meetsma, J. H. Teuben, W. J. J. Smeets, A. L. Spek, *Organometallics* **8**, 2454 (1989).

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<sup>9</sup> The <sup>1</sup>H NMR spectrum of (**1a**), which has no stereogenic centre, can not provide information on N-Ta dissociation / association; see reference [3] for full details about this topic.