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Pentabenzyltantalum: Straightforward Synthesis, X-ray Structure, and Application in the Synthesis of $[O_2N]TaBn_3$-Type and $[O_3N]TaBn_2$-Type Complexes

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Summary: The direct reaction between tantalum pentachloride and benzylmagnesium chloride leads to pentabenzyltantalum, previously prepared by a two-step synthesis. The X-ray structure of pentabenzyltantalum reveals a square-pyramidal geometry. Pentabenzyltantalum was found to be an efficient starting material for the preparation of amine–phenolate complexes via toluene elimination reactions. Thus, its reactions with amine bis(phenolate) and amine tris(phenolate) ligand precursors gave the tribenzyltantalum and dibenzyltantalum complexes, respectively, in quantitative yields.

Pentabenzyltantalum was introduced by Schrock in 1976 alongside related compounds that played a revolutionary role in the development of organometallic chemistry, having led to the discovery of the metal–alkylidene bond and to the development of the well-defined olefin metathesis catalysts.[1,2] Its synthesis relied on a two-step reaction sequence: a reaction between tantalum pentachloride and dibenzylzinc (prepared from BnMgCl) to produce $TaCl_2(benzyl)_3$, which is further reacted with dibenzylmagnesium (also prepared from BnMgCl), giving the homoleptic compound in an overall yield of 51%.[1b] All subsequent preparations of this compound[1c,e] (as well as that of the related $Ta(p\text{-tolyl})_5$)[3] followed this route.[4] Recently, we found that the analogous group IV homoleptic compounds, i.e., $M(benzyl)_4$ (M = Ti, Zr, Hf), serve as convenient entries for making metal–alkyl compounds of various amine–phenolate ligands by direct toluene elimination reactions with the ligand precursors.[5] The latter are synthesized by the straightforward action of 4 equiv of benzylmagnesium chloride on the corresponding metal tetrachloride.[6] It would thus seem plausible that pentabenzyltantalum

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[1] (a) Schrock, R. R. *J. Am. Chem. Soc.* **1974**, *96*, 6796. (b) Schrock, R. R. *J. Organomet. Chem.* **1976**, *122*, 209. (c) Malatesta, V.; Ungold, K. U.; Schrock, R. R. *J. Organomet. Chem.* **1978**, *152*, C53. (d) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. (e) Messerle, L. W.; Jennische, P.; Schrock, R. R.; Stucky, G. *J. Am. Chem. Soc.* **1980**, *102*, 6744.

[2] For a recent review see: Fürstner, A *Angew. Chem., Int. Ed.* **2000**, *39*, 3012.

[3] Piersol, C. J.; Profilet, R. D.; Fanvick, F. E.; Rothwell, I. P. *Polyhedron* **1993**, *12*, 1779.

[4] Notably, Thiele reported in the same year that the action of benzylmagnesium chloride on tantalum pentachloride led to a mixture of compounds, none being the desired pentabenzyl: Von Köhler, E.; Jacob, K.; Thiele, K.-H. *Z. Anorg. Allg. Chem.* **1976**, *421*, 129.

[5] (a) Tshuva, E. Y.; Goldberg, I.; Kol, M.; Goldschmidt, Z. *Organometallics* **2001**, *20*, 3017. (b) Tshuva, E. Y.; Groysman, S.; Goldberg, I.; Kol, M.; Goldschmidt, Z. *Organometallics* **2002**, *21*, 662. (c) Tshuva, E. Y.; Goldberg, I.; Kol, M. *J. Am. Chem. Soc.* **2000**, *122*, 10706. (d) Groysman, S.; Goldberg, I.; Kol, M.; Genizi, E.; Goldschmidt, Z. *Inorg. Chim. Acta* **2003**, *345*, 137.

[6] Zucchini, U.; Alizzati, E.; Giannini, U. *J. Organomet. Chem.* **1971**, *26*, 357.

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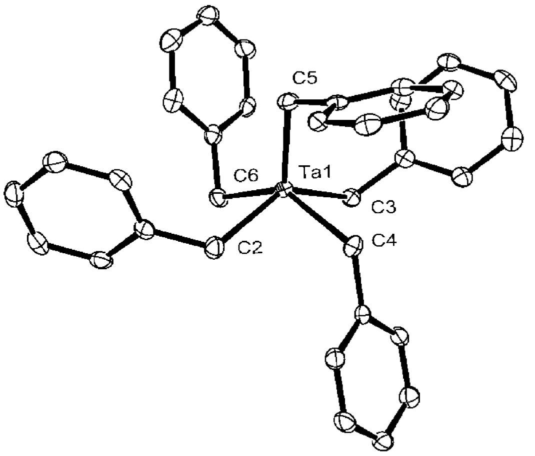


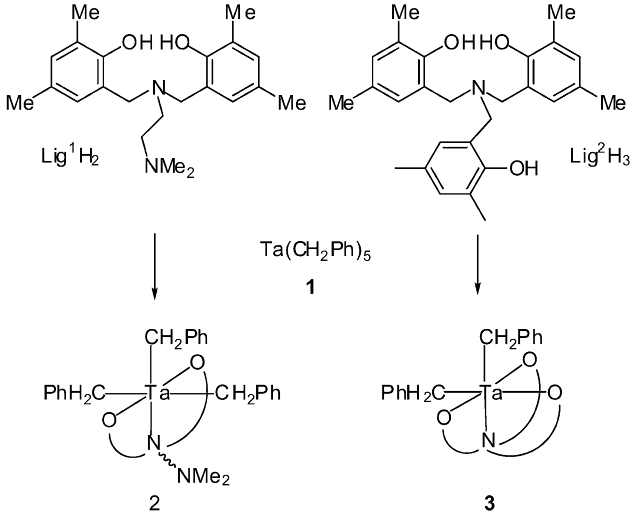
Figure 1. Molecular structure (ORTEP drawing, 50% probability ellipsoids) of **1**. Selected bond lengths (Å) and angles (deg): Ta−C5 = 2.167(4), Ta−C4 = 2.181(4), Ta−C2 = 2.205(4), Ta−C6 = 2.218(4), Ta−C3 = 2.221(4); C5−Ta−C4 = 104.32(14), C5−Ta−C3 = 113.29(14), C4−Ta−C2 = 81.85(15), C4−Ta−C3 = 82.15(14), C4−Ta−C6 = 138.13(14), C2−Ta−C3 = 138.59(14).

may be a useful starting material for the synthesis of various benzyl complexes via the toluene elimination reaction; however, to our knowledge, it has never been employed as such before. In this paper we report a straightforward synthesis of Ta(benzyl)$_5$, its X-ray structure, and its successful application as a starting material for the synthesis of [O_2N]Ta(benzyl)$_3$-type and [O_3N]Ta(benzyl)$_2$-type compounds.

Our wish for a quicker access to Ta(benzyl)$_5$ prompted us to retry the Grignard reagent route,[4] which, gratifyingly, worked out very well. Thus, a slow addition of 5.0 equiv of commercial 1.0 M benzylmagnesium chloride in ether to a stirred, precooled suspension of tantalum pentachloride in ether resulted in an immediate yellow to red-brown color change, and the reaction mixture was stirred at room temperature for 2 h. NMR characterization of the crude product indicated that it consisted of ca. 85% of the desired product and several impurities. Employing less than 5.0 equiv of BnMgCl simplifies the purification of $Ta(CH_2Ph)_5$ (**1**), which is isolated in pure form after workup in ca. 60% yield (see the Supporting Information). The ^1H and ^{13}C NMR spectra of **1** are identical with those reported by Schrock.[1b] Interestingly, the X-ray structure of this fundamental compound had not been reported before. Thus, we grew deep red crystals of **1** from a saturated pentane solution at −35 °C and solved its structure (see Figure 1 and the Supporting Information). The bond distances and angles of $Ta(CH_2Ph)_5$ were found to closely resemble those of the related Ta(*p*-tolyl)$_5$, [3] and the overall geometry around the metal is that of a distorted square pyramid.

Pentabenzyltantalum was reported to start decomposing within a few minutes of heating to 40 °C.[1c] However, we found that when it is stored at −35 °C under a nitrogen atmosphere it does not exhibit appreciable decomposition for weeks and may be employed successfully in toluene elimination reactions with amine−phenolate ligand precursors. Two prototypical ligand skeletons were chosen for the preliminary investigation: Lig$^1H_2$ is an [ONNO]-type dianionic ligand precursor bearing a dimethylamino donor on the sidearm, and Lig$^2H_3$ is an [O_3N]-type trianionic ligand precursor (Scheme 1). Both ligands feature methyl substituents in the 2,4-positions of the phenolate rings.

Scheme 1



Lig$^1H_2$ reacted smoothly with **1** to afford the tribenzyl complex Lig$^1Ta(CH_2Ph)_3$ (**2**) as a yellow solid in quantitative yield. The ^1H NMR spectrum supports a C_s symmetrical binding of the [ONO] core to the metal, as evident from the AB system for the N−CH_2 protons, and a single set of peaks for the two substituted phenolate groups. Somewhat surprisingly, the three benzyl groups are nearly equivalent on the NMR time scale at room temperature, giving rise to two broad absorptions of the methylene protons that coalesce to a broad singlet upon heating to 45 °C. The ^{13}C NMR spectrum exhibits the same pattern: only one flat peak is detected at room temperature for the benzylic carbon, which sharpens as the temperature increases. Cooling a toluene-d_8 solution of **2** to ca. −50 °C shows three distinct resonances for the Ta−CH_2 protons. It thus seems that a fluxional process equilibrates the benzyl groups, without affecting the mode of binding of the amine bis(phenolate) core. Single crystals of Lig$^1Ta(CH_2Ph)_3$ were obtained from cold ether, and the solid-state structure was determined by X-ray crystallography (see Figure 2 and the Supporting Information). The geometry at the Ta center is

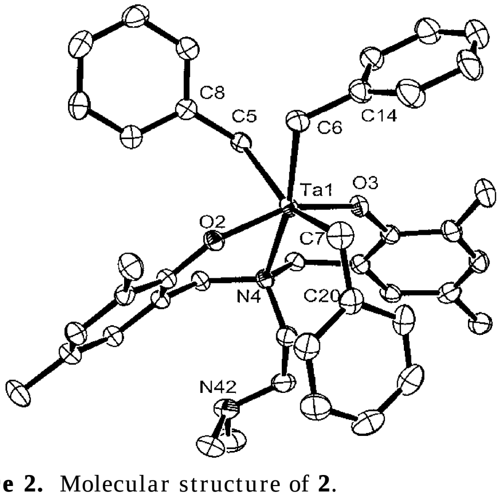


Figure 2. Molecular structure of **2**.

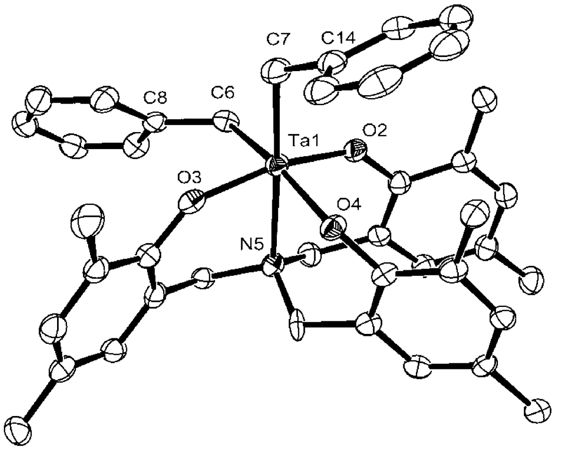


Figure 3. Molecular structure of Lig^{2}Ta(CH$_2$Ph)$_2$ (**3**).

that of a distorted octahedron. The amine bis(phenolate) ligand wraps around the metal in a meridional fashion, with the sidearm dimethylamino donor unbound. The central nitrogen-to-metal bond is very weak, it being the longest (2.513 Å) amid analogous distances in all previously reported metal complexes of this family. The Ta−C bond distances and Ta−C−C bond angles lie in the ranges of 2.248−2.279 Å and 103.60−122.88°, respectively, and clearly indicate η^1 binding of all benzyl groups.

The reaction of the amine tris(phenolate) ligand precursor Lig^{2}H$_3$ with **1** generated the corresponding dibenzyl complex Lig^{2}Ta(CH$_2$Ph)$_2$ (**3**) quantitatively. **3** may also be synthesized (albeit in a lower yield) by reacting Lig^{2}TaCl$_2$ with 2 equiv of BnMgCl; however, this approach is less advantageous, as the synthesis of Lig^{2}TaCl$_2$ is somewhat tedious.[7,8] The ^{1}H NMR spectrum of **3** displays a singlet for the N−CH_2 protons and a singlet for the benzyl CH_2 protons, thereby denoting a highly fluxional complex of C_{3v} symmetry on the NMR time scale. In contrast, all previously studied [O$_3$N]-TaX$_2$-type complexes (i.e. Lig^{2}TaCl$_2$, Lig^{2}Ta(OEt)$_2$, and Lig^{2}Ta(NMe$_2$)$_2$, etc.), feature C_s symmetry on the NMR time scale, indicating that no fluxional process occurs at room temperature.[7,9] Upon cooling to as low as −80 °C, only the disappearance of the benzyl CH_2 signals is observed, supporting a slowing but not complete arresting of the fluxional process. The crystal structure of Lig^{2}Ta(CH$_2$Ph)$_2$ (Figure 3), however, is closely related to those of the previously reported [O$_3$N]-TaX$_2$-type complexes, featuring an overall octahedral geometry and an approximate C_s symmetry.[7,9] Obviously, the barrier for the fluxional process in the complexes of the [O$_3$N]TaX$_2$ type is reduced substantially for X = benzyl.

In conclusion, this convenient one-step synthesis of Ta(CH$_2$Ph)$_5$ and its efficient transformations into two novel types of amine phenolate complexes via toluene elimination reactions demonstrate that, much like its group IV analogues, Ta(CH$_2$Ph)$_5$ may serve as a useful entry for the synthesis of tantalum−alkyl complexes. We are currently investigating the reactivity of the newly prepared complexes.

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Supporting Information Available: Text giving experimental procedures and spectroscopic and crystallographic data for **1**−**3**; data for the crystal structures of **1**−**3** are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM034066P

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[7] Groysman, S.; Segal, S.; Shamis, M.; Goldberg, I.; Kol, M.; Goldcshmidt, Z.; Hayut-Salant, E. *J. Chem. Soc., Dalton Trans.* **2002**, 3425.

[8] Interestingly, the related [N$_3$N]TaCl$_2$ complex featuring the tripodal triamidoamine ligand leads to a benzylidene rather than to a dibenzyl complex upon reaction with benzylmagnesium chloride: Freundlich, J. S.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3643.

[9] Kim, Y.; Kapoor, P. N.; Verkade, J. G. *Inorg. Chem.*, **2002**, *41*, 4834.