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Preparation and Reactions of Tantalum Alkylidene Complexes Containing Bulky Phenoxide or Thiolate Ligands. Controlling Ring-Opening Metathesis Polymerization Activity and Mechanism through Choice of Anionic Ligand

Kevin C. Wallace, Andy H. Liu, John C. Dewan, and Richard R. Schrock*

Contribution from the Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received October 1, 1987*

Abstract: Addition of LiDIPP (DIPP = $O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$) to $Ta(CH\text{-}t\text{-}Bu)(THF)_2Cl_3$ yields $Ta(CH\text{-}t\text{-}Bu)(DIPP)_3(THF)$ (**1**) in high yield. $Ta(CH\text{-}t\text{-}Bu)(DMP)_3(THF)$ (**3**; DMP = $O\text{-}2,6\text{-}C_6H_3Me_2$) and $Ta(CH\text{-}t\text{-}Bu)(TIPT)_3(THF)$ (**5**; TIPT = $S\text{-}2,4,6\text{-}C_6H_2\text{-}i\text{-}Pr_3$) can be prepared by analogous methods. **1** reacts rapidly with 1 equiv of styrene to give the tantalacyclobutane complex $Ta[CH(Ph)CH(t\text{-}Bu)CH_2](DIPP)_3$. $Ta[CH(Ph)CH(t\text{-}Bu)CH_2](DIPP)_3$ belongs to the space group $P2_1/n$ with $a = 21.338\ (11)$ Å, $b = 11.699\ (5)$ Å, $c = 37.198\ (23)$ Å, $\beta = 102.66\ (5)°$, $Z = 8$, M_r 887.03 g, $V = 9060.1$ Å^3, ρ(calcd) = 1.301 g cm^{-3}. The overall structure is a distorted square pyramid. The TaC_3 ring is slightly bent (25.2°) with the phenyl and *tert*-butyl groups trans to one another. The TaC_3 ring is elongated in the $Ta\cdots C_\beta$ direction compared to trigonal-bipyramidal tantalacycle and tungstacycle complexes in which the MC_3 ring is bound in equatorial positions. An analogous reaction between **1** and vinyltrimethylsilane gives $Ta(CHSiMe_3)(DIPP)_3(THF)$ or $Ta[CH(SiMe_3)CH(SiMe_3)CH_2](DIPP)_3$ depending upon reaction conditions; the two are in ready equilibrium. **1** reacts smoothly with ethylene to give $Ta(CH_2CH_2CH_2)(DIPP)_3$ in high yield, but treatmment of **1** with olefins such as propylene or 1-butene did not lead to any characterizable species. Addition of excess *cis*-2-pentene to **1** results in rapid metathesis (100 equiv to equilibrium in <15 min), but activity is short-lived. In contrast to reactions between **1** and olefins, $Ta(CH\text{-}t\text{-}Bu)(TIPT)_3(THF)$ does not react with ordinary olefins and will not metathesize them. Tantalacyclobutane complexes containing the DIPP ligand react with the carbonyl functionality to give a mixture of insertion chemistry (oxytantalacyclohexane complexes) and Wittig-like reactivity, depending upon the carbonyl compound, the tantalacycle, and the temperature. **1** reacts with norbornene to give an isolable tantalacyclobutane complex, $Ta[CH(C_5H_8)CHCH(t\text{-}Bu)](DIPP)_3$, a crystal structure study of which showed it to be a trigonal-bipyramidal species analogous to $W[CH(SiMe_3)CH(SiMe_3)CH_2](N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCMe(CF_3)_2]_2$. (Crystal data are space group $P2_1/n$, $a = 11.587\ (4)$ Å, $b = 20.795\ (4)$ Å, $c = 18.388\ (4)$ Å, $V = 4416.6$ Å^3, $Z = 4$, M_r 877.03 g, ρ(calcd) = 1.319 g cm^{-3}.) Norbornene is polymerized by $Ta[CH(C_5H_8)CHCH(t\text{-}Bu)](DIPP)_3$ in a reaction that is zero order in norbornene (characteristic of rate-limiting opening of the TaC_3 ring followed by rapid capture of the incipient alkylidene complex by NBE) until ~1 equiv of NBE remains, at which point it becomes first order in NBE. Analogous reactions between $Ta(CH\text{-}t\text{-}Bu)(TIPT)_3(py)$ and NBE are first order in NBE, and loss of pyridine is required. The living polymer in the TIPT case is an alkylidene complex. In each system the polymer can be cleaved from the metal with benzaldehyde and shown to be monodisperse. Only in the TIPT system is secondary metathesis (after NBE has been consumed) negligible.

We have reported a variety of high oxidation state, electronically unsaturated alkylidyne[1] and (more recently) alkylidene[2] complexes of tungsten and molybdenum that contain bulky alkoxide ligands. Examples are $W(CR)(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3$,[1b] $Mo(CR)[OCMe(CF_3)_2]_3$,[1e] $W(CHR)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCMe(CF_3)_2]_2$,[2b] and $Mo(CHR)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(O\text{-}t\text{-}Bu)_2$.[2c] It is becoming clear that bulky alkoxide ligands not only can protect a four- or five-coordinate metal complex against deleterious bimolecular decomposition reactions but also can closely *control* the reactivity of the metal complex in acetylene[1a,3] and olefin[4] metathesis reactions.[5] For example, $W(CHR)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCMe(CF_3)_2]_2$ complexes are extremely efficient olefin metathesis catalysts (lower limit ~10^3 turnovers of *cis*-2-pentene per minute at 25 °C)[2b] while $W(CHR)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(O\text{-}t\text{-}Bu)_2$ is *virtually inactive* as a metathesis catalyst for *cis*-2-pentene.[4] ($M(CHR)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(O\text{-}t\text{-}Bu)_2$ complexes (M = Mo or W) *will* react with strained olefins such as norbornene, a fact that makes them extremely useful as catalysts for controlled ring-opening metathesis reactions[8] to give monodisperse polymers.[4,7])

We decided to test whether some of the principles we had uncovered in tungsten and molybdenum chemistry could be used to advantage in tantalum chemistry, especially since $Ta(CH\text{-}t\text{-}Bu)(THF)_2Cl_3$ can be prepared in high yield in two relatively easy steps from $TaCl_5$.[9] Tantalum alkylidene complexes have been useful for outlining the principles of olefin metathesis,[10,11] but none has been long-lived enough to be practical for metathesis of ordinary olefins. Therefore we felt we had a better chance of preparing reagents for Wittig-like reactions[12] or catalysts for the controlled ring-opening of strained cyclic olefins.[4,7,13] We also

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[1] (a) Schrock, R. R. *Acc. Chem. Res.* **1986**, *19*, 342. (b) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554. (c) Freudenberger, J. H.; Schrock, R. R.; Churchill, M. R.; Rheingold, A. L.; Ziller, J. W. *Organometallics* **1984**, *3*, 1563. (d) Listemann, M. L.; Schrock, R. R. *Organometallics* **1985**, *4*, 74. (e) McCullough, L. G.; Schrock, R. R.; Dewan, J. C.; Murdzek, J. S. *J. Am. Chem. Soc.* **1985**, *107*, 5987.

[2] (a) Schrock, R. R. *J. Organomet. Chem.* **1986**, *300*, 249. (b) Schaverien, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2771. (c) Murdzek, J. S.; Schrock, R. R. *Organometallics* **1987**, *6*, 1373.

[3] Krouse, S. A.; Schrock, R. R.; Cohen, R. E. *Macromolecules* **1987**, *20*, 903.

[4] Schrock, R. R.; Feldman, J.; Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1987**, *20*, 1169.

[5] For other recent examples of alkoxide-based olefin metathesis catalysts see ref 6.

[6] (a) Kress, J.; Wesolek, M.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1982**, 514. (b) Kress, J.; Osborn, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6346. (c) Quignard, F.; Leconte, M.; Basset, J.-M. *J. Chem. Soc., Chem. Commun.* **1985**, 1816. (d) Idem. *J. Mol. Catal.* **1985**, *28*, 27.

[7] Murdzek, J. S.; Schrock, R. R. *Macromolecules* **1987**, *20*, 2640.

[8] (a) Ivin, K. J. *Olefin Metathesis*; Academic: London, 1983. (b) Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring-Opening Polymerization of Cyclo-Olefins*, 2nd ed.; Wiley-Interscience: New York, 1985.

[9] Rupprecht, G. A.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6236.

[10] Rocklage, S. M.; Fellmann, J. D.; Rupprecht, G. A.; Messerle, L. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 1440.

[11] Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.

[12] (a) Schrock, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 5399. (b) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (c) Clift, S. M.; Schwartz, J. *J. Am. Chem. Soc.* **1984**, *106*, 8300. (d) Hartner, F. W., Jr.; Schwartz, J.; Clift, S. M. *J. Am. Chem. Soc.* **1983**, *105*, 640. (e) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270. (f) Stille, J. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 855.

[13] (a) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733. (b) Kress, J.; Osborn, J. A.; Greene, R. M. E.; Ivin, K. J.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* **1985**, 874. (c) Kress, J.; Osborn, J. A.; Greene, R. M. E.; Ivin, K. J.; Rooney, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 899.

0002-7863/88/1510-4964$01.50/0

Table I. NMR Data for the Alkylidene Ligands in Tantalum Alkylidene Complexes of the Type $Ta(CHR)X_3(S)^a$

compd	CHR	X	S	δ H_α	δ C_α	J_{CH}
1	CH-*t*-Bu	DIPP	THF	5.73	227.1	95
2	CH-*t*-Bu	DIPP	py	6.29	231.2	96
3	CH-*t*-Bu	DMP	THF	6.93	237.4	107
4	CH-*t*-Bu	DMP	py	7.51	241.9	107
5	CH-*t*-Bu	TIPT	THF	c	251.9[b]	76
6	CH-*t*-Bu	TIPT	py	4.09	252.4	94
8	CHPh	DIPP	THF	8.49	221.1	114
9	$CHSiMe_3$	DIPP	THF	7.73	210.6	102
16	CHR[d]	DIPP	THF	7.69[b]		

[a] Solvent = C_6D_6 and T = 25 °C unless otherwise noted. [b] THF-d_8. [c] Not observed. [d] R = $(C_5H_8)CH{=}CH$-*t*-Bu.

wanted to compare various other supporting ligand systems with alkoxides in order to uncover major differences that might be useful in controlling metathesis activity. In this paper we report the preparation and a comparison of the reactivity of complexes of the type Ta(CH-*t*-Bu)X_3(THF) where X is a bulky phenoxide or benzenethiolate ligand. We have found that differences between phenoxide and benzenethiolate systems are dramatic; the choice determines both activity and mechanism. Some of these results have been reported in preliminary form.[14]

Results

Preparation and Wittig-like Reactions of DIPP, DMP, and TIPT Neopentylidene Complexes. Yellow Ta(CH-*t*-Bu)$(DIPP)_3$(THF) (**1**; eq 1; DIPP = 2,6-diisopropylphenoxide) is formed in high yield upon treating isolated Ta(CH-*t*-Bu)$(THF)_2Cl_3$[9] with 3 equiv of LiDIPP. It also can be prepared from Ta(CH-*t*-Bu)$(THF)_2Cl_3$ that has been generated in situ in ether by addition of excess THF to $Ta(CH_2$-*t*-$Bu)_2Cl_3$, although yields are comparable to those employing isolated Ta(CH-*t*-Bu)$(THF)_2Cl_3$ only when the reaction is performed on a small scale (<5 g). Ta(CH-*t*-Bu)$(DIPP)_3$(THF) appears to be stable as a solid (under dinitrogen), but it decomposes slowly over a period of several days in C_6D_6. We have not been able to remove THF from **1** in the solid state in vacuo at 25 °C, and it begins to decompose when heated. An analogous pyridine adduct (**2**; eq 2) is easily prepared by treating **1** with several equivalents of pyridine. Note that Ta(CH-*t*-Bu)(O-*t*-$Bu)_3$, the only other example of a Ta(CH-*t*-Bu)$(OR)_3$ complex, is base-free, could not be isolated as a solid, and is unstable in solution.[10]

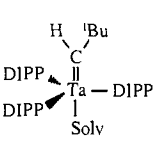
$$\mathrm{Ta(CH\text{-}\mathit{t}\text{-}Bu)(THF)_2Cl_3 + 3LiX \rightarrow 3LiCl + Ta(CH\text{-}\mathit{t}\text{-}Bu)X_3(THF)} \quad (1)$$

1; X = DIPP
3; X = DMP
5; X = TIPT

$$\mathrm{Ta(CH\text{-}\mathit{t}\text{-}Bu)X_3(THF) + pyridine \rightarrow THF + Ta(CH\text{-}\mathit{t}\text{-}Bu)X_3(py)} \quad (2)$$

2; X = DIPP
4; X= DMP
6; X = TIPT

The ^1H and ^{13}C NMR spectra of **1** and **2** show the expected neopentylidene H_α resonances at 5.73 and 6.29 ppm and C_α resonances at 227.1 and 213.2 ppm, respectively (Table I). The relatively low values for J_{CH} (95 and 96 Hz, respectively) suggest that the neopentylidene ligand in each case is distorted,[11] with a $Ta{=}C_\alpha{-}C_\beta$ angle of perhaps 150–160°. The DIPP resonances in **1** are relatively sharp at 25 °C in C_6D_6 but become broader and more complex as a sample (in toluene-d_8) is cooled. When 6 equiv of THF are added to a sample of **1** in C_6D_6, rapid exchange of coordinated THF with free THF is evident in the ^1H NMR spectrum at 25 °C. The DIPP resonances in the NMR spectrum of **2** at 25 °C are broader than they are in **1** at 25 °C. Four likely structures for **1** (we assume for now that the structure of **2** is analogous) are **A** through **D** (Solv = THF or pyridine). If the structure is of type **A** then the broadening of the DIPP signals (observed at low temperature for **1** and at 25 °C for **2**) must be the result of a slowing down of rotation of the phenyl rings about the C–O bonds for steric reasons. If the structures are of type **B**, C, or **D**, then the broadening of the DIPP resonances can be attributed largely to the fact that two types of DIPP ligands are present in the static structure where Solv is held tightly. We favor C, since the geometry about the metal is analogous to that in $[Ta(DIPP)_3(THF)]_2(\mu\text{-}N_2)$[15a] and to that in the alkylidene complex, Ta[C(Me)C(Me)=CH-*t*-Bu]$(DIPP)_3$(py).[15b]



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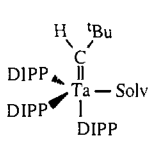

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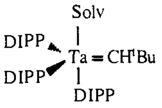
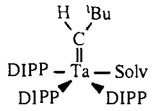


C



D

Ta(CH-*t*-Bu)$(DMP)_3$(THF) (**3**; eq 1; DMP = 2,6-dimethylphenoxide) can be prepared by treating Ta(CH-*t*-Bu)$(THF)_2Cl_3$ with 3 equiv of LiDMP, but the yield is lower than that of **1**. Surprisingly, **3** is less crystalline, more soluble in hydrocarbons, and significantly less stable in hydrocarbons than **1**. The reasons for the instability of **3** are unclear. One possibility is that the major decomposition pathway of Ta(CH-*t*-Bu)$(OAr)_3$(THF) complexes is intermolecular and that therefore they decompose more rapidly when OAr is a relatively small phenoxide. (In a related system, Rothwell and Chamberlain[16] observed formation of Ta(O-2,6-C_6H_3-*t*-$Bu_2)_2(CH_2)(CH_3)$ upon irradiation of Ta(O-2,6-C_6H_3-*t*-$Bu_2)_2(CH_3)_3$, but although methane was observed upon irradiation of $Ta(O\text{-}2,6\text{-}C_6H_3Me_2)_2(CH_3)_3$ (indicative of α-hydride abstraction), no analogous methylene species was observed. They suggested that a methylene complex forms (possibly $Ta(DMP)_2(CH_2)(CH_3)$), but that it decomposes much more rapidly than Ta(O-2,6-C_6H_3-*t*-$Bu_2)_2(CH_2)(CH_3)$.) A pyridine adduct (**4**; eq 2) can be prepared straightforwardly by treating **3** with pyridine, but like **3**, **4** does not analyze well, we believe because of some slow decomposition in the solid state. The ^1H and ^{13}C NMR spectra of **3** and **4** are similar to those for **1** and **2** (Table I). Because of the instability and poor physical properties of **3**, we have not investigated DMP complexes in as much depth as DIPP complexes.

Ta(CH-*t*-Bu)$(TIPT)_3$(THF) (**5**; eq 1; TIPT = 2,4,6-triisopropylbenzenethiolate) can be prepared by treating Ta(CH-*t*-Bu)$(THF)_2Cl_3$ with 3 equiv of LiTIPT in ether. (A byproduct that is formed in small amounts is believed to be [Ta(CH-*t*-Bu)$(TIPT)_3]_2$; details may be found in the Experimental Section.) Ta(CH-*t*-Bu)$(TIPT)_3$(py) (**6**) is prepared straightforwardly from Ta(CH-*t*-Bu)$(TIPT)_3$(THF). Both **5** and **6** are stable as solids, but **5** appears to decompose slowly in C_6D_6 at 25 °C. The ^1H NMR spectrum of **5** at 25 °C displays resonances for only one type of thiolate ligand. Since the THF ligand in **5** is demonstrably exchanging rapidly with free THF at 25 °C (by ^1H NMR), and since the ^1H NMR spectrum of **6** displays broad TIPT resonances, we believe the TIPT ligands are inequivalent in both **5** and **6**. In all structurally characterized examples of TBP complexes that contain three bulky arenethiolate ligands the thiolates are found in equatorial positions with one pointed toward one axial ligand

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[14] (a) Wallace, K. C.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1986**, *5*, 2162. (b) Wallace, K. C.; Schrock, R. R. *Macromolecules* **1987**, *20*, 448.

[15] (a) Schrock, R. R.; Wesolek, M.; Liu, A. H.; Wallace, K. C.; Dewan, J. C. *Inorg. Chem.*, in press. (b) Wallace, K. C., unpublished results. Ta[C(Me)C(Me)=CH-*t*-Bu]$(DIPP)_3$(py) is prepared by treating Ta(CH-*t*-Bu)$(DIPP)_3$(THF) with 2-butyne to give the tantalacyclobutene complex Ta(C(Me)C(Me)CH-*t*-Bu)$(DIPP)_3$, to which pyridine is added; these results will be reported separately.

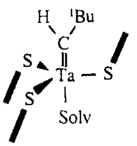
[16] Chamberlain, L. R.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **1987**, 163.

Table II. Proton and Carbon NMR Data for the TaC_3 Ring in Tantalacyclobutane Complexes[a]

compound	H_α	H_β	C_α (J_{CH})	C_β (J_{CH})
Ta[CH(Ph)CH(*t*-Bu)CH_2](DIPP)$_3$ (**7**)	3.10–2.85 (2) 2.17 (1)	1.57	81.9 (d, 133) 63.8 (t, 129)	42.9 (125)
Ta[CH($SiMe_3$)CH($SiMe_3$)CH_2](DIPP)$_3$ (**10**)	4.98 (t) 3.64 (t) 2.95 (d)	−0.33	108.1 (t, 145) 99.3 (d, 128)	6.41 (131)
Ta($CH_2CH_2CH_2$)(DIPP)$_3$ (**11a**)	3.86	0.48	96.1 (147)	−0.68 (150)
Ta($CH_2CH_2CH_2$)(DIPP)$_3$(py) (**11b**)	2.95	2.00	78.0 (120)	36.3 (129)
Ta[CH(C_5H_8)CHCH(*t*-Bu)](DMP)$_3$ (**12**)	5.21 (H_1) 3.72 (H_2)	0.84 (H_3)	132.5 (132) 135.0 (142)	30.2 or 29.0 (149[b])
Ta[CH(C_5H_8)CHCH(*t*-Bu)](DIPP)$_3$ (**13**)	5.32 (H_1) 3.88 (H_2)	0.88 (H_3)		
Ta[CH(C_5H_8)CHCH(C_5H_8CH=CH-*t*-Bu)](DIPP)$_3$ (**15**)	5.23 (H_1) 3.85 (H_2)	obscured		

[a] Solvent = C_6D_6 and T = 25 °C unless otherwise noted. [b] For 29.0 ppm resonance.

and two toward the other axial ligand ("two down, one up") with M–S–C angles of ~110°.[15a,17,18] One of the members of this list is $[Ta(S\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3(THF)]_2(\mu\text{-}N_2)$.[15a] Therefore we propose that the structures of **5** and **6** are as shown (**E**), and that rotation about Ta–S bonds is slow. (**Note Added in Proof**: This proposal has now been confirmed by an X-ray study of the diethyl sulfide derivative.) The TIPT ligands become equivalent when solvent is lost to give Ta(CH-*t*-Bu)(TIPT)$_3$, although the equilibrium between, e.g., **5** and Ta(CH-*t*-Bu)(TIPT)$_3$ must lie far toward **5** in order to slow down the formation of [Ta(CH-*t*-Bu)(TIPT)$_3$]$_2$ (see Experimental Section). Analogous results were observed in complexes of the type M(C-*t*-Bu)(TIPT)$_3$ (M = Mo or W).[19] If our proposals are correct then the basic structures of **1**(C) and **5**(E) are fundamentally different.



E

The ^1H NMR spectrum of **5** shows no obvious neopentylidene H_α resonance, while the spectrum of **6** shows an H_α resonance at 4.09 ppm. We suspect that the α proton resonance in the spectrum of **5** occurs at slightly higher fields than it does in **4** and therefore is obscured by some nearby resonances for the TIPT ligand. ^{13}C NMR spectra show a resonance for the neopentylidene α carbon atom at 251.9 ppm with J_{CH} = 76 Hz in **5** (in THF-d_8) and at 252.4 ppm with J_{CH} = 94 Hz in **6** (in C_6D_6). The low value for J_{CH} and relatively high field chemical shift for H_α suggest that the alkylidene ligand probably is more distorted in **5** and **6** than it is in **1** and **2**. Since early studies showed that neopentylidene ligands are more distorted in iodide complexes than in bromide complexes, and more in bromide complexes than in chloride complexes,[20] one might expect the neopentylidene ligand in thiolate complexes to be more distorted than in analogous phenoxide complexes.

Both the phenoxide and the thiolate neopentylidene complexes react readily with the carbonyl functionality (1–2 equiv in ether or a hydrocarbon at ~20 mM in Ta). **1** reacts with acetone rapidly at 25 °C to give 2,4,4-trimethyl-2-pentene; after 1 h the GC yield was found to be 95% of theory. The reaction between **1** and benzaldehyde gave a 96% GC yield of a 1.9:1 mixture of trans:cis Wittig products in 4 h at 40 °C. Benzophenone reacts with **1** more slowly (8 h at 40 °C, 88% yield by NMR) and *N,N*-dimethylformamide slower still (10 h at 40 °C, 95% yield by NMR, all trans). The tantalum product in all cases is a white powder that is insoluble in common solvents. We believe it must be [Ta(O)(DIPP)$_3$]$_x$ in which bridging oxo ligands form the backbone of the polymer chain. The reaction between **5** and benzaldehyde at 25 °C gives the expected Wittig products (1.0:1.0 trans:cis ratio) in 82% yield after 25 min. We presume the tantalum product is an oxo complex; under these conditions it was an orange oil and was not characterized. These Wittig-like reactions are analogous to those observed in studies involving Ta(CH-*t*-Bu)(CH_2-*t*-Bu)$_3$.[12a]

Table III. Selected Bond Distances (Å) and Angles (deg) in Ta[CH(Ph)CH(*t*-Bu)CH_2](DIPP)$_3$ (**7**)

Ta–O(11)	1.893 (13)	O(21)–Ta–O(31)	120.2 (7)
Ta–O(21)	1.820 (14)	C(41)–Ta–O(11)	90.3 (7)
Ta–O(31)	1.864 (15)	C(41)–Ta–O(21)	106.7 (7)
Ta–C(41)	2.168 (24)	C(41)–Ta–O(31)	128.8 (7)
Ta···C(42)	2.782 (24)	C(43)–Ta–O(11)	150.9 (8)
Ta–C(43)	2.188 (24)	C(43)–Ta–O(21)	96.7 (7)
C(41)–C(42)	1.593 (30)	C(43)–Ta–O(31)	89.3 (8)
C(42)–C(43)	1.473 (36)	C(43)–Ta–C(41)	64.4 (9)
Ta–C(41)–C(42)	94.2 (1.4)	C(41)–C(42)–C(43)	98.4 (18)
Ta–C(43)–C(42)	97.0 (1.5)	Ta–O(11)–C(11)	157.0 (13)
O(11)–Ta–O(21)	104.7 (6)	Ta–O(21)–C(21)	154.5 (13)
O(11)–Ta–O(31)	96.6 (6)	Ta–O(31)–C(31)	146.3 (15)

Reactions of DIPP Complexes with Acyclic Olefins. Ta(CH-*t*-Bu)(DIPP)$_3$(THF) reacts rapidly with 1 equiv of styrene to give a molecule whose ^1H and ^{13}C NMR spectra suggest that it is a tantalacyclobutane complex that contains one α and one β substituent (**7**). The α-proton resonances are found at 3.10–2.85 (area 2) and 2.17 ppm (area 1), and the β-proton resonance at 1.57 ppm (Table II). The α-carbon resonances are found at 81.9 ppm (J_{CH} = 133 Hz) and 63.8 ppm (J_{CH} = 129 Hz), and the β-carbon resonance is found at 42.9 ppm (J_{CH} = 125 Hz). In C_6D_6 at 25 °C all DIPP ligands appear to be equivalent, although the DIPP methyl groups are diastereotopic. These results are those to be expected for either Ta[CH(*t*-Bu)CH(Ph)CH_2](DIPP)$_3$ or the less logical Ta[CH(Ph)CH(*t*-Bu)CH_2](DIPP)$_3$. In either molecule a fluxional process must readily interconvert the DIPP ligands, but no plane of symmetry can be generated in the process.

An X-ray study showed that **7** is actually the less logical of the two possibilities (i.e., Ta[CH(Ph)CH(*t*-Bu)CH_2](DIPP)$_3$). The structure is of poor quality, so we cannot place too much emphasis on detailed comparisons. Bond distances and angles are listed in Table III, and a drawing of one of the two crystallographically independent molecules is provided as Figure 1. One can argue that **7** is best described as a distorted square pyramid with O(21) at the apex. The largest interligand angle is C(43)–Ta–O(11) (150.9 (8)°) followed by C(41)–Ta–O(31) (128.8 (7)°) and O(21)–Ta–O(31) (120.2 (7)°). If O(21)–Ta–O(31) were between 100 and 110 °C then the structure would be close to an ideal square pyramid. This ill-defined geometry contrasts with the fairly rigorous trigonal-bipyramidal geometry found in W[CH($SiMe_3$)CH($SiMe_3$)CH_2](NAr)[OCMe(CF_3)$_2$]$_2$ (NAr = N-

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(17) (a) Koch, S. A.; Millar, M. *J. Am. Chem. Soc.* **1983**, *105*, 3362. (b) Blower, P. J.; Dilworth, J. R.; Hutchinson, J. P.; Zubieta, J. A. *J. Chem. Soc., Dalton Trans.* **1985**, 1533. (c) Bishop, P. T.; Dilworth, J. R.; Hutchinson, J.; Zubieta, J. A. *J. Chem. Soc., Dalton Trans.* **1986**, 967. (d) Dilworth, J. R.; Hutchinson, J.; Zubieta, J. A. *J. Chem. Soc., Chem. Commun.* **1983**, 1034.

(18) (a) Walborsky, E. C.; Wigley, D. E.; Roland, E.; Dewan, J. C.; Schrock, R. R. *Inorg. Chem.* **1987**, *26*, 1615. (b) de Vries, N.; Dewan, J. C.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1988**, *27*, 1574.

(19) Murdzek, J. S.; Blum, L.; Schrock, R. R. *Organometallics* **1988**, *7*, 436.

(20) (a) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210. (b) Churchill, M. R.; Wasserman, H. J.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 1710.

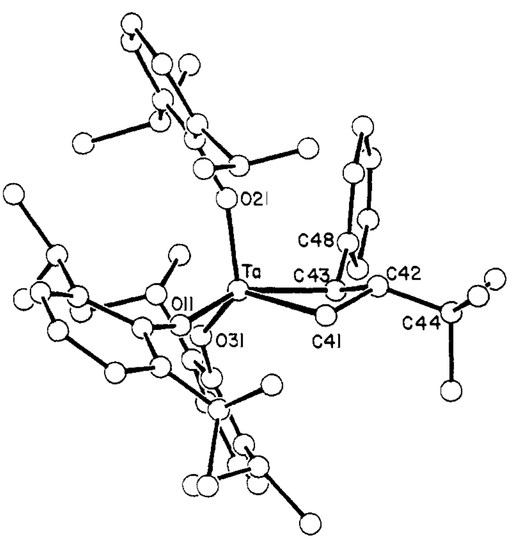


Figure 1. A view of Ta[CH(Ph)CH(*t*-Bu)CH$_2$](DIPP)$_3$ (7) (molecule 1). Spheres of arbitrary radius are employed in order to allow a clear view of the ligand system.

2,6-C$_6$H$_3$-*i*-Pr$_2$),[2b,21a] W(CH$_2$CH$_2$CH$_2$)(NAr)[OC(CF$_3$)$_2$(CF$_2$CF$_2$CF$_3$)]$_2$,[21a] and closely related Ta[CH(C$_5$H$_8$)CHCH(*t*-Bu)](DIPP)$_3$ (see later) where the MC$_3$ ring occupies equatorial coordination sites. Square-pyramidal structures are found occasionally in tantalum(V) chemistry.[21b,c] The reason why the structure of 7 is relatively far from an ideal is unclear at this point. It is interesting to speculate, however, that 7 might more readily lose an olefin than an analogous TBP complex, and since these molecules are so fluxional, that intermolecular packing forces may dictate the structure. Since we now know that square-pyramidal tungstenacyclobutane complexes are sometimes the most stable form[21d] (one has been characterized structurally), a square-pyramidal structure for a metallacyclobutane complex perhaps should always be considered as a distinct alternative to a trigonal-bipyramidal structure in metathetical reactions. We will come back to some of these points later.

The Ta–O and Ta–C bond lengths in the structure of 7 are not unusual, although the shortest Ta–O distance (1.820 (14) Å) is marginally shorter than the Ta–O distance (1.836 (4) Å) reported by Rothwell for Ta(O-2,6-C$_6$H$_3$-*t*-Bu$_2$)$_2$Cl$_3$ and said to be the shortest Ta(V)–aryl oxide bond to date.[21c] The Ta–O–C angles also are not unusual, the range being 146.3 (15) to 157.0 (13)°, characteristic of alkoxides bound to relatively electron-deficient early transition metals.[22] The Ta–C bond lengths are at the lower end of the range for Ta–C single bonds (2.15–2.25 Å).

The TaC$_3$ ring is slightly bent with the α (phenyl) and β-(*tert*-butyl) substituents trans to one another. The dihedral angle between the C(41)/C(42)/C(43) and Ta/C(41)/C(43) planes of 25.2° places the α and β substituents in pseudoequatorial positions.[23] The long C–C bonds within the TaC$_3$ ring also are characteristic of (all carbon) metallacycles of d^0 metals,[24b,d] although the large esd's in this particular case prevent our knowing whether these bond lengths fall in the upper or lower end of the range. One potentially important feature of this MC$_3$ ring system relative to those found in TBP complexes is that it is elongated in the Ta···C$_\beta$ direction, i.e., C(41)–Ta–C(43) = 64.4 (9)°, Ta–C(41)–C(42) = 94.2 (14)°, Ta–C(43)–C(42) = 97.0 (15)°, C(41)–C(42)–C(43) = 98.4 (18)°, and Ta···C(42) = 2.782 (24) Å. These values are compared in Figure 2 with those found in the TaC$_3$ ring in Ta[CH(C$_5$H$_8$)CHCH(*t*-Bu)](DIPP)$_3$ (see later) and the WC$_3$ ring in W[CH(SiMe$_3$)CH(SiMe$_3$)CH$_2$](NAr)[OCMe(CF$_3$)$_2$]$_2$.[2b,21a] We ascribe this elongated ring shape to the fact that 7 is *not* a trigonal-bipyrammidal species; a smaller C$_\alpha$–Ta–C$_{\alpha'}$ angle and longer Ta···C$_\beta$ distance would be expected if the ring carbons occupy basal positions in a square pyramid than if they occupy equatorial positions in a trigonal bipyramid.

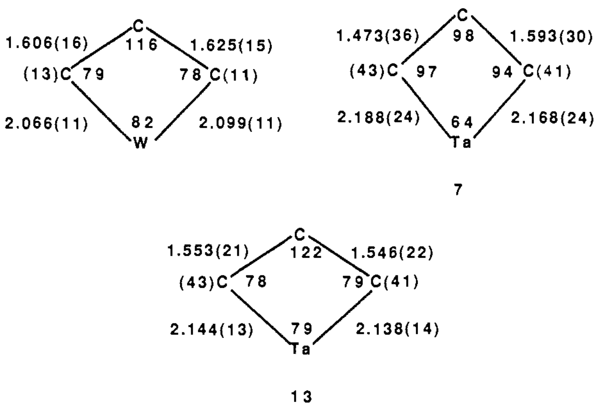
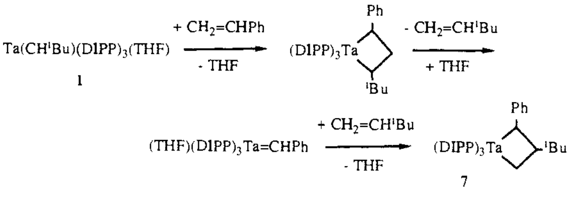


Figure 2. A comparison of metallacyclobutane rings in W[CH(SiMe$_3$)CH(SiMe$_3$)CH$_2$](N-2,6-C$_6$H$_3$-*i*-Pr$_2$)[OCMe(CF$_3$)$_2$]$_2$, 7, and 13.

Most likely the initial tantalacycle that forms when 1 reacts with styrene loses *tert*-butylethylene, which then adds back to the incipient benzylidene complex to give 7 (eq 3). If we ignore electronic factors then we might predict this result on steric grounds alone, assuming that formation of a tantalacycle is readily reversible in the presence of THF, i.e., the two ring substituents should be located in pseudo-equatorial positions as far from the bulky alkoxide ligands as possible (on α and β carbon atoms), and the more bulky of the two should reside on the β-carbon atom.[24a]



(3)

The addition of THF to 7 yields Ta(CHPh)(DIPP)$_3$(THF) (**8**) and *tert*-butylethylene, reversibly (eq 4). In a typical reaction **7** and **8** are in equilibrium in C$_6$D$_6$ in the presence of several

$$\underset{\mathbf{7}}{\mathrm{Ta[CH(Ph)CH(}t\mathrm{\text{-}Bu)CH_2](DIPP)_3}} \underset{-\mathrm{THF}\,+\,\mathrm{CH_2{=}CH\text{-}}t\mathrm{\text{-}Bu}}{\overset{+\mathrm{THF}\,-\,\mathrm{CH_2{=}CH\text{-}}t\mathrm{\text{-}Bu}}{\rightleftharpoons}} \underset{\mathbf{8}}{\mathrm{Ta(CHPh)(DIPP)_3(THF)}} \quad (4)$$

equivalents of THF. Ta(CHPh)(DIPP)$_3$(THF) can be isolated by treating **1** with styrene in the presence of a large excess of THF, followed by removal of *tert*-butylethylene in vacuo. The chemical shift of H$_\alpha$ in **8** (8.49 ppm) is substantially greater than that in **1** (5.73 ppm) and J_{CH} (114 Hz) is the largest of any molecule of this type (Table I).

Ta(CHCMe$_3$)(DIPP)$_3$(THF) reacts with 1 equiv of vinyltrimethylsilane to give Ta(CHSiMe$_3$)(DIPP)$_3$(THF) (**9**) in high yield (eq 5). The formation of **9** is significantly *accelerated* when the reaction is performed in the presence of excess THF. We

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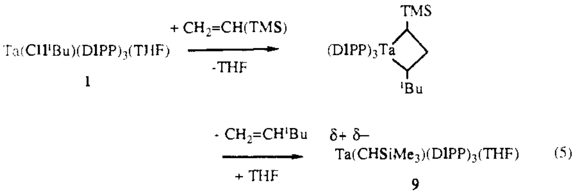
(21) (a) Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423. (b) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 2575. (c) Chamberlain, L. R.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Chem. Soc., Dalton Trans.* **1987**, 155. (d) Feldman, J., unpublished results.

(22) (a) Chisholm, M. H. *Polyhedron* **1983**, *2*, 681 and references therein. (b) Chisholm, M. H.; Rothwell, L. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R., McCleverty, J. A., Eds.; Pergamon: New York, 1987; Vol. 2.

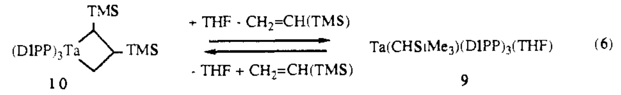
(23) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982, Vol. 8, Chapter 54.

(24) (a) Straus, D. A.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1658. (b) Lee, J. B.; Gajda, G. J.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 7358. (c) Erker, G.; Czisch, P.; Krüger, C.; Wallis, J. M. *Organometallics* **1985**, *4*, 2059. (d) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 7357. (e) Seetz, J. W. F. L.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 248. (f) Seetz, J. W. F. L.; Van de Heisteeg, B. J. J.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Mol. Catal.* **1985**, *28*, 71.

postulate that vinyltrimethylsilane in effect displaces THF from Ta(CHR)(DIPP)$_3$(THF) and that olefin is ejected from the intermediate tantalacycle when it is attacked by THF (eq 5). It is not unexpected to find that **9** is favored over **1**, a result that would be consistent with the well-known ability of silicon to stabilize an adjacent negative charge on the alkylidene α-carbon atom.



When **9** is treated with one or more additional equivalents of vinyltrimethylsilane, or when **1** is treated with several equivalents of vinyltrimethylsilane over a period of several hours, colorless Ta[CH(SiMe$_3$)CH(SiMe$_3$)CH$_2$](DIPP)$_3$ (**10**) can be isolated in good yield. Addition of THF to **10** yields solutions that contain both **9** and **10**, suggesting that the equilibrium shown in eq 6 is readily attained. (A ^{1}H NMR spectrum of a C$_6$D$_6$ solution containing **10** ($\sim$50 mM) and 4 equiv of THF showed a mixture of 84% **10** to 16% **9** at 25 °C and 73% **10** to 27% **9** at 50 °C.)



^{1}H and ^{13}C NMR data suggest that the substituents in **10** are located on α and β ring carbon atoms (Table II), probably mutually trans to one another, as found in W[CH(SiMe$_3$)CH(SiMe$_3$)CH$_2$](N-2,6-C$_6$H$_3$-*i*-Pr$_2$)[OCMe(CF$_3$)$_2$]$_2$.[2b,21a] The ^{1}H NMR spectrum of **10** displays broad resonances for the DIPP ligands, but the ring protons give rise to relatively sharp signals at 4.98 (t, 1), 3.64 (t, 1), 2.95 (d, 1), and -0.33 (m, 1). A ^{13}C NMR spectrum displayed resonances for the ring carbons at 108.1 (t, C$_\alpha$), 99.3 (d, C$_\alpha$), and 6.41 (d, C$_\beta$) ppm. ^{1}H NMR decoupling experiments provided further support for an α,β substituted ring. The 4.98- and 3.64-ppm resonances can be ascribed to inequivalent α methylene protons, the -0.33-ppm resonance to β C*H*(TMS) and the 2.95-ppm resonance to α C*H*(TMS).

Close examination of NMR spectra of **10** suggests that a small amount of the α,α' substituted isomer ($\sim$15%) may be present. (A ^{1}H NMR multiplet at 3.93 ppm can be assigned to α C*H*SiMe$_3$ and a ^{13}C NMR doublet at 106.2 ppm (J_{CH} = 122 Hz) to α *C*HSiMe$_3$.) In the related tungsten complex, W[CH(SiMe$_3$)CH(SiMe$_3$)CH$_2$](N-2,6-C$_6$H$_3$-*i*-Pr$_2$)[OCMe(CF$_3$)$_2$]$_2$,[2b,21a] only the α,β isomer is observed, and on the basis of a crystal structure it could be argued that the α,α' isomer should be unfavorable for steric reasons in that case. The DIPP ligands in **10**, however, could be more tolerant of the sterically demanding α,α' disubstitution since the molecule is not stereochemically rigid and may not be rigorously trigonal bipyramidal.

Ta(CHCMe$_3$)(DIPP)$_3$(THF) reacts virtually instantaneously with 30 psi of ethylene to give colorless Ta(CH$_2$CH$_2$CH$_2$)(DIPP)$_3$ (**11a**) and 0.90 equiv of *tert*-butylethylene (eq 7). Ta[CH(*t*-Bu)CH$_2$CH$_2$](DIPP)$_3$, the presumed intermediate in this reaction, has never been observed under these conditions. In the ^{1}H NMR

$$\mathrm{Ta(CHCMe_3)(DIPP)_3(THF) + C_2H_4 \xrightarrow[-THF]{} \underset{\mathbf{11a}}{Ta(CH_2CH_2CH_2)(DIPP)_3} + \mathit{t}\text{-}BuCH{=}CH_2} \quad (7)$$

spectrum of **11a** (in C$_6$D$_6$) the α-proton resonance consists of a doublet of doublets at 3.86 ppm, and the β-proton resonance as a multiplet at 0.48 ppm. A ^{13}C NMR spectrum shows a resonance for the α ring carbon atom at 96.1 ppm (J_{CH} = 147 Hz) and for the β ring carbon atom at -0.68 ppm (J_{CH} = 150 Hz). In both ^{1}H and ^{13}C NMR spectra, only a single set of DIPP ligand resonances is observed at 25 °C.

THF does not react readily with **11a**, although pyridine does react readily with **11a** to give what appears to be an adduct, Ta(CH$_2$CH$_2$CH$_2$)(DIPP)$_3$(py) (**11b**). **11b** is the only example of a base adduct of a tantalacyclobutane complex that we have observed. Similar adducts may be intermediates in reactions of various other tantalacycles with donor ligands, or in reactions of alkylidene complexes with olefins, although it is impossible to predict how stable such intermediates might be, and therefore whether they should be included as part of a mechanism. Substitution of the TaC$_3$ ring is likely to significantly increase steric crowding about the metal, perhaps to the extent that a six-coordinate THF adduct would have virtually no stability.

The NMR data for **11b** need to be looked at closely, since we now have good reason to believe that ^{1}H and ^{13}C NMR chemical shifts (and probably also CH coupling constants) are sensitive to the overall structure of the metallacyclobutane complex, and in particular to the detailed structure of the metallacyclic ring, i.e., whether the metal$\cdots$C$_\beta$ distance is "long" (as in **7**) or "short" (as in trigonal-bipyramidal metallacyclobutane complexes). A ^{1}H NMR spectrum of **11b** at 25 °C (C$_6$D$_6$) displays resonances for the α protons at 2.95 ppm and the β protons at 2.00 ppm. Since only one set of resonances is observed when free pyridine is added to the sample we believe that pyridine is lost readily from **11b** to give **11a**. Upon heating a sample of **11b** the α-proton resonance shifts downfield and the β-proton resonance shifts upfield, further suggesting that **11b** is in equilibrium with **11a** and pyridine. Unfortunately, spectra at low temperatures were too complex to allow us to conclude whether **11b** is a single isomer or not, and if it is a single isomer, what its structure might be. Nevertheless, the fact that the average α and average β proton resonances in **11b** are not as disparate as they are in **11a** we believe is consistent with a now higher coordinate metallacycle in which the metal$\cdots$C$_\beta$ distance is significantly longer and the C$_\alpha$–M–C$_\alpha$ angle is significantly smaller than it is in five-coordinate, trigonal-bipyramidal species. Analogous trends are observed in the ^{13}C NMR spectra of **11b**. The α-carbon resonance is found at 78.0 ppm (J_{CH} = 120 Hz) and the β-carbon resonance at 36.3 ppm (J_{CH} = 129 Hz), in sharp contrast to what is found for **11a** (96.1 and -0.68 ppm, respectively; Table II). Neither **11a** nor **11b** is stable in solution over an extended period of time. They (especially **11b**) slowly decompose to give dark solutions in which no product has yet been identified. In one instance in the process of collecting ^{13}C NMR data on **11b** we observed a triplet resonance at 217.4 ppm with J_{CH} = 135 Hz that almost certainly can be ascribed to a methylene complex, perhaps Ta(CH$_2$)(DIPP)$_3$(py)$_2$ (cf. δ C$_\alpha$ = 252.2 ppm with J_{CH} = 145 Hz in W(CH$_2$)(N-2,6-C$_6$H$_3$-*i*-Pr$_2$)[OCMe(CF$_3$)$_2$]$_2$(PMe$_3$)[21a]). However, this species also decomposed readily, and no attempt was made to isolate it.

Ta(CHCMe$_3$)(DIPP)$_3$(THF) reacts rapidly with propylene or 1-butene to give nearly colorless solutions initially. However, these solutions begin to darken rapidly upon workup. We have tried to identify products in situ, but so far without success. We believe that tantalacyclobutane complexes form, but alkylidene complexes of the type Ta(CHR)(DIPP)$_3$(THF) in which the alkylidene ligand contains β hydrogen atoms probably are unstable. Addition of excess *cis*-2-pentene to **1** in ether or a hydrocarbon results in a lightening of the solution and rapid metathesis (100 equiv to equilibrium in <15 min). However, addition of a second aliquot of *cis*-2-pentene showed that the catalyst was no longer active, further evidence that intermediate alkylidene complexes are unstable. These findings are analogous to those in earlier systems employing phosphine-substituted niobium and tantalum complexes.[10] It is also possible that intermediate tantalacyclobutane rings rearrange to olefins,[10] although we think this a less likely possibility in view of what appears to be the relatively high stability of the tantalacyclobutane complexes that we have isolated so far. The activity of the Ta(CHR)(DIPP)$_3$(THF) system qualitatively is significantly greater than the activity of the phosphine-substituted catalysts.[10] One possible explanation is that Ta(CHR)(DIPP)$_3$(THF) complexes actually *are* more stable toward rearrangement to an olefin than tantalum alkylidene complexes that contain phosphine ligands.

Ta(CH-*t*-Bu)(DMP)$_3$(THF) does not react cleanly with ethylene. No products could be isolated, and a ^{1}H NMR spectrum

Table IV. Products of the Reactions of Tantalacyclobutane Complexes with Organic Carbonyls

compd	carbonyl	conditions	insertion (%)	Wittig (% by NMR)
7	1.5 Me_2CO	C_6D_6, 25 °C, 60 min	*a*	86 ($Me_2C{=}CHPh$) 91 (t-$BuCH{=}CH_2$)
11a	1.5 Me_2CO	C_6D_6, 25 °C, 60 min	100 (NMR)	*b*
11a	1.5 Me_2CO	C_6D_6, 60 °C, 30 min	75 (NMR)	19 ($Me_2C{=}CH_2$)
11a	1.0 t-BuCHO	ether, 25 °C, 12 h[c]	100 (NMR)	*b*
11a	1.5 Ph_2CO	C_6D_6, 25 °C, 60 min	45 (NMR)	46 ($Ph_2C{=}CH_2$)
11a	1.5 Ph_2CO	C_6D_6, 60 °C, 30 min	24 (NMR)	71 ($Ph_2C{=}CH_2$)
11b	1.5 Me_2CO	ether, 25 °C, 45 min[c]	100 (NMR)	*b*
11b	1.0 PhCHO	ether, 25 °C, 60 min[c]	80 (isolated)	*b*
11b	1.2 t-BuCHO	C_6D_6, 25 °C, 30 min	100 (NMR)	*b*
11b	1.5 Ph_2CO	C_6D_6, 70 °C, 35 min	<6 (NMR)	86 ($Ph_2C{=}CH_2$)

[a] No insertion products observed by NMR. [b] No Wittig products observed. [c] Reaction was initiated at −30 °C.

of the crude reaction mixture showed many unidentifiable resonances. We speculate that DMP ligands probably are small enough to behave as donors in intermolecular reactions that result in loss of ethylene and subsequent decomposition of the incipient methylene complex.

Reactions of TIPT Complexes with Acyclic Olefins. The TIPT complex **5** *does not react* with ordinary olefins (e.g., *cis*-3-hexene) over a period of several hours at 25 °C. Likewise, **5** does not metathesize 2-pentenes at 25 or 50 °C. A similar lack of reactivity (relative to the corresponding phenoxide species) has been documented for some benzenethiolate alkylidyne complexes of molybdenum and tungsten.[19] The reasons why **5** is relatively unreactive toward ordinary olefins may not be straightforward (see Discussion). Lack of reactivity of TIPT complexes with acyclic olefins is a disadvantage to the extent that it prevents us from preparing other types of alkylidene complexes from **5**. However, this lack of reactivity can be turned into an asset, as we shall see later when we discuss reactions of neopentylidene complexes with norbornene.

Reactions of Metallacycles with the Carbonyl Functionality. Since tantalacyclobutane complexes react with THF or pyridine to give alkylidene complexes, we thought that they probably would react with organic compounds that contain the carbonyl functionality to give Wittig products via an incipient tantalum alkylidene complex.[12] This turns out to be the case, but the situation is complicated by direct reaction of the carbonyl compound with the tantalacycle to give oxytantalacyclohexane complexes via insertion of the organic carbonyl into a tantalum–carbon bond. In this section we discuss various examples of reactions of tantalacycles with carbonyl compounds. We have not explored this subject deeply since at this stage we are interested primarily in determining trends, and in particular, in determining what carbonyl compound yields Wittig products most efficiently.

Upon exploring reactions involving **11a** and **11b** (Table IV) we noticed that they react similarly with ketones and aldehydes, a result that suggests that the reactive species is the base-free tantalacycle (eq 8; DIPP ligands omitted). Reaction of the base-free tantalacycle with the carbonyl compound via path A then competes with loss of ethylene and reaction of the incipient methylene complex (path B). We must consider the possibility that path B also proceeds under some circumstances via a carbonyl adduct of the tantalacycle, i.e., loss of ethylene is promoted by coordination of the carbonyl. For benzophenone the reaction follows mostly path B, while for acetone, benzaldehyde, or pivaldehyde the reaction proceeds primarily via path A. Most tantalacyclohexane insertion products (the exception being that formed from benzophenone) are quite stable thermally, showing little, if any, decomposition after being heated overnight in C_6D_6 at 70 °C. We are assuming that the insertion reaction proceeds so as to place the oxygen in the ring next to the metal, and that the carbonyl carbon atom is still bound to that oxygen. Related insertion reactions have been reported previously,[24c,e,f,25] and one X-ray study[25] shows that the oxygen is bound to zirconium. Proton and carbon NMR data for oxytantalacyclohexane complexes can be found in the Experimental Section.

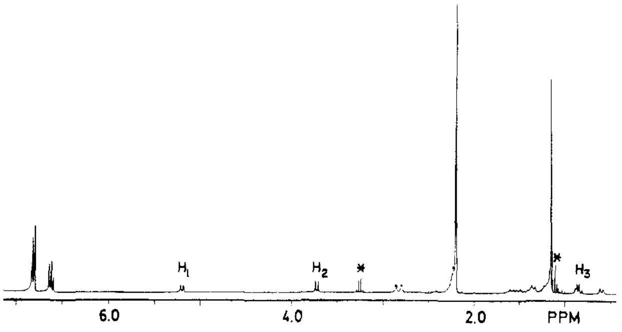
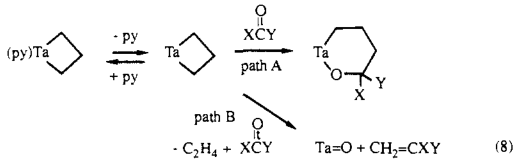


Figure 3. The ^1H NMR spectrum of $Ta[CH(C_5H_8)CHCH(t\text{-}Bu)](DMP)_3$ (**12**) in C_6D_6 (* = diethyl ether).

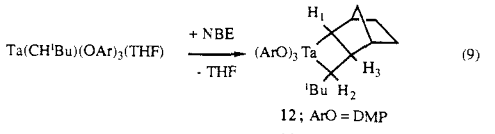


(8)

The second trend that we have observed for reactions involving **11a** and **11b** is that at higher temperatures more Wittig products are observed (Table IV), consistent with a greater entropic contribution to the temperature dependence of the rate constant for path B.

Third, one might predict that an olefin is lost more readily from a more crowded disubstituted tantalacycle and that therefore little or no insertion chemistry of such tantalacycles should be observed. Indeed, **7** reacts with acetone at 25 °C to give ~90% Wittig products, with no sign of any insertion reaction. We will show later that a trisubstituted tantalacycle reacts even with benzaldehyde to give only the Wittig product.

Isolable Tantalacyclobutane Complexes Prepared by Reaction of Ta(CH-*t*-Bu)(OAr)$_3$(THF) (OAr = DIPP or DMP) with Norbornene. Addition of 1 equiv of norbornene at −30 °C to **3** in ether produces a yellow solution from which a yellow oil is obtained by removing all solvent in vacuo. Very pale yellow microcrystals that are extremely soluble in pentane can be obtained in 31% yield from concentrated solutions at −30 °C. The NMR spectra of the oil and the crystals are identical except for minor impurity peaks in the former. A ^1H NMR spectrum of the crystals is shown in Figure 3. It is consistent with the product being the tantalacyclobutane complex **12** (eq 9; ring stereochemistry unknown). The most characteristic features of the spectrum are



(9)

12; ArO = DMP
13; ArO = DIPP

the resonances at δ 5.21 (d), 3.72 (d), and 0.84 (t), assignable

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[25] Tikkanen, W. R.; Petersen, J. L. *Organometallics* **1984**, *3*, 1651.

Table V. Selected Bond Distances (Å) and Angles (deg) in $Ta[CH(C_5H_8)CHCH(t\text{-}Bu)](DIPP)_3$ (**13**)

Ta-O(1)	1.917 (8)	O(2)-Ta-O(3)	87.5 (3)
Ta-O(2)	1.904 (9)	C(41)-Ta-O(1)	89.2 (5)
Ta-O(3)	1.909 (8)	C(41)-Ta-O(2)	136.1 (5)
Ta-C(41)	2.138 (14)	C(41)-Ta-O(3)	93.1 (5)
Ta···C(42)	2.382 (16)	C(43)-Ta-O(1)	95.3 (4)
Ta-C(43)	2.144 (13)	C(43)-Ta-O(2)	145.1 (6)
C(41)-C(42)	1.546 (22)	C(43)-Ta-O(3)	88.9 (4)
C(42)-C(43)	1.553 (21)	C(43)-Ta-C(41)	78.7 (7)
Ta-C(41)-C(42)	78.8 (9)	C(41)-C(42)-C(43)	122.4 (13)
Ta-C(43)-C(42)	78.4 (8)	Ta-O(1)-C(11)	161.0 (8)
O(1)-Ta-O(2)	88.1 (3)	Ta-O(2)-C(21)	159.3 (8)
O(1)-Ta-O(3)	175.5 (3)	Ta-O(3)-C(31)	163.7 (7)

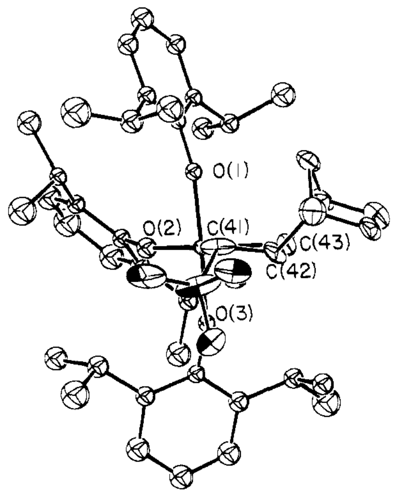


Figure 4. A view of $Ta[CH(C_5H_8)CHCH(t\text{-}Bu)](DIPP)_3$ (**13**).

to protons H_1, H_2, and H_3, respectively. (The H_1 and H_2 resonances can be distinguished on the basis of the reaction of **13** with norbornene-*2,3-d*$_2$; see later.) In a similar titanacyclobutane complex, $Cp_2Ti[CH(R)CH(C_5H_8)CH]$ ($R = Me_2CCH{=}CH_2$), these signals are found at 3.72, 2.63, and 0.08 ppm.[13a] The ^{13}C NMR spectrum of **12** shows signals for all 15 carbon atoms, the tantalacycle ring carbon resonances being observed at δ 132.5, 135.0, and 29.0 or 30.2 (Table II; cf. 110.9, 104.4, and 24.2 ppm in $Cp_2Ti[CH(R)CH(C_5H_8)CH]$[13a]).

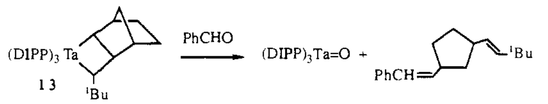
An analogous reaction between **1** and norbornene yields more crystalline, colorless **13** in 64% isolated yield (recrystallized from ether). NMR spectra of **13** are analogous to those of **12** as far as the TaC_3 ring is concerned (Table II). However, the DIPP resonances are broad, characteristic of an intermediate rate of a fluxional process in a tantalacyclobutane complex in which they are not all equivalent. **13** is stable as a solid at 25 °C, but it decomposes to the extent of 10–20% after 1 day in C_6D_6.

An X-ray structure study showed **13** to have a geometry close to trigonal bipyramidal (Figure 4; Table V) with O–Ta–O angles of only slightly less than 90° or 180°. All of the Ta–O bond lengths are similar (~1.91 Å; Table V) as are all Ta–O–C angles (159–164°). All values are within the range of metal–oxygen and metal–O–C angles that are normally observed for early transition metal phenoxide complexes.[22] The two ring α carbon atoms lie essentially in the equatorial plane with C_α–Ta–O_{ax} bond angles of near 90° and C_α–Ta–O_{eq} bond angles of 136.1 (5)° and 145.1 (6)°.

The tantalacyclic ring system in **13** is remarkably similar to the tungstacyclic ring system in $W[CH(SiMe_3)CH(SiMe_3)CH_2](N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCMe(CF_3)_2]_2$ (Figure 2).[21a] The main difference between the ring system in **13** and that in **7** is that the ring in **7** is much more elongated (as we mentioned earlier); the Ta···C_β bond distance in **7** is 2.782 (24) Å, while it is 2.382 (16) Å in **13**. We assume, therefore, that the ring systems in $W[CH(SiMe_3)CH(SiMe_3)CH_2](N\text{-}2,6\text{-}C_6H_6\text{-}i\text{-}Pr_2)[OCMe(CF_3)_2]_2$ and **13** are characteristic of complexes in which the overall structure is close to trigonal bipyramidal. There are three other tungstacyclobutane complexes that have been structurally elucidated; two are trigonal bipyramids and have ring systems closely analogous to that found in **13**,[21a] and the third is a square pyramid with a ring closely analogous to that found in **7**.[21d] The ring in **13** is bent less (~15.5°) than the ring in **7**, perhaps in part because the geometry about the C(42)–C(43) bond is necessarily cis.

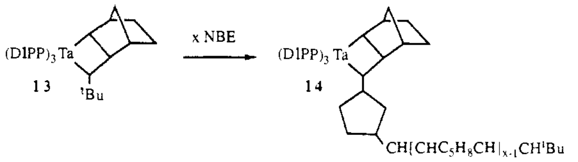
Figure 5. The ^1H NMR spectrum of **14** in C_6D_6 at 50 °C (* = mesitylene internal standard).

The trisubstituted tantalacycle **13** reacts with benzaldehyde to give the expected Wittig products, as shown in eq 10 (reaction with 3 equiv of benzaldehyde is complete within ~30 min at 50 °C in C_6D_6 at a concentration of **13** of ~50 mM). The observed pattern for the olefinic proton resonance on the phenyl-substituted end is consistent with a 2.7/1.0 trans/cis mixture of isomers, based on spin simulation experiments performed with the analogous complex **14** (see below). We cannot tell what the double bond geometry is at the other end by NMR; we presume it is all trans since the *tert*-butyl group is trans to the norbornane ring in **13**.



(10)

Polymerization of Norbornene by DIPP Complexes. When **13** is heated with excess NBE in C_6D_6, resonances characteristic of polynorbornene (~55% trans) are observed, and resonances for the tantalacycle **14** appear (H_1 at 5.22 ppm and H_2 at 3.85 ppm) as those for **13** disappear (eq 11; it should be understood that there is the normal distribution of chain lengths about $x - 1$). The reaction can be taken to completion (Figure 5) with no sign of degradation of the catalyst. The polymerization can be stopped by cooling the reaction mixture (from 50 to 25 °C). After reheating it to 50 °C the polymerization resumes at the same rate as before. In the absence of NBE **14** decomposes to the extent of ~5 to ~10% after 24 h at 25 °C, but in the presence of NBE it does not decompose to any extent observable by NMR (<5%) in the same time period. In the absence of NBE the cis double bonds in the polymer isomerize slowly. For example, in reactions in which x = 10–20 the trans content increases from 55% to ~65% in 5 days in C_6D_6. We assume that isomerization results from metathesis reactions and that either some decomposition product or the alkylidene formed by ring-opening of **14** is the catalyst. (As we shall show later the polydispersity of the polynorbornene increases with time, characteristic of metathesis reactions involving the double bonds in the polymer chain.) Polynorbornene is readily cleaved from the metal center in **14** by treatment with carbonyl compounds, preferably benzaldehyde. Addition of 3 equiv of benzaldehyde to **14** at 65 °C in C_6D_6 results in essentially quantitative formation of $PhCH(CHC_5H_8CH)_{x+1}CH\text{-}t\text{-}Bu$ within 20 min. The stereochemistry at the site of cleavage (i.e., in the phenyl-substituted double bond) is 68% trans and 32% cis, based on spin simulation studies (Figure 6; details in Experimental Section).



(11)

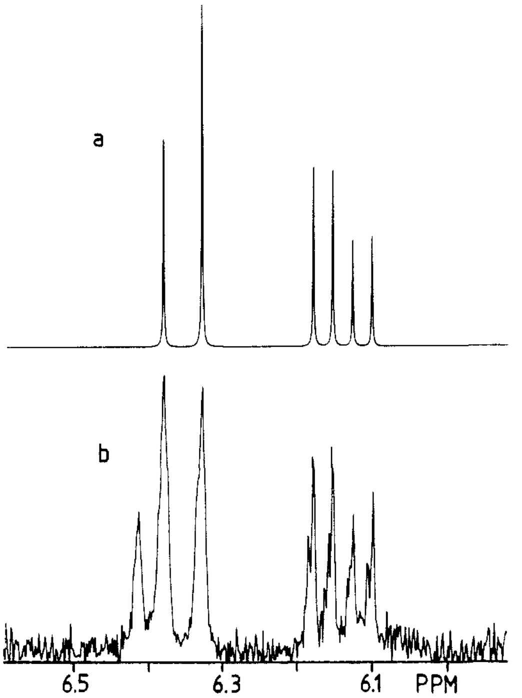


Figure 6. (a) Calculated spectrum for the olefinic protons in the *trans*-phenyl-substituted portion of the Wittig product produced upon treating **14** with benzaldehyde. (b) Experimental spectrum for the olefinic protons in the phenyl-substituted cap in the Wittig product produced upon treating **14** with benzaldehyde. (See Experimental Section for details.)

Table VI. The Results of GPC Analysis of Polynorbornenes

run no.	catalyst	equiv of NBE	M_n(uncorr)	M_w/M_n
1	**13**	100	22 000	1.63
2	**13**	200	48 000	1.66
3	**13**	500	127 000	1.73
4[a,b]	**13**	200	32 100	1.04
5[d]	**13**	150	31 500	1.95
6	**5**	50	13 200	1.08
7	**5**	100	26 200	1.09
8	**5**	200	58 800	1.10
9	**6**	95	18 800	1.07
10	**12**	100	10 700	2.71
11	**1**	200	146 000	4.41
12[c]	**5**	200	59 100	1.05
13[c]	**5**	200	57 600	1.07

[a] The reaction was taken to ~75% completion. [b] The polymer with the expected molecular weight made up ~94% of the sample; ~6% of a fraction with a relatively high molecular weight could be resolved as a separate peak in this GPC trace. [c] A sample for run 12 was taken after 20 min, at which time the polymerization was complete; a sample for run 13 was taken from the same reaction after 55 min. [d] The reaction was heated at the polymerization temperature for several extra hours after all of the NBE had been consumed.

Table VII. Kinetic Data for the Polymerization of NBE by **13** and **6**

catalyst	[Ta] (mM)	$[NBE]_0$ (mM)	T (K)	10^3k
13	10.9	111	308.4	0.64 s^{-1}
13	5.59	80	317.9	2.0 s^{-1}
13	5.59	55	323.3	3.5 s^{-1}
13	6.84	183	323.3	3.9 s^{-1}
13	7.98	189	323.3	3.9 s^{-1}
13	2.91	46	323.3	3.8 s^{-1}
13	5.59	45	330.0	7.1 s^{-1}
13	5.70	177	330.0	7.6 s^{-1}
13	9.32	87	333.1	12 s^{-1}
13	5.59	200	337.8	23 s^{-1}
6	9.08	166	313.0	48 M^{-1} s^{-1}
6	9.08	134	322.2	80 M^{-1} s^{-1}
6	17.8	199	322.4	94 M^{-1} s^{-1}
6	18.1	122	323.1	79 M^{-1} s^{-1}
6[a]	19.3	272	323.0	0.2 M^{-1} s^{-1}

[a] Polymerization carried out in the presence of 3 equiv of pyridine and monitored over ~1 half-life.

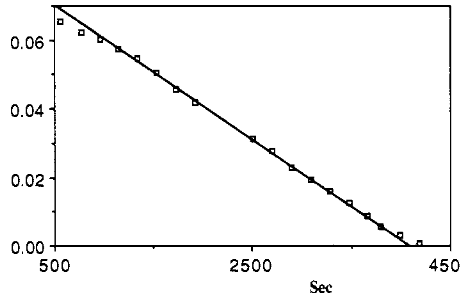
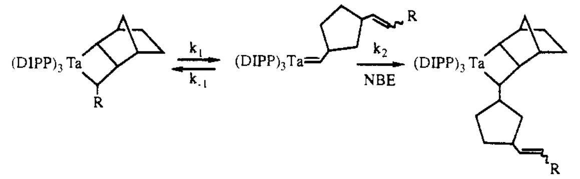


Figure 7. A plot of the consumption of 20 equiv of NBE by **13** at 50 °C in C_6D_6.

It is relatively simple to prepare samples of polynorbornene employing **13** as the catalyst in toluene in the presence of norbornene. The reaction is heated and the consumption of NBE is monitored. After polymerization is complete 20–30 equiv of benzaldehyde are added, $[Ta(O)(DIPP)_3]_x$ is filtered off, and the resulting polymer is analyzed by gel permeation chromatography. The results are summarized in Table VI; a representative GPC trace is displayed in Figure 9b. The molecular weight of the polynorbornene increases linearly with the number of equivalents of monomer, as expected for a living catalyst system. The higher than desired polydispersities (e.g., for 100 equiv of NBE, M_n = 22 000 and d = 1.63) can be ascribed to slow secondary metathesis reactions after all norbornene has been consumed. When a sample was heated for several hours after all of the monomer had been consumed, a polydispersity of 1.95 was observed (run 5). In one case (run 4) the polymerization was stopped at ~75% completion, and the polydispersity in that case (1.04) was what one would expect for a well-behaved living polymerization. Polydispersities increase as a result of metathesis (and accompanying isomerization) reactions after all NBE is consumed.

Kinetic studies demonstrated that the rate-limiting step in this reaction is ring-opening of the metallacycle followed by a rapid reaction of the incipient alkylidene with NBE (eq 12 and 13). Kinetic data are listed in Table VII. A typical plot is shown in Figure 7. In the beginning of a typical run the rate of consumption of NBE is slightly less than the maximum value and increases to that value after ~5 equiv of NBE have been consumed, consistent with a slightly slower initial step (when R = *tert*-butyl) relative to that when R is the growing polymer chain. The zero-order dependence on [NBE] (k_2[NBE] ≫ k_{-1}) continues throughout the reaction until 1 to 2 equiv of NBE remain. Thereafter k_2[NBE] ≪ k_{-1}. At 57 °C a ln [NBE] plot begun when ~1 equiv of NBE remained yielded $k_2/k_{-1} \approx 150\ M^{-1}$ (estimated error ±50 M^{-1}).



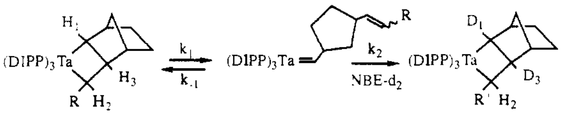
(12)

$$-\frac{d\,[NBE]}{dt} = \frac{k_1k_2[Ta][NBE]}{k_{-1} + k_2[NBE]} \tag{13}$$

The rate of consumption of **13** was monitored at 35.0 °C by following the disappearance of the proton signal ascribed to H_2 at 3.88 ppm. A plot of ln [**13**] versus time yielded $k_1 = 3.9 \times 10^{-4}\ s^{-1}$. The maximum rate of consumption of NBE (by **14**) at 35.2 °C was found to be $6.3 \times 10^{-4}\ s^{-1}$. Therefore the rate of chain growth is approximately 50% faster than the rate of chain initiation. A detailed explanation is not possible since two propagating tantalacycles are involved, one in which the growing chain is trans to the C_5H_8 ring (as the *tert*-butyl group is in **13**, i.e., $\mathbf{14}_{trans}$) and another "all cis" tantalacycle ($\mathbf{14}_{cis}$). We assume that $\mathbf{14}_{trans}$ gives rise to the trans C=C bond in the polymer, and $\mathbf{14}_{cis}$ to the cis C=C bond in the polymer, i.e., $k_1(obsd)[Ta_{total}] = k_1(\mathbf{14}_{trans})[Ta_{trans}] + k_1(\mathbf{14}_{cis})[Ta_{cis}]$. We would expect k_1 for **13**

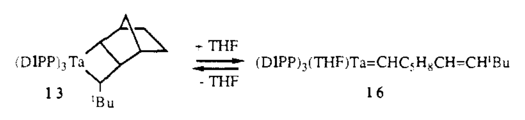
(k_1(**13**)) to be greater than k_1(**14**$_{trans}$) since the *tert*-butyl group in **13** for steric reasons should speed up opening of the ring. We propose that the difference between k_1(**13**) and k_1(**14**$_{trans}$) is more than negated by a relatively large value for k_1(**14**$_{cis}$), so that propagation ultimately is faster than initiation. Fortunately, the difference in the rate of propagation versus initiation has a negligible effect on the dispersity of polynorbornenes prepared in this manner.

It is possible (but difficult) to isolate the "second insertion product", $Ta[CH(C_5H_8)CHCH(C_5H_8CH{=}CH\text{-}t\text{-}Bu)](DIPP)_3$ (**15**), by treating **13** with 1 equiv of NBE followed by heating the mixture to 60 °C. A sample of **15** could be isolated as an *extremely* soluble white powder from concentrated pentane solutions. The ^{1}H NMR spectrum of **15** at 25 °C displays broad resonances for the DIPP ligands but relatively sharp signals for the α protons of the ring (H_1 at 5.23 ppm (d), H_2 at 3.85 ppm (~t)), about the same chemical shifts as the resonances for H_1 and H_2 in the spectrum of **14**; the β-proton resonance in the spectrum of **15** is obstructed by other upfield resonances. The rate of ring-opening of **15** can be determined by monitoring the disappearance of the H_1 resonance at 5.23 ppm (H_1) upon treating **15** with NBE-*2,3-d*$_2$. The H_1 resonance was chosen because it is replaced by deuterium upon reaction with 1 equiv of NBE-*2,3-d*$_2$ (eq 14), while conversion of H_2 to deuterium requires 2 equiv of NBE-*2,3-d*$_2$. A plot of ln [**15**] versus time at 35.0 °C gave k_1(**15**) = 9.8×10^{-4} s^{-1} (cf. k_1(**13**) = 3.9×10^{-4} s^{-1} at 35.0 °C and k_1(**14**) = 6.3×10^{-4} s^{-1} for consumption of NBE at 35.2 °C by **14**$_{cis}$ plus **14**$_{trans}$). The only way we can explain the large value for k_1(**15**) relative to k_1(**14**) (the observed rate for NBE bulk polymerization) is to assume that isolated **15** is *not representative* of the mixture of cis plus trans tantalacycles in solution, i.e., it contains a significantly higher percentage of the cis tantalacycle, the rate of opening of which must be faster than the rate of opening of the trans tantalacycle, as noted above.



(14)

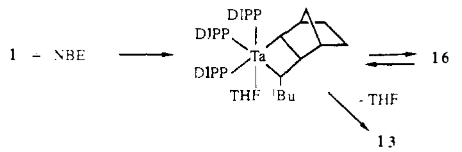
Upon heating a solution of **13** in THF-d_8 at 65 °C signals characteristic of an alkylidene complex (δ H_α = 7.69 ppm, J_{HH} = 8.6 Hz; δ H_β = 4.54 ppm (m)) grow in slowly. We propose that this alkylidene complex is **16** (eq 15), and that it is formed by rate-limiting ring-opening of **13** followed by trapping of the incipient alkylidene by THF. The consumption of NBE at elevated temperatures in the presence of 5–10 equiv of THF is the same as in the absence of THF, a fact that suggests that ring-opening *in this case* (see earlier examples to the contrary) is rate limiting and that NBE is a significantly better trap for the incipient alkylidene complex than THF is. In solvents other than THF (ether, pentane, C_6D_6) **16** loses THF and **13** reforms.



(15)

There is one last observation that deserves some comment. Addition of excess NBE to **1** at 25 °C leads to rapid formation of polynorbornene and complete consumption of **1** (eq 16), even in neat THF. We speculate that an initial six-coordinate tantalacycle forms that is in equilibrium with **16** and that *relatively* slowly loses THF to give **13** (eq 17). If excess NBE is present then **16** reacts rapidly to give another six-coordinate tantalacycle that ring-opens readily, etc., i.e., a kinetically distinct "base-on" mechanism can be operative. Once "base-free" *five*-coordinate tantalacycles form (**13** and **14**), then polymerization of norbornene proceeds via the mechanism involving rate-limiting ring-opening in these five-coordinate tantalacycles (a much slower process). GPC analysis of a polynorbornene polymer sample prepared by adding 200 equiv of NBE to **1** in toluene (Table VI, run 11) supports this speculation. The polynorbornene has a high molecular weight and large polydispersity (M_n = 146 000; d = 4.41) along with a low molecular weight tail, features that could arise from a highly active polymerization catalyst that is deactivated over the course of the polymerization reaction by formation of **13** and **14**, species that are relatively inactive at room temperature.

$$Ta(CH\text{-}t\text{-}Bu)(DIPP)_3(THF) \xrightarrow[25\ °C,\ very\ fast]{excess\ NBE} polymer \quad (16)$$



(17)

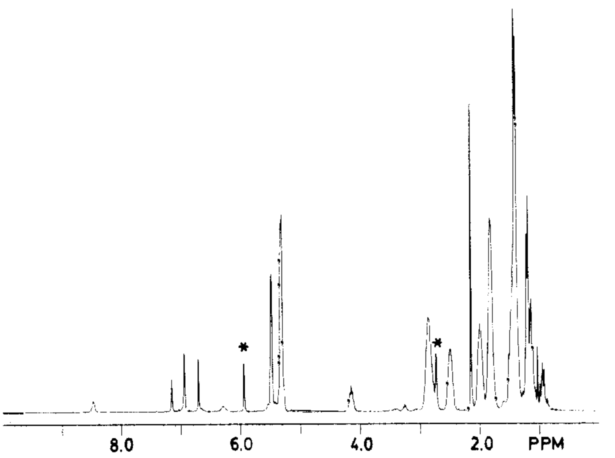
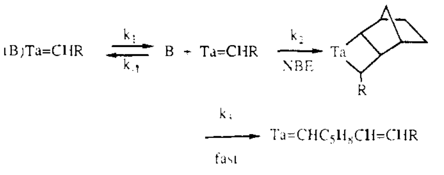


Figure 8. The ^{1}H NMR spectrum of **6** after reaction with ~15 equiv of NBE in C_6D_6 at 50 °C (* = NBE).

Reactions of TIPT Complexes with Acyclic Olefins and NBE. As mentioned previously, neither **5** nor **6** reacts with ordinary olefins such as *cis*-3-hexene or 2-pentenes. However, **5** does react rapidly with NBE at 25 °C in ether or toluene to give polynorbornene (~70% cis). When **5** was treated with 10 equiv of NBE in ether, the ^{1}H NMR spectrum of the resulting product (in C_6D_6) showed only resonances consistent with the formation of $Ta[(CHC_5H_8CH)_xCH\text{-}t\text{-}Bu](TIPT)_3(THF)$, none for **5**. The α-proton resonance was not located in the spectrum of $Ta[(CHC_5H_8CH)_xCH\text{-}t\text{-}Bu](TIPT)_3(THF)$; it was not in the spectrum of **5** either (see above). Neither **5** nor $Ta[(CHC_5H_8CH)_xCH\text{-}t\text{-}Bu](TIPT)_3(THF)$ reacts with NBE at 25 °C in THF, a fact that suggests that activity probably depends on the accessibility of a base-free intermediate (i.e., $Ta(CH\text{-}t\text{-}Bu)(TIPT)_3$; eq 18, TIPT ligands omitted). At no time do we see ^{1}H NMR resonances characteristic of a tantalacyclobutane complex. Therefore we propose that k_3 is fast.



(18)

There is other evidence for the "base-free" mechanism. The pyridine adduct **6** does not react with NBE at 25 °C in toluene, pentane, or ether. At elevated temperatures where a base-free intermediate is present in much higher concentration, **6** does react with excess NBE to give polymer (~65% cis). In a typical spectrum, the α-proton resonance for **6** disappears as new resonances for what we believe to be $Ta[(CHC_5H_8CH)_xCH\text{-}t\text{-}Bu](TIPT)_3(py)$ appear (Figure 8); **6** is consumed completely by 5–6 equiv of NBE. As in reactions involving **5** the alkylidene α-proton resonances in $Ta[(CHC_5H_8CH)_xCH\text{-}t\text{-}Bu](TIPT)_3(py)$ were not positively identified in the ^{1}H NMR spectrum, but the alkylidene α-carbon resonance can be seen at 249.3 ppm in the ^{13}C NMR spectrum of $Ta[(CHC_5H_8CH)_xCH\text{-}t\text{-}Bu](TIPT)_3(py)$ in C_6D_6 at 25 °C. As one would expect the rate of consumption of NBE at 50 °C in the presence of 3 equiv of added pyridine ([**6**] = 19 mM) was drastically reduced (by a factor of ~400; Table VII)

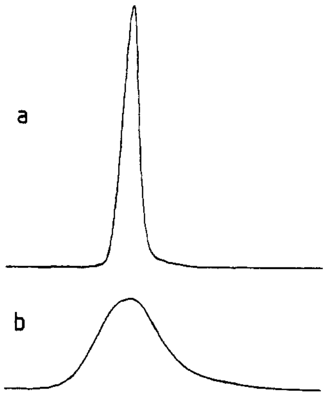


Figure 9. GPC traces for the benzylidene-capped polynorbornene produced by adding 100 equiv of NBE to **5** (a) (polydispersity 1.09) and **13** (b) (polydispersity 1.63).

compared to that in the absence of added pyridine.

According to the mechanism shown in eq 18 the rate of consumption of NBE should follow first-order kinetics under any given set of conditions (eq 19). This was the case for the rate of disappearance of NBE in the presence of **6** in C_6D_6 at 39.8 °C ($k_{obsd} = 4.8 \times 10^{-2}$ M^{-1} s^{-1}) and 49.0 °C ($k_{obsd} = 8.0 \times 10^{-2}$ M^{-1} s^{-1}) (see also Table VII). The relatively small value of k_1/k_{-1} makes a detailed study of the rate versus [B] impractical.

$$-\frac{d\,[\mathrm{NBE}]}{dt} = \frac{k_1k_2[\mathrm{Ta}][\mathrm{NBE}]}{k_1 + k_{-1}[\mathrm{B}]} \tag{19}$$

Reaction of $Ta[(CHC_5H_8CH)_xCH\text{-}t\text{-}Bu](TIPT)_3(THF)$ (or **6** at elevated temperatures) with 3 equiv of benzaldehyde in C_6D_6 at 25 °C results in a complete cleavage of the polymer chain within 30 min. The configuration in the phenyl-capped double bond was found to be 64% cis on the basis of spin simulation studies (see Experimental Section for details). The results of GPC analysis of the benzylidene-capped polynorbornene samples prepared with **5** and **6** are shown in Table VI. Consistent with a living polymerization system in which the rate of propagation is of the same magnitude as the rate of initiation, the molecular weights of the polynorbornene samples increase linearly with the number of monomer equivalents employed, and in all cases the polydispersities are representative of essentially monodisperse samples (a typical trace is shown in Figure 9a). In contrast to what was found with the DIPP catalysts, additional reaction time does *not* significantly affect polydispersity: 200 equiv of NBE polymerized by **5** gave $M_n = 59\,100$ ($d = 1.05$) after 20 min (the consumption was complete at this time) and $M_n = 57\,600$ ($d = 1.07$) when a reaction was allowed to run for 55 min before being quenched with benzaldehyde. Therefore, the polymerization of NBE by **5** or **6** is well-behaved, yielding monodisperse polymers that are *not* subject to isomerization by the catalyst (cf. the DIPP system).

Polymerization of Norbornene by the DMP System. The DMP tantalacyclobutane complex **12** reacts with NBE in a manner that in some respects is similar to the mode of reactivity observed for **13**. When **12** is heated with excess NBE in C_6D_6 new resonances indicative of the tantalacycle $Ta[CH(C_5H_8)CHCH(P)](DMP)_3$ (P = polymer; 55% trans) are observed. **12** is consumed by 5 equiv of NBE. However, the rate of consumption of NBE by **12** was found to be neither cleanly zero order nor first order in NBE in experiments in which $[\mathbf{12}]_0 \approx 5$ mM and $[\mathrm{NBE}]_0 = 50\text{–}75$ mM. For this reason we have not attempted to study the DMP catalyst system in any detail.

A NBE polymerization reaction catalyzed by **12** can be taken to completion and left at 50 °C with no sign of degradation of $Ta[CH(C_5H_8)CHCH(P)](DMP)_3$. Solutions of $Ta[CH(C_5H_8)CHCH(P)](DMP)_3$ in C_6D_6 in the absence of NBE show no *obvious* signs of decomposition even after several days at 25 °C, although the double bonds in the polymer isomerize to ~70% trans during this time ($x = 10\text{–}20$). Polymerization of 100 equiv of NBE by **12** yields a polymer that by GPC analysis has $M_n = 10\,700$ and $d = 2.71$ (Table VI). We could ascribe the high polydispersity to a greater metathesis activity toward double bonds in the polymer chain (after consumption of NBE), although mechanistic complications hinted at by the lack of well-behaved kinetics (see above) might also lead to broadening of the molecular weight distribution.

Discussion

There are some results in the literature that correlate olefin metathesis activity with the electron-withdrawing power of the alkoxide ligand. In complexes of the type $M(CHR')(NAr)(OR)_2$ (M = Mo or W; Ar = $2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$), the activity of the catalysts for a given metal increases significantly in the series $OCMe_3 < OCMe_2(CF_3) < OCMe(CF_3)_2$.[2,4,21a] Related observations had been made in acetylene metathesis reactions catalyzed by well-characterized alkylidyne complexes of the type $M(CR')(OR)_3$ (M = Mo or W).[1] In both olefin and acetylene metathesis systems intermediate metallacycles *in general* appear to be more stable toward loss of olefin (or acetylene) when electron-withdrawing alkoxide ligands are present. Finally, virtually no acetylene metathesis activity was observed for complexes of the type $M(CR')(SAr)_3$ (M = Mo or W; Ar = $2,4,6\text{-}C_6H_2\text{-}i\text{-}Pr_3$ or $2,4,6\text{-}C_6H_2Me_3$).[19] The trend that is appearing (at least for Mo and W) is that electron-withdrawing ligands in general (but not without exception even at this stage[21a]) activate the metal toward reaction with a carbon–carbon multiple bond and stabilize metallacycles.

The results reported here are consistent with the trend noted above if we assume that a thiolate ligand is overall a much better donor of electron density to the metal than an analogous alkoxide ligand, and that greater electron donor ability alone dictates the chemistry in the phenoxide and TIPT systems discussed here. But we have some evidence that at least the second of these assumptions is in fact incorrect. $Ta(CH\text{-}t\text{-}Bu)(DIPP)_3(THF)$ probably reacts in an associative fashion with an olefin (at least norbornene), one that perhaps involves attack at an equatorial position next to the neopentylidene ligand in C (see first section). In contrast $Ta(CH\text{-}t\text{-}Bu)(TIPT)_3(THF)$ probably reacts dissociatively to yield incipient $Ta(CH\text{-}t\text{-}Bu)(TIPT)_3$ which an olefin attacks so as to produce an intermediate in which the alkylidene and the olefin are bound trans to one another in axial positions of the trigonal bipyramid. This trans TBP intermediate would have to rearrange to a cis intermediate in order to form the required metallacyclobutane ring. Therefore the generalization that complexes that contain thiolate ligands are poor metathesis catalysts is probably correct, but the reasons may be more subtle and varied than we anticipated initially. More studies will be required before a wholly satisfactory answer to this question is possible.

There are now several catalyst systems that will polymerize norbornene in a well-defined manner. (NBE is extremely reactive and polymerization of it by classical catalysts is well-studied;[8,23] NBE therefore is the logical monomer for studying potentially controllable ring-opening metathesis polymerization reactions by new catalysts.) The first was the titanocene system developed by Grubbs where opening of the titanacyclobutane ring is rate limiting.[13a] The DIPP tantalacyclobutane system we report here is remarkably similar in that respect; Grubbs reported $\Delta H^{\ddagger} = 27.1$ (0.5) kcal/mol, $\Delta S^{\ddagger} = 9$ (4) eu, and $\Delta G^{\ddagger}_{338} = 24$ (1) kcal/mol compared to $\Delta H^{\ddagger} = 24.0$ (0.9) kcal/mol, $\Delta S^{\ddagger} = 4.8$ (2.8) eu, and $\Delta G^{\ddagger}_{338} = 22.4$ (1.3) kcal/mol for the tantalum system. Grubbs assumed, as we have, that the trans to cis ratio in the polynorbornene results from competitive cleavage of trans and cis metallacycles, although in neither system is it possible to know what the individual rate constants for cleavage of the trans and cis metallacycles actually are. We have some evidence that the "all cis" tantalacycle opens significantly more rapidly than the trans tantalacycle, and that chain propagation is faster than chain initiation because **13** (the initiator) is trans while propagating tantalacycles contain a large fraction of cis isomer. We feel that the similarities between the tantalum DIPP system and the titanium system investigated by Grubbs are purely circumstantial; they are both well-behaved examples of catalysts in which ring-opening is rate limiting.

Several other systems are known that will polymerize norbornene. The Osborn catalyst system ($W(CHR')(OCH_2\text{-}t\text{-}Bu)_2(halide)_2$/Lewis acid) has been shown to react with various norbornenes to yield living intermediates;[13b] under some circumstances metallacycles can be observed at the same time as alkylidene complexes.[13c] The $M(CHR')(NAr)(OR)_2$ catalyst systems (M = Mo[7] or W[4]) can be tuned to react only with norbornene by employing OR = *tert*-butoxide. The $Mo(CHR')(NAr)(O\text{-}t\text{-}Bu)_2$ catalyst will tolerate ~100 equiv of ester during the course (~15 min) of a polymerization of 5,6-dicarbomethoxynorbornene. In two cases[4,7] the polynorbornene that is produced has been shown to be monodisperse, as one would expect for well-behaved living polymerization catalysts. Although metallacycle stability will vary widely with the degree of substitution on the ring, and the nature of the ligands in Mo and W systems, the data available so far suggest that metallacyclobutane rings become less stable toward loss of olefin (ring-opening) as one moves from group 4 to group 6 metals.

We were surprised to find such a large variation in the behavior of the three basic types of catalysts (DIPP, TIPT, DMP). Even the (presumably solely steric) differences between the DMP and DIPP ligands are extremely important if one is concerned with controlling ring-opening polymerization reactions. The DMP catalyst system is clearly unsuitable, although we do not know why in any detail. The two most significant problems with the DIPP system are the possibility of a competitive "base one" mechanism under some conditions (eq 17) and some activity for metathesis of ordinary olefins (i.e., isomerization of the double bonds and broadening of the molecular weight distribution). The TIPT system is the best behaved overall from the practical point of view of preparing well-defined polymers through ring-opening reactions, since tantalacycles are unstable, living alkylidene complexes (containing a β proton) appear to be relatively stable (as base adducts, at least), and there is potentially a great deal of control over the rate of the ring-opening reaction by choosing the appropriate base, solvent (possibly also a coordinating ligand), and temperature. We plan to employ the thiolate catalysts in future studies of ring-opening polymerization reactions by tantalum.

Finally, we want to emphasize again the potential significance of the two quite different types of metallacyclobutane rings found in the two structures reported here. The evidence is beginning to accumulate in the tungsten alkylidene catalyst system[21a,d] that TBP metallacyclobutane complexes are not necessarily always the most stable or even the most common. It also makes sense using both steric and electronic arguments that the short $M \cdots C_\beta$ distance (and concomitantly relatively large $C_\alpha\text{–}M\text{–}C_\alpha$ angle) found in TBP metallacyclic complexes must lengthen (and the $C_\alpha\text{–}M\text{–}C_\alpha$ angle must decrease) in a square-pyramidal metallacyclic complex in which the ring occupies basal positions, or in a octahedral metallacyclic complex. We stress that the important question concerning how an olefin approaches a M=C bond remains unanswered; our working proposal is that an olefin approaches the metal so that its C—C axis is more perpendicular than parallel to the M=C bond to give a roughly square-pyramidal transition state. Structures like that of **7** therefore may prove to be more relevant in that they can more readily lose an olefin to give a pseudotetrahedral alkylidene complex than can the more ideal trigonal-bipyramidal metallacyclic complexes. The situation is more complex in this particular system because of the important role a base undoubtedly plays in several steps of a metathetical reaction.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques. Reagent grade ether, tetrahydrofuran, and toluene were distilled from sodium benzophenone ketyl under nitrogen. Pentane was washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was distilled from calcium hydride under nitrogen. All deuteriated NMR solvents were passed through a column of activated alumina.

$Ta(CH_2\text{-}t\text{-}Bu)_2Cl_3$,[20a] $Ta(CH\text{-}t\text{-}Bu)(THF)_2Cl_3$,[9] and $2,4,6\text{-}C_6H_2\text{-}i\text{-}Pr_3SH$ (HTIPT)[26] were prepared as described in the literature. $LiDIPP{\cdot}Et_2O$, LiDMP, and LiTIPT were prepared from the appropriate phenol or thiol and *n*-butyllithium in ether (for $LiDIPP{\cdot}Et_2O$) or pentane (for LiDMP and LiTIPT). Norbornene-*2,3-d*$_2$ was provided by J. K. Stille via R. H. Grubbs. All other reagents were purchased from commercial sources and purified by standard techniques.

Chemical shifts are listed in ppm downfield from TMS. Coupling constants are quoted in hertz. Routine coupling constants and multiplicities are not listed. The NMR solvent is benzene-d_6, the temperature 25 °C, and the field between 250 and 400 MHz (^1H), unless otherwise noted. All polymer samples were analyzed in toluene (0.3% by weight polynorbornene in solution) at 25 °C versus polystyrene standards ($1260\text{–}1.030 \times 10^6$ MW) on a Waters 150C instrument equipped with three Styragel columns (10^3, 10^4, and 10^5 Å) and a refractive index detector. Molecular weight distributions were calculated by an accompanying Waters Data Module. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory (Woodside, NY) or Spang Microanalytical Laboratory (Eagle Harbor, MI).

Preparation of Compounds. $Ta(CH\text{-}t\text{-}Bu)(DIPP)_3(THF)$ (DIPP = $O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$) (1). $Ta(CH_2\text{-}t\text{-}Bu)_2Cl_3$ (2.00 g, 4.66 mmol) was dissolved in ether (50 mL) and the solution was cooled to −30 °C. THF (12 g) was added dropwise. As this solution was allowed to warm at room temperature the color changed from yellow to violet. After 2 h the solution was again cooled to −30 °C and stirred while solid $LiDIPP{\cdot}Et_2O$ (3.62 g, 14.0 mmol) was added. As the solution warmed to room temperature the color changed from violet to yellow-orange. The total reaction time (including the time of addition) was 20 min. The mixture was then filtered through Celite, and the solvent was removed in vacuo. The resulting yellow-orange solid was dissolved in pentane, and the solution was filtered through Celite to remove any remaining LiCl. The solvent was removed in vacuo and the residue dissolved in ether. Orange-yellow crystals were obtained by cooling the solution to −30 °C (3.58 g, 90%): ^1H NMR δ 7.32 (d, 6, H_m), 7.15 (t, 3, H_p), 5.73 (s, 1, $CHCMe_3$), 3.99 (m, 10, $CHMe_2$ and THF), 1.48 (d, 36, $CHMe_2$), 1.31 (s plus m, 13, $CHCMe_3$ and THF); ^{13}C NMR δ 227.1 (d, J_{CH} = 95, $CHCMe_3$), 159.0 (s, C_{ipso}), 137.4 (s, C_o), 123.6 (d, C_m), 121.7 (d, C_p), 73.8 (m, THF), 45.0 (s, $CHCMe_3$), 35.7 (q, $CHCMe_3$), 27.1 (d, $CHMe_2$), 25.6 (m, THF), 24.5 (q, $CHMe_2$). Anal. Calcd for $TaC_{45}H_{69}O_4$: C, 63.20; H, 8.15; Cl, 0.00. Found: C, 63.13; H, 8.09; Cl <0.5. On a larger scale best yields are obtained if $Ta(CH\text{-}t\text{-}Bu)(THF)_2Cl_3$ is isolated before being treated with $LiDIPP{\cdot}Et_2O$ (in ether; no added THF). **1** has been isolated in 85% yield on a 20-g scale.

$Ta(CH\text{-}t\text{-}Bu)(DIPP)_3(py)$ (2). $Ta(CH\text{-}t\text{-}Bu)(DIPP)_3(THF)$ (0.50 g, 0.58 mmol) was dissolved in ether (10 mL) and the solution was cooled to −30 °C. While this solution was stirred, pyridine (280 μL, excess) was added. After 10 min at 25 °C the solution had changed color from orange-yellow to orange. The solvent was removed in vacuo and the residue recrystallized from ether at −30 °C to give 0.38 g of orange crystals (75%): ^1H NMR δ 8.70 (py H_o), 7.06 (unresolved, H_m), 6.92 (unresolved, H_p), 6.51 (py H_p), 6.29 ($CHCMe_3$), 6.22 (py H_m), 3.83 (unresolved, $CHMe_2$), 1.22 (unresolved, $CHCMe_3$ and $CHMe_2$); ^{13}C NMR δ 231.2 (d, J_{CH} = 96, $CHCMe_3$), 157.0 (C_{ipso}), 151.0 (py C_o), 137.8 (py C_p), 137.6 (C_o), 124.4 (py C_m), 123.7 (C_m), 121.7 (unresolved, C_p), 45.2 ($CHCMe_3$), 35.4 ($CHCMe_3$), 27.1 ($CHMe_2$), 24.4 ($CHMe_2$). Anal. Calcd for $TaC_{46}H_{66}NO_3$: C, 64.08; H, 7.73. Found: C, 64.27; H, 7.78.

$Ta(CH\text{-}t\text{-}Bu)(DMP)_3(THF)$ (DMP = $O\text{-}2,6\text{-}C_6H_3Me_2$) (3). $Ta(CH\text{-}t\text{-}Bu)(THF)_2Cl_3$ (2.00 g, 3.99 mmol) was dissolved in a mixture of ether (110 mL) and THF (10 mL), and the solution was cooled to −30 °C. This solution was stirred while solid LiDMP (1.53 g, 11.9 mmol) was added. While this mixture was stirred at room temperature for 20 min, LiCl precipitated and the color changed from purple to orange-yellow. The reaction mixture was then filtered through Celite, and the solvent was removed in vacuo. The resulting yellow-orange oil was dissolved in ether and the solution filtered again through Celite. Partial removal of the solvent in vacuo yielded an orange-yellow precipitate (1.25 g). An additional 0.32 g was obtained by cooling the filtrate to −30 °C for 12 h (total yield 57%): ^1H NMR δ 7.01 (H_m), 6.93 ($CHCMe_3$), 6.77 (H_p), 3.58 (THF), 2.46 (DMP Me groups), 1.15 ($CHCMe_3$), 1.01 (THF); ^{13}C δ 237.4 (d, J_{CH} = 107, $CHCMe_3$), 161.7 (C_{ipso}), 128.8 (C_m), 126.7 (C_o), 120.7 (C_p), 74.5 (THF), 43.1 ($CHCMe_3$), 36.0 ($CHCMe_3$), 25.3 (THF), 18.2 (DMP Me). Anal. Calcd for $TaC_{33}H_{45}O_4$: C, 57.71; H, 6.62. Found: C, 57.02; H, 6.38. Low analytical results are believed due to some decomposition in the solid state.

$Ta(CH\text{-}t\text{-}Bu)(DMP)_3(py)$ (4). Pyridine (280 μL, 3.48 mmol) was added via syringe to a stirred solution of $Ta(CH\text{-}t\text{-}Bu)(DMP)_3(THF)$ (0.80 g, 1.16 mmol) in ether (150 mL) at −30 °C. The solution was stirred at room temperature for 10 min, during which time the color changed from orange to orange-red. The solvent was removed in vacuo from the filtrate, and the resulting oil was dissolved in a minimal amount of a 1:1 mixture of ether and pentane. Dark yellow crystals were isolated from this solution at -30 °C (0.49 g, 61%): ^{1}H NMR δ 8.54 (py H$_o$), 7.51 (C*H*CMe$_3$), 7.1–6.1 (br m, py and DMP ring protons), 2.45 (DMP Me groups), 1.25 (CHC*Me*$_3$); ^{13}C NMR δ 241.9 (d, J_{CH} = 107, *C*HCMe$_3$), 160.0, 128.8, 126.9, and 120.8 (DMP ring carbons), 150.9 (py C$_o$), 137.9 (py C$_p$), 124.5 (py C$_m$), 43.4 (CH*C*Me$_3$), 35.7 (CHC*Me*$_3$), 18.3 (DMP Me). Anal. Calcd for $TaC_{34}H_{42}NO_3$: C, 58.86; H, 6.11. Found: C, 57.70; H, 5.93. We believe decomposition of the sample is responsible for the low results.

Ta(CH-*t*-Bu)(TIPT)$_3$(THF) (TIPT = S-2,4,6-C$_6$H$_2$-*i*-Pr$_3$) (5). A solution of LiTIPT (1.45 g, 5.98 mmol) in ether (25 mL) was added dropwise to a solution of Ta(CH-*t*-Bu)(THF)$_2$Cl$_3$ (1.00 g, 1.99 mmol) in ether (50 mL) at room temperature. As the solution was stirred at room temperature, the color changed from purple to orange-red. After 20 min the mixture was filtered through Celite, and the solvent was removed from the filtrate in vacuo. The resulting oil was dissolved in pentane, and the solution was cooled to -30 °C to give a yellow powder (1.25 g, 61%): ^{1}H NMR δ 7.15 (H$_m$), 3.95 (br septet, 6, ortho C*H*Me$_2$), 3.65 (br, 4, THF), 2.82 (septet, 3, para C*H*Me$_2$), 1.36 (d, 36, ortho CH*Me*$_2$), 1.23 (d plus m, 22, para CH*Me*$_2$ and THF), 0.98 (s, 9, CHC*Me*$_3$); ^{13}C NMR (THF-d_8) δ 251.9 (d, J_{CH} = 76, *C*HCMe$_3$), 149.6, 148.9, and 148.0 (C$_{ipso}$, C$_o$, and C$_p$), 121.1 (d, C$_m$), 48.3 (s, CH*C*Me$_3$), 35.2 (d, para *C*HMe$_2$), 33.0 (d, ortho *C*HMe$_2$), 31.9 (CHC*Me*$_3$), 24.8 and 24.3 (ortho and para CH*Me*$_2$). Coordinated THF resonances were assumed to be coincident with the solvent resonances. Anal. Calcd for $TaC_{54}H_{87}OS_3$: C, 62.99; H, 8.53. Found: C, 62.94; H, 8.70.

During the original workup of **5**, and upon recrystallization, small amounts of a deep red microcrystalline compound that is more soluble in pentane than **5** can be isolated. So far we have not discovered a systematic method of preparing it in high yield. Analytical, ^{1}H NMR, and ^{13}C NMR data are all consistent with it being "Ta(CH-*t*-Bu)(TIPT)$_3$". We speculate that it is actually [Ta(CH-*t*-Bu)(TIPT)$_3$]$_2$ on the basis of the fact that it reacts only slowly with ~50 equiv of pyridine at 50 °C in C$_6$D$_6$ to give **6** in ~15% yield in 15 min. (Related compounds of the type Mo(CCMe$_3$)(SAr)$_3$ and W(CCMe$_3$)(SAr)$_3$ are also believed to be dimers.[19]) However, if so, [Ta(CH-*t*-Bu)(TIPT)$_3$]$_2$ must be in rapid equilibrium with a minute amount of Ta(CH-*t*-Bu)(TIPT)$_3$, since both ^{1}H and ^{13}C NMR spectra at room temperature show a single set of TIPT resonances. We also did not find an alkylidene α-carbon resonance, consistent with a monomer/dimer equilibrium of the order of the NMR time scale at room temperature and quite different chemical shifts for the alkylidene α-carbon resonance in each: ^{1}H NMR δ 7.15 (H$_m$), 3.80 (ortho C*H*Me$_2$), 2.82 (para C*H*Me$_2$), 1.80 (C*H*CMe$_3$), 1.26 (para CH*Me*$_2$), 1.22 (ortho CH*Me*$_2$), 1.08 (CHC*Me*$_3$); ^{13}C NMR δ 149.4, 148.7, and 140.8 (C$_{ipso}$, C$_o$, and C$_p$), 121.5 (C$_m$), 37.5 (CH*C*Me$_3$), 34.6 (para *C*HMe$_2$), 33.8 (CHC*Me*$_3$), 33.0 (ortho *C*HMe$_2$), 24.5 and 24.2 (ortho and para CH*Me*$_2$). The C$_\alpha$ resonance could not be observed at room temperature. Anal. Calcd for $TaC_{50}H_{79}S_3$: C, 62.73; H, 8.32; S, 10.05. Found: C, 63.12; H, 8.29; S, 10.09.

Ta(CH-*t*-Bu)(TIPT)$_3$(py) (6). Pyridine (70 μL, 0.87 mmol) was added to a stirred solution of Ta(CH-*t*-Bu)(TIPT)$_3$(THF) (0.30 g, 0.29 mmol) in ether (10 mL) at room temperature. After 20 min the solution was filtered through Celite, and the solvent was removed in vacuo, leaving the product as an orange-yellow powder (0.21 g, 70%): ^{1}H NMR (60°) δ 6.84 (br, H$_m$), 4.2–4.0 (br, ortho C*H*Me$_2$), 4.09 (C*H*CMe$_3$), 2.72 (m, para C*H*Me$_2$), 1.38 (ortho CH*Me*$_2$), 1.24 (CHC*Me*$_3$), 1.13 (para CH*Me*$_2$); ^{13}C NMR δ 252.4 (d, J_{CH} = 94, *C*HCMe$_3$), 150.3 (py C$_o$), 135.2 (py C$_p$), 123.5 (py C$_m$), 150–118 (br resonances, TIPT ring carbons), 47.1 (s, CH*C*Me$_3$), 34.5 (para *C*HMe$_2$), 32.4 (br, ortho *C*HMe$_2$), 31.4 (CHC*Me*$_3$), 24.7 (para CH*Me*$_2$), 24.5 (br, ortho CH*Me*$_2$). Anal. Calcd for $TaC_{55}H_{84}NS_3$: C, 63.73; H, 8.19. Found: C, 64.10; H, 8.30.

Ta[CH(Ph)CH(*t*-Bu)CH$_2$](DIPP)$_3$ (7). A solution of styrene (200 μL, 1.74 mmol) in ether (20 mL) was cooled to -30 °C and added dropwise to a stirred solution of Ta(CH-*t*-Bu)(DIPP)$_3$(THF) (1.50 g, 1.75 mmol) in ether (40 mL) at -30 °C. The solution was warmed to 25 °C and stirred for 30 min. The deep orange solution was then filtered through Celite and the solvent removed in vacuo to give an orange oil. The oil was dissolved in minimal pentane and the solution was cooled to -30 °C to yield orange crystals (0.87 g, 57%): ^{1}H NMR δ 7.05 (H$_m$) 7.0–6.6 (m, H$_p$ and phenyl protons), 3.47 (C*H*Me$_2$), 3.10–2.85 (m, 2, α C*H*$_2$), 2.17 (d, 1, J_{HH} = 12, α C*H*Ph), 1.57 (m, 1; β C*H*CMe$_3$), 1.19 (18, CH*Me*$_2$), 1.18 (18, CH*Me*$_2$), 0.94 (CHC*Me*$_3$); ^{13}C NMR δ 157.5 (C$_{ipso}$), 147.9 (C$_{ipso}$ phenyl), 138.1 (C$_o$), 128.2, 127.8, and 123.2 (phenyl carbons), 123.9 (C$_p$), 123.7 (C$_m$), 81.9 (d, J_{CH} = 133, *C*HPh), 63.8 (t, J_{CH} = 129, *C*H$_2$), 42.9 (d, J_{CH} = 125, *C*HCMe$_3$), 39.3 (CH*C*Me$_3$), 28.1 (*C*HMe$_2$), 27.7 (CHC*Me*$_3$), 24.0 (CH*Me*$_2$). Anal. Calcd for $TaC_{49}H_{69}O_3$: C, 66.34; H, 7.86. Found: C, 66.61; H, 7.63.

Ta(CHPh)(DIPP)$_3$(THF) (8). A solution of styrene (110 μL, 0.96 mmol) in ether (3 mL) was cooled to -30 °C and added dropwise to a solution of Ta(CH-*t*-Bu)(DIPP)$_3$(THF) (0.80 g, 0.94 mmol) in a mixture of ether (12 mL) and THF (5 mL) at -30 °C. The solution was warmed to 25 °C and stirred for 1 h, during which time the color changed from orange-yellow to dark orange. The mixture was filtered through Celite and the solvent was removed in vacuo to yield a dark orange oil. The oil was dissolved in pentane and the solution was cooled to -30 °C to give dark orange crystals (0.37 g, 45%): ^{1}H NMR δ 8.49 (C*H*Ph), 7.23 (phenyl H$_m$), 7.10 (H$_m$), 6.95–6.90 (m, H$_p$ and phenyl H$_o$), 6.62 (phenyl H$_p$), 3.74 (m, C*H*Me$_2$ and THF), 1.23 (CH*Me*$_2$), 1.00 (m, THF); ^{13}C NMR δ 221.1 (d, J_{CH} = 114, *C*HPh), 157.9 (C$_{ipso}$), 145.7 (phenyl C$_{ipso}$), 137.7 (C$_o$), 129.0, 127.3, and 124.1 (unresolved, phenyl carbons), 123.6 (C$_m$), 122.0 (C$_p$), 74.9 (THF), 27.3 (*C*HMe$_2$), 25.4 (unresolved, THF), 24.3 (CH*Me*$_2$). Decomposition of **8** upon recrystallization thwarted all attempts at analysis.

Ta(CHSiMe$_3$)(DIPP)$_3$(THF) (9). A solution of trimethylsilylethylene (56 μL, 0.39 mmol) in ether (4 mL) was cooled to -30 °C and added dropwise to a solution of Ta(CH-*t*-Bu)(DIPP)$_3$(THF) (0.30 g, 0.35 mmol) in a mixture of ether (8 mL) and THF (2 mL) at -30 °C. The solution was warmed to room temperature and stirred for 40 min, during which time the color changed from orange-yellow to yellow. It was filtered through Celite, and the solvent was removed in vacuo from the filtrate to give a yellow oil. The yield is virtually quantitative by ^{1}H NMR. Yellow crystals were obtained by crystallization from pentane at -30 °C: ^{1}H NMR δ 7.73 (C*H*SiMe$_3$), 7.11 (H$_m$), 6.94 (H$_p$), 3.85–3.65 (m, C*H*Me$_2$ and THF), 1.27 (CH*Me*$_2$), 1.12 (m, 4, THF), 0.17 (CHSi*Me*$_3$); ^{13}C NMR δ 210.6 (d, J_{CH} = 102, *C*HSiMe$_3$), 158.3 (C$_{ipso}$), 137.6 (C$_o$), 123.7 (C$_m$), 122.2 (C$_p$), 73.2 (THF), 27.2 (*C*HMe$_2$), 25.4 (unresolved, THF), 24.4 (CH*Me*$_2$), 4.08 (CHSi*Me*$_3$). Anal. Calcd for $TaC_{44}H_{69}O_4Si$: C, 60.66; H, 8.00. Found: C, 60.76; H, 8.01.

Ta[CH(SiMe$_3$)CH(SiMe$_3$)CH$_2$](DIPP)$_3$ (10). A solution of trimethylsilylethylene (134 μL, 0.92 mmol) in ether (4 mL) was cooled to -30 °C and added dropwise to a solution of Ta(CHSiMe$_3$)(DIPP)$_3$(THF) (0.40 g, 0.46 mmol) in ether (6 mL) at -30 °C. The solution was warmed to room temperature and stirred for 15 min, during which time the solution became colorless. Filtration through Celite followed by removal of the solvent in vacuo from the filtrate yielded a colorless oil. A white precipitate formed upon cooling a pentane solution to -30 °C (0.29 g, 71%): ^{1}H NMR δ 6.96 (H$_m$), 6.82 (m, H$_p$), 4.98 (t, 1, J_{HH} = 10.1, α CH$_2$), 3.64 (t, 1, J_{HH} = 10.7, α CH$_2$), 3.6–3.2 (br, C*H*Me$_2$), 2.95 (d, 1, J_{HH} = 14.5, α C*H*SiMe$_3$), 1.5–0.5 (br multiplet, CH*Me*$_2$), 0.24 (SiMe$_3$), 0.14 (SiMe$_3$), -0.33 (m, 1, β C*H*SiMe$_3$); ^{13}C NMR δ 160–120 (ring carbons), 108.1 (t, J_{CH} = 145, α CH$_2$), 99.3 (d, J_{CH} = 128, α *C*HSiMe$_3$), 28–22 (m, *C*HMe$_2$ and CH*Me*$_2$), 6.41 (d, J_{CH} = 131, β *C*HSiMe$_3$), 2.31 (SiMe$_3$), 0.82 (SiMe$_3$). Anal. Calcd for $TaC_{45}H_{73}O_3Si_2$: C, 60.11; H, 8.18. Found: C, 60.43; H, 8.24. A small amount of another isomer (~15%), possibly Ta[CH(SiMe$_3$)CH$_2$CH(SiMe$_3$)](DIPP)$_3$, is present according to ^{1}H and ^{13}C NMR spectra.

Ta(CH$_2$CH$_2$CH$_2$)(DIPP)$_3$ (11a). A solution of Ta(CH-*t*-Bu)(DIPP)$_3$(THF) (1.50 g, 1.75 mmol) in ether (20 mL) was placed in a pressure bottle. The bottle was then pressurized at 30 psi of ethylene for 10 min, during which time the solution became nearly colorless. The solution was filtered through Celite and the solvent removed from the filtrate in vacuo to give a colorless oil. This oil was dissolved in pentane and the solution cooled to -30 °C to yield colorless crystals (0.95 g, 72%): ^{1}H NMR δ 6.99 (H$_m$), 6.84 (H$_p$), 3.86 (m, 4, α CH$_2$), 3.52 (C*H*Me$_2$), 1.12 (CH*Me*$_2$), 0.48 (m, 2, β CH$_2$); ^{13}C NMR δ 156.6 (C$_{ipso}$), 137.6 (C$_o$), 123.4 (C$_m$), 122.2 (C$_p$), 96.1 (t, J_{CH} = 147, α CH$_2$), 27.7 (*C*HMe$_2$), 23.8 (CH*Me*$_2$), -0.68 (t, J_{CH} = 150, β CH$_2$). Anal. Calcd for $TaC_{39}H_{57}O_3$: C, 62.05; H, 7.63. Found: C, 62.21; H, 7.58.

Ta(CH$_2$CH$_2$CH$_2$)(DIPP)$_3$(py) (11b). Ta(CH-*t*-Bu)(DIPP)$_3$(THF) (7.00 g, 8.19 mmol) was dissolved in ether (150 mL) and placed in a Schlenk flask sealed with a septum. The flask was attached to a Schlenk line, and ethylene was vigorously bubbled through the solution via a needle for ~60 s. During this time the color changed from yellow-orange to very pale yellow. The solution was then filtered through Celite, and the solvent was removed from the filtrate in vacuo. The resulting oil was dissolved in pentane and the solution was cooled to -30 °C. Pyridine (1.98 mL, 24.6 mmol) was added dropwise while the solution was stirred. A white precipitate formed quickly. After the mixture was stirred for 10 min at room temperature this precipitate was collected and washed with cold pentane. Additional product was obtained by reducing the volume of the filtrate and cooling to -30 °C (total 4.90 g, 72%): ^{1}H NMR δ 8.58 (py H$_o$), 7.06 (H$_m$), 6.90 (H$_p$), 6.80 (py H$_p$), 6.45 (py H$_m$), 3.57 (C*H*Me$_2$), 2.95 (m, 4, α CH$_2$), 2.00 (m, 2, β CH$_2$), 1.15 (CH*Me*$_2$); ^{13}C NMR δ 156.6 (C$_{ipso}$), 150.1 (py C$_o$), 138.0 (C$_o$), 136.0 (unresolved, py C$_p$), 123.8 (py C$_m$), 123.6 (C$_m$), 122.3 (C$_p$), 78.0 (t, J_{CH} = 120, α CH$_2$), 36.3 (t, J_{CH} = 129, β CH$_2$), 27.6 (*C*HMe$_2$), 24.0 (CH*Me*$_2$). Anal. Calcd for $TaC_{44}H_{62}NO_3$: C, 63.37; H, 7.49. Found: C, 63.85; H, 8.05.

Ta[CH(C$_5$H$_8$)CHCH(*t*-Bu)](DMP)$_3$ (12). A solution of norbornene (0.055 g, 0.58 mmol) in ether (20 mL) was cooled to -30 °C and added to a solution of Ta(CH-*t*-Bu)(DMP)$_3$(THF) (0.40 g, 0.58 mmol) in ether

(40 mL) at −30 °C. The solution rapidly turned from orange-yellow to yellow. After 15 min at −30 °C the solvent was removed in vacuo to give a yellow oil. This oil was taken up in pentane and the solution was cooled to −30 °C to yield a pale yellow precipitate (0.13 g, 31%). A ^{1}H NMR spectrum of the crude oil showed the product to be formed in high yield; the low isolated yield is thought to arise from the high solubility of the compound: ^{1}H NMR δ 6.8 (H_m), 6.62 (H_p), 5.21 (d, 1, J_{HH} = 9.6, α $C\mathit{H}C_5H_8$), 3.72 (d, 1, J_{HH} = 10.0, α $C\mathit{H}CMe_3$), 2.86 and 2.80 (each a br d, 1 each, CH's of C_5H_8), 2.21 (DMP Me groups), 1.7–1.4 (m, 4, CH_2's of C_5H_8), 1.35 and 0.60 (each a br d, 1 each, bridgehead H's of C_5H_8), 1.16 ($C\mathit{Me}_3$), 0.84 (t, J_{HH} = 9.1, β $C_5H_8C\mathit{H}$); ^{13}C NMR δ 159.6 (C_{ipso}), 135.0 and 132.5 (each a d, J_{CH} = 142 and 132, α C's), 128.5 (C_m), 127.1 (C_o), 121.2 (C_p), 45.7 and 45.0 (each a d, CH's of C_5H_8), 38.6 ($\mathit{C}Me_3$), 34.5 and 34.6 (each a t, CH_2's of C_5H_8), 33.1 ($C\mathit{Me}_3$), 30.2 (t, bridgehead C of C_5H_8), 29.0 (d, J_{CH} = 149, β C_5H_8CH), 18.0 (DMP Me). We were never able to obtain a satisfactory elemental analysis, presumably because of sample decomposition (as judged visually).

Ta[CH(C_5H_8)CHCH(*t*-Bu)](DIPP)$_3$ (13). A solution of norbornene (0.077 g, 0.82 mmol) in ether (10 mL) was added to a stirred solution of Ta(CH-*t*-Bu)(DIPP)$_3$(THF) (0.70 g, 0.82 mmol) in ether (30 mL) at −30 °C. The reaction rapidly turned colorless from yellow-orange. The solution was stirred at room temperature for 30 min, and the solvent was removed in vacuo to yield a white powder. Crystallization from ether yielded a microcrystalline white powder (0.46 g, 64%): ^{1}H NMR δ 7.1–6.8 (m, H_m and H_p), 5.32 (d, 1, J_{HH} = 9.6, α $C\mathit{H}C_5H_8$), 3.88 (d, 1, J_{HH} = 10.1, α $C\mathit{H}CMe_3$), 3.8–3.2 (br, $C\mathit{H}Me_2$), 3.00 and 2.82 (each a br s, 1 each, CH's of C_5H_8), 0.88 (br t, 1, J_{HH} unresolved, β $C_5H_8C\mathit{H}$), 1.6–0.5 (br, no other specific assignments could be made); a ^{13}C NMR spectrum at room temperature displayed broad resonances. Anal. Calcd for $TaC_{48}H_{71}O_3$: C, 65.72; H, 8.18. Found: C, 65.90; H, 8.36.

Ta[CH(C_5H_8)CHCH(CHC$_5$H$_8$CH=CH-*t*-Bu)](DIPP)$_3$ (15). A solution of norbornene (0.083 g, 0.88 mmol) in ether (20 mL) was cooled to −30 °C and added to a solution of Ta(CH-*t*-Bu)(DIPP)$_3$(THF) (0.750 g, 0.88 mmol) in ether (30 mL) at −30 °C. The solution was warmed to room temperature and the solvent removed in vacuo after 20 min. The off-white solid was dissolved in toluene (10 mL), and norbornene (0.083 g, 0.88 mmol) in toluene (10 mL) was added. This solution was heated to 60 °C for 25 min. The solution was filtered through Celite, and the solvent was removed in vacuo, leaving behind a colorless oil. This oil was taken up in pentane (it is *extremely* soluble), and the solution was filtered through Celite to remove any undissolved Ta[CH(C_5H_8)CHCH(*t*-Bu)](DIPP)$_3$. After the solution was left to stand for several days at −30 °C, a white precipitate was collected (0.34 g, 40%): ^{1}H NMR δ 6.99 (br d, H_m), 6.84 (br t, H_p), 5.6–5.3 (m, 2, olefinic H's), 5.23 (d, 1, J_{HH} = 9.1, α $C\mathit{H}C_5H_8$), 3.85 (t, 1, J_{HH} = 8.6, α $C\mathit{H}$(C_5H_8CHCH-*t*-Bu)), 3.8–3.1 (br, $C\mathit{H}Me_2$), 1.12 ($C\mathit{Me}_3$). All other resonances were broad and complex, so no other specific assignments could be made. This product is not pure, the major impurity being Ta[CH(C_5H_8)CHCH(*t*-Bu)](DIPP)$_3$ according to ^{1}H NMR spectra.

Ta[CH$_2$CH$_2$CH$_2$CH(Pb)O](DIPP)$_3$(py) (17). A solution of benzaldehyde (61 μL, 0.60 mmol) in ether (5 mL) was cooled to −30 °C and added to a solution of Ta($CH_2CH_2CH_2$)(DIPP)$_3$(py) (0.50 g, 0.60 mmol) in ether (15 mL) at −30 °C. The solution was held at −30 °C for 15 min and then 25 °C for an additional 60 min. A white solid precipitated from the solution but redissolved when the solution reached room temperature. The solution was filtered through Celite and the solvent removed in vacuo to give a white solid that was reprecipitated from pentane at −30 °C (yield 0.45 g, 80%): ^{1}H NMR δ 8.64 (br s), 7.15–6.85 (m, 6), 7.08 (d, 6), 6.93 (t, 3), and 6.61 (t, 2, all pyridine, phenyl, or DIPP ring resonances), 5.56 (d of d, 1, J_{HH} = 2.6 and 10.4, $C\mathit{H}Ph$), 3.66 ($C\mathit{H}Me_2$), 3.2–1.6 (m, 6, α CH_2, β CH_2, and γ CH_2), 1.16 (18, $CH\mathit{Me}_2$), 1.14 (18, $CH\mathit{Me}_2$); ^{13}C NMR δ 157.0 (s), 150.2 (d), 144.8 (s), 138.0 (s), 135.6 (d), 129–125.6 (unresolved), 123.7 (d), and 122.7 (d, all pyridine, phenyl, or DIPP ring carbons), 85.1 (d, J_{CH} = 144, $\mathit{C}HPh$), 66.2 (t, J_{CH} = 120, α CH_2), 42.0 (t, J_{CH} = 126, β CH_2), 27.6 (t, J_{CH} = 127, γ CH_2), 27.4 ($\mathit{C}HMe_2$), 24.3 ($CH\mathit{Me}_2$), 24.0 ($CH\mathit{Me}_2$). Anal. Calcd for $TaC_{51}H_{68}NO_4$: C, 65.15; H, 7.31. Found: C, 64.74; H, 6.87.

Ta[CH$_2$CH$_2$CH$_2$C(Me)$_2$O](DIPP)$_3$ (18). A solution of acetone (7.3 μL, 0.10 mmol) in ether (5 mL) was cooled to −30 °C and added to a solution of Ta($CH_2CH_2CH_2$)(DIPP)$_3$ (0.075 g, 0.10 mmol) in ether (5 mL) at −30 °C. The solution was held at −30 °C overnight, during which time the color did not change and no precipitate was observed. Filtration of the solution followed by removal of the solvent in vacuo yielded a colorless oil in essentially quantitative yield by ^{1}H NMR; the compound can be obtained as a white precipitate when the reaction is performed on a larger scale: ^{1}H NMR δ 7.06 (H_m), 6.91 (H_p), 3.59 ($C\mathit{H}Me_2$), 2.40 (br, 2, α CH_2), 2.23 (br, 2, β CH_2), 1.52 (br, 2, γ CH_2), 1.22 ($CH\mathit{Me}_2$), 0.97 ($C\mathit{Me}_2$); ^{13}C NMR δ 157.5 (C_{ipso}), 137.5 (C_o), 123.6 (C_m), 122.5 (C_p), 82.1 (s, $\mathit{C}Me_2$), 66.9 (t, J_{CH} = 122, α CH_2), 45.4 (t, J_{CH} = 123, β CH_2), 37.5 ($C\mathit{Me}_2$), 29.5 ($CH\mathit{Me}_2$), 27.4 ($\mathit{C}HMe_2$), 23.9 (t, J_{CH} = 127, γ CH_2). Anal. Calcd for $TaC_{42}H_{63}O_4$: C, 62.06; H, 7.81. Found: C, 61.99; H, 7.95.

Ta[CH$_2$CH$_2$CH$_2$CH(*t*-Bu)O](DIPP)$_3$ (19). Pivaldehyde (29 μL, 0.27 mmol) was added to a stirred solution of Ta($CH_2CH_2CH_2$)(DIPP)$_3$ (0.20 g, 0.26 mmol) in ether (5 mL) at −30 °C. After the reaction mixture was left to stand overnight at room temperature, the solvent was removed in vacuo, leaving behind a colorless oil in essentially quantitative yield by NMR. The product could not be obtained in crystalline form, even when the reaction was performed on a large scale: ^{1}H NMR δ 7.07 (H_m), 6.92 (H_p), 4.09 (d of d, 1, J_{HH} = 1.9 and 11.4, $C\mathit{H}CMe_3$), 3.58 ($C\mathit{H}Me_2$), 3.11 (m, 1, α CH_2), 2.63 (d of t, 1, J_{HH} unresolved, α CH_2), 1.9–1.5 (multiplet, 4, β CH_2 and γ CH_2), 1.23 (18, $CH\mathit{Me}_2$), 1.19 (18, $CH\mathit{Me}_2$), 0.71 ($CHC\mathit{Me}_3$); ^{13}C NMR δ 157.1 (C_{ipso}), 137.7 (C_o), 123.6 (C_m), 122.7 (C_p), 91.8 (d, J_{CH} = 140, $\mathit{C}HCMe_3$), 66.8 (t, J_{CH} = 123, α CH_2), 35.1 ($CH\mathit{C}Me_3$), 33.3 (t, J_{CH} = 123, β CH_2), 27.6 (t, J_{CH} = 129, γ CH_2), 27.4 ($\mathit{C}HMe_2$), 26.0 ($CHC\mathit{Me}_3$), 24.3 ($CH\mathit{Me}_2$), 24.1 ($CH\mathit{Me}_2$).

X-ray Structure of Ta[CH(Pb)CH(*t*-Bu)CH$_2$](DIPP)$_3$ (7). Data were collected at −65 °C on an Enraf-Nonius CAD4F-11 diffractometer equipped with a liquid-nitrogen low-temperature device and with Mo Kα radiation. Axial photographs were taken on the diffractometer about each of the reciprocal axes to check that the unit cell lengths were correct. The program TRACER run on the unit cell (which was calculated with 25 high-angle reflections (2θ > 30°)) revealed no higher symmetry. Data collection, reduction, and refinement procedures can be found elsewhere.[27] A total of 11816 reflections were collected in the range 3° < 2θ < 45° with the 7831 having $F_o > 4\sigma(F_o)$ being used in the structure refinement which was carried out in two blocks (224 variables each) with SHELX-76. Final R_1 = 0.084 and R_2 = 0.115. A semiempirical absorption correction was applied (μ = 5.8 cm^{-1}). Two crystallographically independent but closely analogous molecules are present in the asymmetric unit. Only the Ta atoms were refined anisotropically. Most hydrogen atoms could be placed in calculated positions (C–H = 0.95 Å) and constrained to ride on their respective carbon atoms. Hydrogen atoms on the TaC_3 ring carbon atoms could not be located and were ignored. A final difference Fourier map showed no significant features. The crystal data are the following: space group $P2_1/n$ with a = 21.338 (11) Å, b = 11.699 (5) Å, c = 37.198 (23) Å, β = 102.66 (5)°, Z = 8, M_r 887.03 g, V = 9060.1 Å^3, ρ(calcd) = 1.301 g cm^{-3}.

X-ray Structure of Ta[CH(C_5H_8)CHCH(*t*-Bu)](DIPP)$_3$ (13). Data were collected at −65 °C on an Enraf-Nonius CAD4F-11 diffractometer equipped with a liquid-nitrogen low-temperature device and with Mo Kα radiation. Data collection, reduction, and refinement procedures have been detailed elsewhere.[27] A total of 7749 reflections (+h,+k,±l) were collected in the range 3° ≤ 2θ ≤ 50° with the 4679 having $F_o > 4\sigma(F_o)$ being used in the structure refinement which was by full-matrix least-squares techniques (278 variables) with SHELX-76 with final R_1 = 0.068 and R_2 = 0.061. The tantalum and all the non-hydrogen atoms of the metallacyclobutane ring were refined anisotropically. All remaining non-hydrogen atoms in the complex were refined isotropically. The three hydrogen atoms on the metallacyclobutane ring were omitted, but all remaining hydrogen atoms were placed in calculated positions and were constrained to ride on their respective carbon atoms. A final difference-Fourier map showed no chemically significant features. The crystal data are the following: space group $P2_1/n$, a = 11.587 (4) Å, b = 20.795 (4) Å, c = 18.388 (4) Å, Z = 4, M_r 877.03 g, V = 4416.6 Å^3, ρ(calcd) = 1.319 g cm^{-3}, μ = 24.0 cm^{-1}. A semiempirical absorption correction was applied.

Preparation of Polynorbornene with 5, 6, 12, and 13. In a typical reaction, a solution of **13** (20 mg) in toluene was mixed with a solution of norbornene in toluene such that the total volume was 15–20 mL. The resulting solution was heated in an oil bath to 65 °C, and the reaction was monitored by GLC. After all norbornene was consumed, excess benzaldehyde or acetone (~50 μL) was added, and the mixture was heated to 65 °C for another 15 min. The solvent was removed in vacuo and the polymer sample was rinsed with 20–30 mL of methanol (containing a small amount of BHT, 2,6-di-*tert*-butyl-4-methylphenol) and dried in vacuo. When **5** was employed as the catalyst, the polymerization and capping reactions were done at 25 °C.

Kinetics of Polymerization of Norbornene. Stock solutions of norbornene in benzene-d_6 and the catalyst (e.g., **13**) in benzene-d_6 (with a few equivalents of mesitylene as internal standard) were prepared. In a typical run, aliquots of each solution were added to an NMR tube and additional benzene-d_6 added such that the total volume was 1 mL. The NMR tube was sealed and kept at −30 °C. The sample was placed in the probe of a Varian XL-300 NMR spectrometer maintained at the

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(26) Pearson, D. E.; Caine, D.; Field, L. *J. Org. Chem.* **1960**, *25*, 867.

(27) Silverman, L. D.; Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 3379.

J. Am. Chem. Soc. **1988**, *110*, 4977-4982

reaction temperature (determined before and after the run with ethylene glycol). After allowing 10 min for equilibration of the sample, and after all the initial **13** had been consumed, the disappearance of the olefinic protons of norbornene was monitored relative to the internal standard. A plot of [NBE] versus time gave k_{obsd}, where $k_{obsd} = k_1[\mathbf{13}]$. All runs were monitored for at least 3 half-lives, and in all cases acceptable R values were obtained from the subsequent kinetic plots. An analogous procedure was employed for the reactions of **12** and **6** with norbornene, except that the signal from C_6D_5H was utilized as the internal standard. For **6**, a plot of ln [NBE] versus time gave $k_{obsd}[\mathbf{6}]$. For the reaction of **15** with NBE-*2,3-d*$_2$, samples were prepared as described above employing stock solutions of NBE-*2,3-d*$_2$ in toluene-d_8 and **15** in benzene-d_6. The rate of ring opening of **15** was determined by monitoring the disappearance of the α proton at 5.23 ppm.

Capping Living Polymers; Spin Simulation Experiments. A sample of **14** ($x_{av} = 7$) was treated with 3 equiv of benzaldehyde in C_6D_6 at 65 °C. A ^{1}H NMR spectrum of the resulting $PhH_AC{=}CH_B[C_5H_8CH{=}CH]_x$-*t*-Bu displayed olefinic resonances in the region 6.0–6.5 ppm for H_A and H_B (Figure 5b). On the basis of related studies[28] in which only the trans isomer (of the phenyl-substituted capping olefin group) is observed, the resonances at 6.38 and 6.33 ppm were assigned to H_A, and those at 6.18–6.10 ppm were assigned to H_B of the trans isomer. Using the values $\delta\ H_A = 1905$ Hz and $\delta\ H_B = 1841$ Hz at 300 MHz, $J_{AB} = 16$ Hz and $J_{BX} = 8$ Hz (H_X is the first cyclopentyl tertiary proton), a theoretical spectrum for the trans isomer was calculated (Figure 6a), utilizing a software program based on the iterative spin simulation program LAME. The results of the calculated spectrum suggest that resonances for $H_{A,cis}$ isomer overlap with those for $H_{A,trans}$ isomer between 6.30 and 6.45 ppm in the observed spectrum (Figure 6b). The resonances for $H_{B,cis}$ isomer are assumed to occur upfield of those for $H_{B,trans}$ resonances at 6.18–6.10 ppm and are obstructed by polynorbornene resonances at ~5.2–5.6 ppm. This type of shift is generally observed for an olefinic proton trans to a phenyl group ($H_{B,cis}$) relative to one cis to a phenyl group ($H_{B,trans}$). For example, using a general formula,[29] $H_{B,cis}$ is calculated to resonate at 5.62 ppm, while $H_{B,trans}$ is calculated to resonate at 6.09 ppm, consistent with what we propose. Utilizing the above data the trans/cis capped polymer ratio can be easily determined by comparing the integrations of the resonances at 6.30–6.45 ppm ($H_{A,trans}$ plus $H_{A,cis}$) with those for the resonances at 6.18–6.10 ppm ($H_{B,trans}$). In this way the double bond formed by reaction of **14** with benzaldehyde was determined to be 68% trans and 32% cis. In an analogous manner the terminal double bond formed by reaction of $Ta[(CHC_5H_8CH)_xCH$-*t*-Bu](TIPT)$_3$(THF) ($x_{av} = 10$) with 3 equiv of benzaldehyde in C_6D_6 at 25 °C was determined to be 64% cis and 36% trans.

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Supplementary Material Available: Tables of final atomic coordinates and temperature factors and a fully labeled figure for $Ta[CH(C_5H_8)CHCH($*t*-Bu$)](DIPP)_3$ (5 pages); listing of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page. Supplementary material for $Ta[CH(Ph)CH($*t*-Bu$)CH_2](DIPP)_3$ was provided in a preliminary communication.[14a]

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[28] Krouse, S. A., unpublished results.

[29] Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; John Wiley and Sons: New York, 1981; p 227.

Titanium(III) Tetrahydroborates. Preparation and Crystal Structure of $Ti(BH_4)_3(PMe_3)_2$ Containing an Unusual Ti···H···B Agostic Interaction

James A. Jensen, Scott R. Wilson, and Gregory S. Girolami*

Contribution from the School of Chemical Sciences, The University of Illinois at Urbana—Champaign, 505 South Mathews, Urbana, Illinois 61801.

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Abstract: The reaction of trialkylphosphines with $Ti(BH_4)_3(Et_2O)$, prepared in situ from $TiCl_4$ and $LiBH_4$ in diethyl ether, gives dark blue adducts of stoichiometry $Ti(BH_4)_3(PR_3)_2$, where PR_3 is PMe_3, PEt_3, PMe_2Ph, or $P(OMe)_3$. Magnetic susceptibility and ESR measurements indicate that these are monomeric titanium(III) species. An X-ray crystal structure of $Ti(BH_4)_3(PMe_3)_2$ (orthorhombic; *Pnma*; $a = 10.757$ (1), $b = 11.145$ (2), $c = 14.270$ (3) Å; $V = 1710.8$ (8) Å^3; $Z = 4$; $R_F = 6.4\%$; $R_{wF} = 4.8\%$) reveals an approximate trigonal-bipyramidal geometry, with the phosphines occupying the axial positions: Ti–P = 2.571 (3), 2.539 (3) Å; P–Ti–P = 170.27 (9)°. One of the three equatorial BH_4^- groups is bidentate, $Ti–H_b = 1.90$ (6) Å, Ti···B = 2.40 (1) Å, $B–H_b = 1.03$ (7) Å, B–H = 1.00 (8) Å, whereas the other two BH_4^- groups possess unusual geometries involving interaction of the titanium center with one B–H bond in a "side-on" manner, $Ti–H_b = 1.73$ (7) Å, Ti–B = 2.27 (1) Å, $B–H_b = 0.95$ (6) Å, $B–H_t = 0.96$ (6) Å. This unusual interaction may be a type of Jahn–Teller distortion and closely resembles one proposed transition state for the activation of the isoelectronic molecule methane.

Titanium trichloride and triethylaluminum are the key components of industrial catalysts for the polymerization of olefins.[1-3] The actual active species in these systems are thought to be titanium alkyls that are able to insert olefins sequentially into the Ti–C bond. Although it is not known with certainty which oxidation state of titanium is primarily responsible for the polymerization catalysis, several studies indicate that there is a correlation between the concentration of trivalent titanium and the rate of polymerization.[4-7] Despite the uncertainty in oxidation state,

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[1] Boor, J. *Ziegler-Natta Catalysts and Polymerizations*; Academic: New York, 1979.

[2] Gavens, P. D.; Bottrill, M.; Kelland, J. W.; McMeeking, J. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Chapter 22-5.

[3] Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99–149.

[4] Adema, E. H. *J. Polym. Sci., Part C* **1968**, *16*, 3643–3645.