

Bis(methylidene) Complex of Tantalum Supported by a PNP Ligand

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Summary: Reaction of (PNP)Li with TaF₅ produces pentagonal-bipyramidal (PNP)TaF₄ (**2**). Alkylation of **2** with MeMgBr allows for the isolation of (PNP)TaMe₄ (**3**). (PNP)TaMe₄ (**3**) evolves thermally and/or photochemically into a bis(methylidene) complex (PNP)Ta(=CH₂)₂ (**4**). The identity of the latter has been established by X-ray structural, NMR spectroscopic, and DFT computational studies. It does not appear that **4** possesses agostic interactions in solution.

High oxidation state transition metal complexes containing double metal–carbon bonds (usually termed Schrock¹ carbenes or alkylidenes) have attracted significant attention,² in part because of their importance in catalytic alkene metathesis.³ The majority of alkylidene complexes possess at least one bulky substituent on the alkylidene carbon; this steric protection is important against bimolecular decomposition pathways.⁴ In addition, alkylidenes are often generated via α -abstraction⁴ from a di- or polyalkyl precursor. Such reactions are assisted by steric pressure, and larger alkyls are more prone to α -abstraction than methyls. On the other hand, exploration of the simplest ligands has always been attractive to organometallic chemists. In the context of metal alkylidenes, the CH₂ ligand (methylene or methylidene) is the smallest and simplest possible ligand. Although the first methylidene complex (**A**, Figure 1) was among the first alkylidenes reported,⁵ relatively few methylidene complexes have been reported since.^{2,6} To the best of our knowledge, no complexes with two terminal methylidene ligands attached to the same metal have been unambiguously characterized.⁷ Our group, as well as Mindiola et al., have recently used the ancillary pincer PNP ligand⁸ to support remarkably resilient alkylidene compounds of Ti (**B**) and Zr (**C**), and even a transient Ti alkylidyne in Mindiola's studies, prepared by α -abstraction.⁹ In the PNP system, the steric pressure to promote α -abstraction and steric protection of the bis(alkylidene) products is afforded

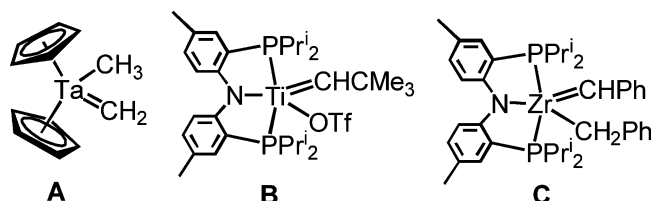
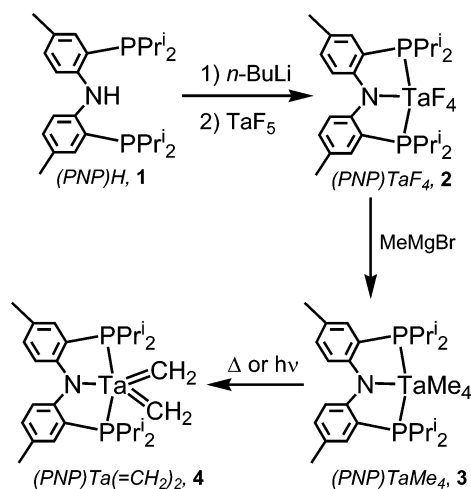


Figure 1. First methylidene complex (**A**) and examples of PNP-supported Ti (**B**) and Zr (**C**) alkylidenes.

Scheme 1. Synthesis of **2**, **3**, and **4**



by the bulky phosphine arms, the coordination of which to the metal is enforced by the rigidity of the PNP construction. We surmised that the PNP ligand should be suitable to support related organometallic compounds of Ta as well. Here we report a well-characterized example of a Ta complex bearing two methylidene ligands.

Reaction of (PNP)Li^{9a} with TaF₅ afforded (PNP)TaF₄ (**2**) in good isolated yield (Scheme 1). We selected a metal fluoride instead of a more traditional metal chloride precursor because of the smaller size of fluorine (and thus more accommodating of the high coordination number in **2**) and the convenience of ¹⁹F NMR. The solid-state structure of **2** was determined in the course of an X-ray diffraction study (Figure 2). The environment about Ta can be described as approximately pentagonal bipyramidal. Two of the fluorides occupy the axial sites, and PNP and the other two fluorides occupy the equatorial sites. Only

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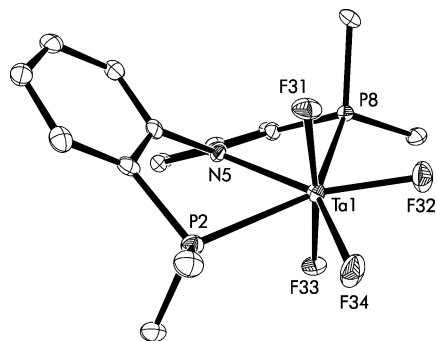


Figure 2. ORTEP¹¹ drawing (50% probability ellipsoids) of **2** showing selected atom labeling. Hydrogen atoms and all methyl groups are omitted for clarity. Selected bond distances (Å) and angles (deg): Ta1–F31, 1.892(2); Ta1–F32, 1.929(2); Ta1–F33, 1.899(2); Ta1–F34, 1.946(2); Ta1–P2, 2.6556(11); Ta1–N5, 2.174(3); Ta1–P8, 2.6663(11); P2–Ta1–P8, 139.61(3).

one ¹⁹F resonance was observed at 22 °C (δ –195.9 ppm) and only one resonance in the ³¹P{¹H} spectrum as a telltale quintet (δ 48 ppm, J_{P-F} = 58 Hz). Upon lowering the temperature to –70 °C, two resonances of equal intensity (δ –187.2, –221.8 ppm) were detected by ¹⁹F NMR, consistent with the presence of two types of F in the solid-state structure. Reaction of (PNP)-TaF₄ with 4 equiv of MeMgBr resulted in complete replacement of four fluorine ligands with methyl groups with formation of (PNP)TaMe₄ (**3**), which was isolated in 60% yield upon workup. Both **2** and **3** display time-averaged C₂ symmetry on the NMR time scale at 22 °C with only a single Ta–Me resonance observable by ¹H (δ 1.12, t, 6 Hz) or ¹³C{¹H} (δ 66.7) NMR.¹⁰

Thermolysis of **3** led to slow conversion to (PNP)Ta(=CH₂)₂ (**4**) via apparent α -abstraction (methane observed by ¹H NMR). **4** can also be produced via photolysis of **3** (λ = 350 nm). The photolytic synthesis of **4** is faster and results in material of greater purity. Photolytic transformations of (P₂N₂)TaMe₃ and (ArO)₂TaMe₃ to give (P₂N₂)Ta(=CH₂)(CH₃)¹² and (ArO)₂Ta(=CH₂)(CH₃),¹³ respectively, have been reported (P₂N₂ is a cyclic bis(phosphine)/bis(amido) ligand). In contrast, (PNP)-ZrMe₃ is thermally stable.^{9a} Presumably, the higher coordination number for Ta^V versus Zr^{IV} is conducive to α -abstraction.

The methylene ¹³C{¹H} NMR resonance (t, J_{CP} = 6 Hz) of **4** was detected at δ 233.9 ppm. The methylene hydrogens of **4** gave rise to two broad resonances in the ¹H NMR spectrum at 22 °C at δ 8.7 and 7.9 ppm. Two well-resolved doublets (J_{HH} = 10 Hz) were observed at –15 °C, indicating nonequivalence of the two hydrogen atoms on the same carbon. We propose that the rotation about the Ta=C bond is responsible for the site exchange. The activation parameters for the exchange were determined (ΔH^\ddagger = 52(2) kJ/mol, ΔS^\ddagger = –29(6) J/(mol·K)) by temperature-dependent NMR line shape analysis in the –15 to +80 °C range.¹⁴ The modest negative value of ΔS^\ddagger supports the notion of an intramolecular process. **4** displayed apparent C₂ symmetry in the NMR spectra in the –15 to +80 °C range.¹⁰

(10) Trigonal bipyramidal (PNP)AlX₂ (X = Cl, alkyl) compounds also display C₂ symmetry in solution by NMR and in the solid state.^{17a} Square-planar PNP complexes (e.g., (PNP)PdCl),¹⁷ on the other hand, display C_{2v} symmetry in solution despite C₂ symmetry in the solid.^{17b}

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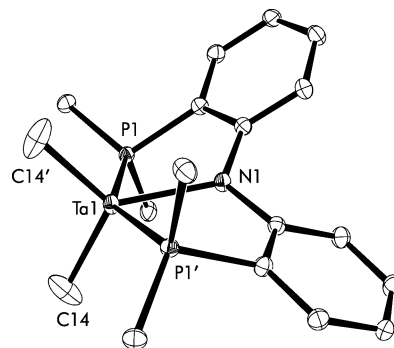


Figure 3. ORTEP¹¹ drawing (50% probability ellipsoids) of **4** showing selected atom labeling. Hydrogen atoms and all methyl groups are omitted for clarity.

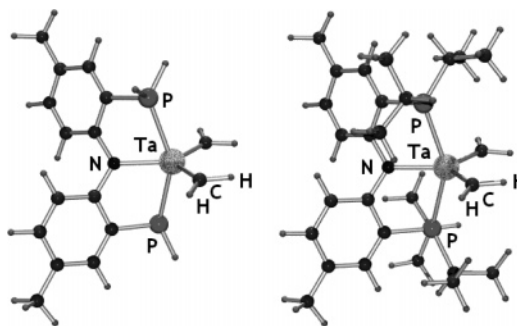


Figure 4. DFT-optimized structures of (PNP^H)Ta(=CH₂)₂ (**5**, left) and of **4** (right).

An X-ray structural determination confirmed the presence of two crystallographically equivalent methylene ligands attached to the Ta center (Figure 3). The coordination environment about the Ta center can be described as a heavily distorted trigonal bipyramid. The greatest distortion is in the P–Ta–P angle (149.201(15)°), presumably a consequence of the chelate constraint. The Ta–C distance of 1.9385(17) Å is well within the range for the known Ta–C double bonds.² In particular, this distance is similar to the Ta=C distances in the range 1.93–2.00 Å for (mesityl)(Me₃P)₂Ta(=CHCMe₃)₂ and (Me₃SiCH₂)-(Me₃P)₂Ta(=CHSiMe₃),¹⁵ the other crystallographically characterized approximately trigonal-bipyramidal tantalum bis(alkylidenes). Crystallographic evidence for a T-shaped arrangement of the CH₂ hydrogen atoms about the alkylidene carbon was found in difference Fourier maps. Although this geometry is typical of agostic alkylidenes and their inclusion improved the refinement statistics, hydrogen atom positions from X-ray diffractometry can be unreliable, particularly when in close proximity to heavy atoms such as Ta. Spectroscopic evidence in solution and DFT calculations (vide infra) do not support this agostic model.

For an agostic CH₂ group, one would expect the ¹J_{CH} values and the chemical shifts corresponding to the two hydrogens to be drastically different. The agostic hydrogens typically exhibit <100 Hz J_{CH} values (substantially lower than a standard J_{CH} for a C(sp²)–H or even a C(sp³)–H bond). A nonagostic hydrogen of a T-shaped methylidene should exhibit a J_{CH} value comparable to a standard J_{CH} value for a C(sp)–H bond. For example, Templeton et al. reported [Tp^W(CO)₂(=CH₂)]BF₄, an agostic cationic methylidene of W^{II}.¹⁶ The agostic and the nonagostic methylidene hydrogens resonated at δ 1.9 (J_{CH} =

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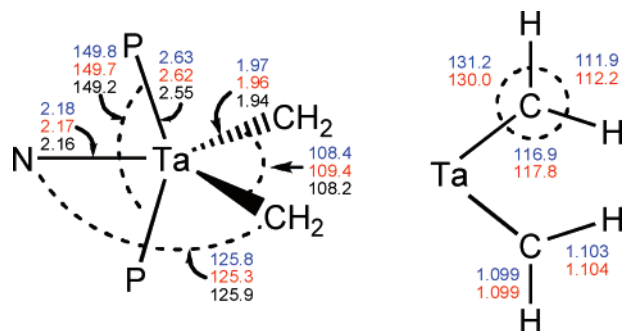


Figure 5. Distances (Å) and angles (deg) from the XRD structure of **4** (bottom numbers, black) and the DFT structures of **5** (middle, red) and **4** (top, blue).

93 Hz) and 9.1 ($J_{\text{CH}} = 191$ Hz) ppm, respectively. This is in contrast to the similar chemical shifts for the two CH₂ hydrogens observed for **4**. Because of the poor solubility of **4**, we were able to determine only the J_{CH} value of 128 Hz for the resonance at δ 8.7 ppm. Although this value is somewhat smaller than is expected for a C(sp²)-H bond, it is too large for an agostic C-H and also too small to correspond to the nonagostic C-H of a T-shaped CH₂ ligand.

To obtain further insight, we resorted to DFT studies. We have optimized structures (Figure 4) of the bis(methylidene) complexes **4** and **5** for both the full ligand and the simplified

PNP^H ligand that bears PH₂ arms. DFT reproduced the XRD-determined positions of the heavy atoms with a great degree of accuracy (Figure 5). While DFT evidences a minor distortion from an idealized trigonal plane for the CH₂ ligands, the geometry is far from T-shaped and probably should not be termed agostic. This is in accord with the solution NMR data.

In summary, we have prepared a rare example of a stable transition metal bis(methylidene) complex, (PNP)Ta(=CH₂)₂ (**4**), with a unsaturated metal center. Agostic interactions with the methylidene hydrogen atoms *exclusively* in the solid state cannot be ruled out, but the solution NMR and DFT evidence is inconsistent with agostic interactions in **4**.

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Supporting Information Available: Crystallographic information for **2** and **4** in the form of CIF files, experimental details, and pictorial NMR spectra for select compounds. This material is available via the Internet free of charge at <http://pubs.acs.org>.

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