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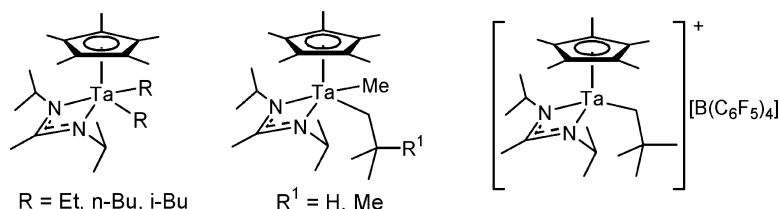
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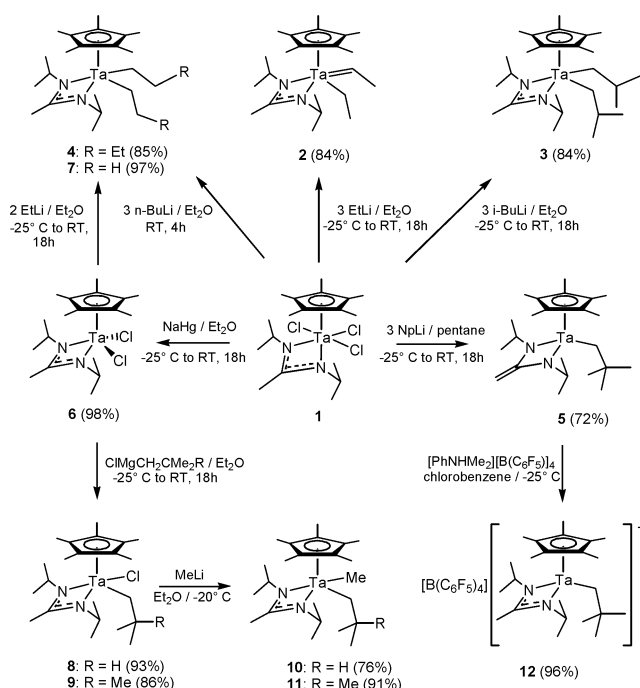
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Transition-metal-catalyzed polymerizations and synthetic (asymmetric) organic transformations will continue to be of dominant importance to society for the foreseeable future. Accordingly, there is great need to continuously develop new fundamental organometallic chemistry that can pave the way for the development of new transition-metal-based catalysts. In this regard, tremendous gaps still exist in our knowledge of the chemistry of the group 5 metals in their highest oxidation states, that is, M(IV) and M(V) (M = V, Nb, and Ta), as it pertains to the stability and reactivity of organometallic complexes with saturated alkyl groups possessing β -hydrogens, and more specifically, those containing M-CH₂CHR_n fragments.¹ Interest in filling this knowledge gap is more than academic in that over the past 30 years there have been, for instance, sporadic reports of Ta-based catalysts for both the Ziegler–Natta polymerization and selective oligomerization of ethylene and the selective dimerization of α -olefins.^{2,3} Indeed, it is through the seminal discovery and detailed mechanistic investigations of this last catalytic system by Schrock and co-workers³ that we have the best evidence to date that such compounds can be stable enough to isolate for structural characterization.⁴ However, it must also be recognized that the increased stability of the Ta(V) metallacyclopentanes that are involved in this process, relative to acyclic alkyl groups, is most likely the result of conformational restrictions imposed by the five-membered metallacyclopentane ring that contribute to a higher barrier for intramolecular β -hydrogen elimination (abstraction).⁵ With respect to the organometallic chemistry of Ta(IV), to the best of our knowledge, the record is completely silent regarding any report of isolable or spectroscopically observable alkyl complexes bearing β -hydrogens. Herein, we now report the successful synthesis and solid-state structural characterization of a family of neutral and cationic d¹ Ta(IV) alkyl complexes that can be isolated in pure form. Importantly, all these new compounds display a remarkable stability toward β -hydrogen and β -methyl eliminations.

Scheme 1 summarizes the synthetic results of the present work in which all the new compounds, **2–12**, have been fully characterized, including determination of their solid-state structures by single-crystal X-ray analysis.⁶ To begin, alkylation of known **1**^{2d} at -25°C with 3 equiv of EtLi in diethyl ether (Et₂O) provided the d⁰ Ta(V) ethyl, ethylidene **2** in a 84% isolated yield. In contrast, carrying out the same reaction using either 3 equiv of *i*-BuLi (at -25°C) or *n*-BuLi (at room temperature)⁷ now provided excellent isolated yields of the paramagnetic d¹ Ta(IV) di(isobutyl) and di(*n*-butyl) compounds, **3** and **4**, respectively. Finally, with 3 equiv of neopentylolithium (NpLi), alkylation of **1** resulted in a 72% yield of the mononeopentyl Ta(IV) complex **5**. While we have not yet attempted to unequivocally elucidate the mechanistic path(s) that lead to each of these structurally distinct products, it seems reasonable to conclude that because of increasing steric demands that occur about the metal center with each successive Cl \rightarrow alkyl exchange, the remaining equivalent(s) of organolithium reagent can

Scheme 1



engage in (1) α -hydrogen deprotonation of an alkyl substituent, to produce a Ta(V) alkylidene,⁸ (2) reductive electron transfer to the metal center to provide Ta(IV) species, and (3) deprotonation of the methyl group of the acetamidinate ligand to produce an eneamidate species.⁹

Although the solution stabilities of the new organotantalum(IV) alkyl compounds, **3–5**, were initially surprising (vide infra), these observations are in keeping with those previously reported by us for the class of structurally analogous neutral and cationic d⁰ group 4 (M = Ti, Zr, Hf) monocyclopentadienylmetal amidinate alkyl complexes that can function as precatalysts and highly active species, respectively, for the living (stereospecific) Ziegler–Natta polymerization of α -olefins.¹⁰ Accordingly, on the basis of this experience, we felt it highly likely that a general route to a much larger variety of Ta(IV) homoleptic and mixed dialkyl compounds built around the monocyclopentadienyl, amidinate ligand combination could be successfully developed. To this end, it was first determined that **1** could be reduced by 1 equiv of sodium amalgam in Et₂O to provide a near quantitative yield of the Ta(IV) dichloride **6**, which was also found to be quite stable in solution and the solid state.⁶ Compound **6** then proved to be an excellent starting material for preparing a range of new, isolable Ta(IV) alkyl derivatives according to Scheme 1. Thus, alkylation of **6** with 2 equiv of EtLi cleanly provided an excellent yield of the desired Ta(IV) diethyl compound **7**. Furthermore, using 1 equiv of *i*-BuMgCl and NpMgCl, controlled monoalkylation of **6** could be carried out to

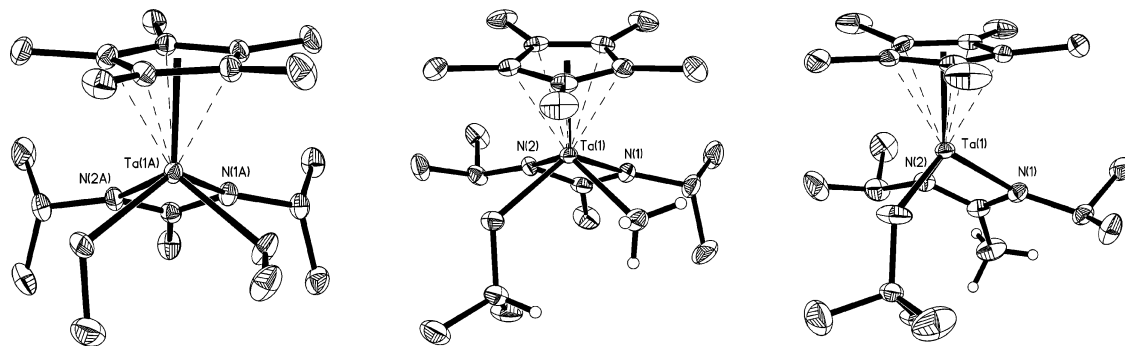
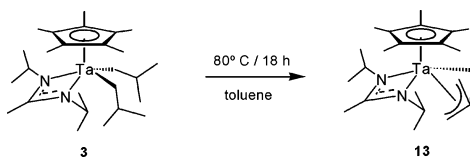


Figure 1. Molecular structures (30% thermal ellipsoids), from left to right, of compounds **7**, **10**, and **12**. The $[\text{B}(\text{C}_6\text{F}_5)_4]$ anion of **12** and all hydrogen atoms, except for selected ones in **10** and **12** that are represented as small spheres of arbitrary size, have been removed for the sake of clarity.

Scheme 2



provide good yields of the corresponding Ta(IV) chloro, alkyl complexes, **8** and **9**, respectively, which, after isolation and purification through recrystallization, were further methylated using 1 equiv of MeLi to provide excellent yields of the final desired mixed Ta(IV) methyl, alkyl complexes, **10** and **11**, respectively.⁶ Finally, in related work with the goal of exploring the possible Ziegler–Natta polymerization activity of well-defined cationic d¹ Ta(IV) alkyl species, it was determined that protonation of the enamidate **5** could be achieved using 1 equiv of $[\text{PhNHMe}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ in chlorobenzene to produce a near quantitative yield of the cationic Ta(IV) neopentyl complex **12** according to Scheme 1. Figure 1 provides a few representative examples of the molecular structures of **3**–**12** that were determined by single-crystal X-ray analyses, and in each case, no structural evidence for any α - or β -hydrogen agostic¹¹ interactions involving the Ta(IV) metal center are observed.⁶

Compounds **3**–**12** were qualitatively all found to be remarkably stable in solution at room temperature for extended periods of time, and in the case of the neopentyl derivatives **11** and **12**, at higher temperatures as well. Indeed, cationic **12** could be recovered nearly quantitatively through crystallization after heating a chlorobenzene solution to 100 °C for 10 h. This degree of thermal stability stands in sharp contrast to other cationic group 4 and 5 metal neopentyl species which are all reported to engage in facile low-temperature β -methyl group elimination.¹² This is not to say, however, that the new Ta(IV) alkyls are devoid of potentially interesting thermal behavior. Indeed, as depicted in Scheme 2, heating a toluene solution of the diisobutyl compound **3** to 80 °C for 18 h resulted in a 50% isolated yield of the trimethylenemethane (TMM) Ta(IV) complex **13** that was also structurally characterized by X-ray analysis. Interestingly, the TMM fragment of **13** appears to adopt a unique η^1, η^3 -bonding mode.^{6,10b} As similar results were obtained upon thermolysis of a Zr(IV) structural analogue,^{10b,13} it is now possible to speculate that a common mode of decomposition for early transition-metal alkyl compounds bearing β -hydrogens involves intra- and intermolecular γ -hydrogen abstraction rather than simple β -hydrogen eliminations/abstractions alone.¹⁴

In conclusion, the present work serves to present a family of neutral and cationic Ta(IV) alkyl complexes that are stable toward β -hydrogen and β -methyl eliminations. Clearly, however, these

preliminary results only provide the barest of introductions to the likely beginnings of a new era of discovery for high-oxidation-state group 5 organometallic chemistry. Further studies regarding the stability and chemical reactivity of all the new compounds reported herein are in progress, the results of which will be reported in due course.

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Supporting Information Available: Experimental details, including crystallographic analyses of **2**–**13**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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