

Hydrogen-Transfer Reactions Which Generate New Imine, Imido, and Trimethylenemethane Complexes of Tantalum

James M. Mayer,¹ Calvin J. Curtis,² and John E. Bercaw*³

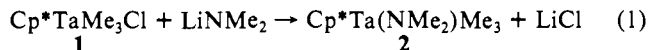
Contribution No. 6722 from the Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125. Received September 17, 1982

Abstract: The reactions of $\text{Cp}^*\text{TaMe}_3\text{Cl}$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) with a variety of alkali-metal alkoxide, alkylamide, and alkyl reagents have been examined. Reaction with LiNMe_2 produces $\text{Cp}^*\text{Ta}(\text{NMe}_2)_3$, which decomposes at 25 °C to an imine (or metallaazirane) complex, $\text{Cp}^*\text{Ta}(\text{CH}_2\text{NMe})\text{Me}_2$. The decomposition is a first-order, unimolecular process with a large kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} = 9.7$). Monoalkylamides (LiNHR) react with $\text{Cp}^*\text{TaMe}_3\text{Cl}$ to form imido complexes $\text{Cp}^*\text{Ta}(\text{NR})\text{Me}_2$. Reaction of $\text{Cp}^*\text{TaMe}_3\text{Cl}$ with lithium diisopropylamide forms a bridging methylene complex, $\text{Cp}^*\text{Ta}(\mu\text{-CH}_2)(\mu\text{-H})_2\text{TaMe}_2\text{Cp}^*$. The alkoxide compounds $\text{Cp}^*\text{Ta}(\text{OR})\text{Me}_3$ ($\text{R} = \text{Me}, \text{CHMe}_2, \text{CMe}_3$) are very stable and decompose only over 100 °C. Alkyl complexes are stable only if the alkyl group does not have β -hydrogens. Treatment of $\text{Cp}^*\text{TaMe}_3\text{Cl}$ with (2-methylallyl)magnesium bromide affords an unstable tantalum 2-methylallyl compound, which decomposes cleanly to the trimethylenemethane complex $\text{Cp}^*\text{TaMe}_2[\eta^4\text{-C}(\text{CH}_2)_3]$. The rates of hydrogen abstraction or elimination processes in this system correlate with the nature of the atom bound to tantalum: for reactions involving a β -hydrogen transfer the order is $\text{C} > \text{N} > \text{O}$, while the facility of α -hydrogen abstraction reactions appear to decrease in the reverse order $\text{N} > \text{C}$. These reactivity patterns appear to reflect the variance in Ta-C, Ta-N, and Ta-O bond energies in this series. Hydrogenation of the imido compounds ($\text{Cp}^*\text{Ta}(\text{NR})\text{Me}_2$) in the presence of phosphine ligands yields new examples of imido hydride complexes $\text{Cp}^*\text{Ta}(\text{NR})\text{H}_2(\text{L})$ ($\text{L} = \text{PMe}_3, \text{PMe}_2(\text{C}_6\text{H}_5)$; $\text{R} = \text{CMe}_3, \text{CH}_2\text{CMe}_3$). A moderately stable alkyl hydride complex, $\text{Cp}^*\text{Ta}(\text{CH}_2\text{NMe})\text{Me}(\text{PMe}_3)\text{H}$, has also been prepared.

Whereas the transformations of hydrocarbon ligands are a primary focus of organotransition-metal chemistry,⁴ those involving organic groups bonded to the metal center through elements other than carbon have received relatively little attention. For example, the reactions of metal alkyl complexes with dihydrogen have been investigated for many years,⁵⁻⁸ but the first clear example of hydrogenolysis of a metal-alkoxide bond has only recently been reported.⁹ α - and β -hydrogen elimination processes have been extensively studied for alkyl ligands,^{10,11} but there are few examples of hydrogen-transfer reactions from dialkylamide or alkoxide ligands. We report herein the synthesis and reactivity of a series of alkyl, allyl, amide, and alkoxide complexes of tantalum. The properties of these compounds depend to a large extent on whether or not an α - or β -hydrogen is present and on the type of atom bound to tantalum.

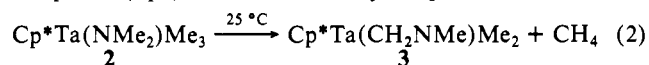
Results

The starting material for the compounds prepared in this study is $\text{Cp}^*\text{TaMe}_3\text{Cl}$, **1** ($\text{Me} \equiv \text{CH}_3$, $\text{Cp}^* \equiv \eta^5\text{-C}_5\text{Me}_5$).¹² Compound **1** reacts rapidly with lithium dimethylamide at 0 °C in diethyl ether to give the expected product $\text{Cp}^*\text{Ta}(\text{NMe}_2)_3$ (**2**), identified by its ¹H and ¹³C NMR spectra (see Table I). **2** can be

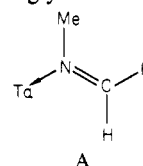


isolated in good yield at 0 °C or below, but at ambient temperatures it decomposes in solution or in the solid state to an imine complex, **3** (eq 2). The stoichiometry of eq 2 has been confirmed

by quantitatively collecting the methane formed and identifying it by IR spectroscopy. The imine complex **3** may be isolated as a microcrystalline material, which has been characterized by IR and NMR spectroscopy, elemental analysis, and a molecular weight measurement. The ¹³C NMR spectrum of **3** indicates the presence of a methylene carbon (δ 65.46 (t, $^1J_{\text{CH}} = 155$ Hz)), in addition to the Cp^* ligand and methyl groups on both tantalum and nitrogen. The high-field chemical shift of the methylene carbon, the low-energy C-N stretch (1265 cm^{-1}), and the equivalence of the methylene hydrogen atoms argue against an η^1 structure (A) and strongly indicate that the imine ligand is



bound to the tantalum through both the carbon and nitrogen atoms.¹³ Such an η^2 geometry has been found crystallographically for a tungsten imine complex,¹⁴ and similar structures have been proposed for imine complexes of tantalum,¹⁵ zirconium,¹⁶ titanium,¹⁷ and group 8 metals.¹⁸ An analogous tantalum acetone



bound to the tantalum through both the carbon and nitrogen atoms.¹³ Such an η^2 geometry has been found crystallographically for a tungsten imine complex,¹⁴ and similar structures have been proposed for imine complexes of tantalum,¹⁵ zirconium,¹⁶ titanium,¹⁷ and group 8 metals.¹⁸ An analogous tantalum acetone

(1) National Science Foundation Predoctoral Fellow, 1978-1981. Present address: Experimental Station E328, E. I. du Pont de Nemours and Company, Wilmington, DE 19898.

(2) Present address: Solar Energy Research Institute, 1617 Cole Boulevard, Golden, CO 80401.

(3) Camille and Henry Dreyfus Teacher-Scholar, 1977-1982.

(4) (a) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980. (b) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978.

(5) Reference 4a, pp 316-384.

(6) Schrock, R. R.; Parshall, G. W. *Chem. Rev.* **1976**, *76*, 243-268.

(7) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 2488-9 and references therein.

(8) Gell, K. I.; Posin, B.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846-1855 and references therein.

(9) Goeden, G. V.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 7354-5.

(10) Reference 4b, pp 246-258, 285-292, and ref 6.

(11) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.

(12) McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 4558.

(13) The chemical shift of the imine carbon (δ 65.46) is close to the range expected for amines ($\text{RCH}_2\text{NR}'_2$, $\delta \sim 50 \pm 10$). We have been unable to find ¹³C NMR data on imines, but aldehyde carbon atoms usually are far downfield (δ 200 \pm 10). Leyden, D. E.; Cox, R. H. "Analytical Applications of NMR"; Wiley Interscience: New York, 1977; p 196.

(14) Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1981**, 2088-2097. Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1980**, *102*, 7979-7980.

(15) (a) Takahashi, Y.; Onoyama, N.; Ishikawa, Y.; Motojima, S.; Sugiyama, K. *Chem. Lett.* **1978**, 525-528. (b) Airoldi, C.; Bradley, D. C.; Vuru, G. *Transition Met. Chem. (Weinheim, Ger.)* **1979**, *4*, 64.

(16) Wolczanski, P. T.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 6450-6452.

(17) Klei, E. Thesis, Rijksuniversiteit, Groningen, The Netherlands, 1981.

(18) (a) Walther, D. Z. *Anorg. Allg. Chem.* **1977**, *431*, 17-30. (b) Browning, J.; Empsall, H. D.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 381-7.

Table I. ^1H and ^{13}C NMR Data^a

compd	assignmt	chemical shift, multiplicity, coupling const	
		^1H NMR	^{13}C NMR
Cp*Ta(NMc ₂)Me ₃ (2) ^b	C ₅ (CH ₃) ₅	1.62 s	10.95 q, $^1J_{\text{CH}} = 127$ Hz
	C ₅ (CH ₃) ₅		113.12 s
	N(CH ₃) ₂	2.37 s	40.90 q, $^1J_{\text{CH}} = 135$ Hz
	Ta(CH ₃)(CH ₃) ₂	0.67 s	51.30 ^c
	Ta(CH ₃)(CH ₃) ₂	0.17 s	45.67 q, $^1J_{\text{CH}} = 112$ Hz
Cp*Ta(CH ₂ NMe)Me ₃ (3) ^d	C ₅ (CH ₃) ₅	1.68 s	10.46 q, $^1J_{\text{CH}} = 127$ Hz
	C ₅ (CH ₃) ₅		115.01 s
	Ta(CH ₃) ₂	0.05 s	51.98 q, $^1J_{\text{CH}} = 118$ Hz
	Ta(CH ₂ NMe)	2.06 s	65.46 t, $^1J_{\text{CH}} = 155$ Hz
	Ta(CH ₂ NCH ₃)	3.91 s	47.20 q, $^1J_{\text{CH}} = 134$ Hz
Cp*Ta(CH ₂ NCH ₂ CH ₂ CH ₃)Me ₂ (4)	C ₅ (CH ₃) ₅	1.73 s	10.59 q, $^1J_{\text{CH}} = 127$ Hz
	C ₅ (CH ₃) ₅		115.17 s
	Ta(CH ₃) ₂	-0.09 s	51.07 q, $^1J_{\text{CH}} = 118$ Hz
	Ta(CH ₂ NCH ₂ CH ₂ CH ₃)	1.83 s	58.22 t, $^1J_{\text{CH}} = 153$ Hz
	Ta(CH ₂ NCH ₂ CH ₂ CH ₃)	4.09 t, $^3J_{\text{HH}} = 7$ Hz	59.96 tt, $^1J_{\text{CH}} = 134$ Hz, $^2J_{\text{CH}} = 5$ Hz
	Ta(CH ₂ NCH ₂ CH ₂ CH ₃)	1.09 m	23.51 q, $^1J_{\text{CH}} = 123$ Hz
	Ta(CH ₂ NCH ₂ CH ₂ CH ₃)	0.96 t, $^3J_{\text{HH}} = 7$ Hz	12.28 q, $^1J_{\text{CH}} = 130$ Hz
	Ta(CH ₂ NCH ₂ CH ₂ CH ₃)	1.88 s	11.19 q, $^1J_{\text{CH}} = 127$ Hz
Cp*Me ₂ Ta(μ-CH ₂)(μ-H) ₂ TaMe ₂ Cp* (5)	C ₅ (CH ₃) ₅		116.59 s
	C ₅ (CH ₃) ₅	0.17 s	44.15 q, $^1J_{\text{CH}} = 120$ Hz
	Ta(CH ₃) ₂	9.72 t, $^3J_{\text{HH}} = 6$ Hz	
	Ta(μ-H) ₂ Ta	0.54 t, $^3J_{\text{HH}} = 6$ Hz	135.76 t, $^1J_{\text{CH}} = 123$ Hz
	Ta(μ-CH ₂)Ta	1.83 s	11.14 q, $^1J_{\text{CH}} = 127$ Hz
Cp*Ta(NCMe ₃)Me ₂ (6)	C ₅ (CH ₃) ₅		115.72 s
	C ₅ (CH ₃) ₅		43.12 q, $^1J_{\text{CH}} = 118$ Hz
	Ta(CH ₃) ₂	0.13 s	64.14 s
	Ta(NCMe ₃)		33.81 q-sept, $^1J_{\text{CH}} = 125$ Hz, $^3J_{\text{CH}} = 4$ Hz
	Ta[NC(CH ₃) ₃]	1.42 s	10.62 q, $^1J_{\text{CH}} = 127$ Hz
Cp*Ta(NCH ₂ CMe ₃)Me ₂ (7)	C ₅ (CH ₃) ₅	1.76 s	
	C ₅ (CH ₃) ₅		114.94 s
	Ta(CH ₃) ₂	0.19 s	44.36 q, $^1J_{\text{CH}} = 118$ Hz
	Ta(NCH ₂ CMe ₃)	3.91 s	70.94 tm, $^1J_{\text{CH}} = 133$ Hz, $^3J_{\text{CH}} = 4$ Hz
	Ta(NCH ₂ CMe ₃)		35.53 s
	Ta[NCH ₂ C(CH ₃) ₃] q	1.13 s	27.92 qm, $^1J_{\text{CH}} = 125$ Hz, $^3J_{\text{CH}} = 5$ Hz
Cp*Ta(NMe)Me ₂ (8)	C ₅ (CH ₃) ₅	1.78 s	10.46 q, $^1J_{\text{CH}} = 127$ Hz
	C ₅ (CH ₃) ₅		114.78 s
	Ta(CH ₃) ₂	0.14 s	43.96 q, $^1J_{\text{CH}} = 118$ Hz
	Ta(NCH ₃)	3.97 s	46.43 q, $^1J_{\text{CH}} = 133$ Hz
	C ₅ (CH ₃) ₅	1.75 s	11.05 q, $^1J_{\text{CH}} = 127$ Hz
Cp*Ta(OCHMe ₂)Me ₃ (11)	C ₅ (CH ₃) ₅		115.60 s
	Ta(CH ₃) ₂ (CH ₃)'		49.91 q, $^1J_{\text{CH}} = 119$ Hz
	Ta(CH ₃) ₂ (CH ₃)'	0.45 br s	53.94 q, $^1J_{\text{CH}} = 120$ Hz
	Ta(OCHMe ₂)	4.53 septet, $^3J_{\text{HH}} = 6$ Hz	75.71 d-sept, $^1J_{\text{CH}} = 144$ Hz, $^2J_{\text{CH}} = 4$ Hz
	Ta[OCH(CH ₃) ₂]	1.14 d, $^3J_{\text{HH}} = 6$ Hz	24.89 q, $^1J_{\text{CH}} = 126$ Hz
	C ₅ (CH ₃) ₅	1.72 s	10.98 q, $^1J_{\text{CH}} = 127$ Hz
Cp*Ta(OMe)Me ₃ (12) ^e	C ₅ (CH ₃) ₅		115.91 s
	Ta(CH ₃) ₂ (CH ₃)'		52.46 q, $^1J_{\text{CH}} = 119$ Hz
	Ta(CH ₃) ₂ (CH ₃)'	0.46 br s	54.97 q, $^1J_{\text{CH}} = 119$ Hz
	Ta(OCH ₃)	3.95 s	59.92 q, $^1J_{\text{CH}} = 143$ Hz

Cp*Ta(CH ₂ CMe ₃)Me ₃ (13)	C ₅ (CH ₃) ₅	1.67 s	11.36 q, ¹ J _{CH} = 128 Hz
	C ₅ (CH ₃) ₅		117.93 s
	Ta(CH ₃) ₃	0.71 br s	71.90 q, ¹ J _{CH} = 119 Hz
	Ta(CH ₂ CMe ₃)	0.30 br s	74.29 t, ¹ J _{CH} = 118 Hz
	Ta(CH ₂ CMe ₃)		35.19 s
Cp*Ta(CH ₂ C ₆ H ₅)Me ₃ (14)	Ta[CH ₂ C(CH ₃) ₃]	1.35 s	35.84 q-sept, ¹ J _{CH} = 124 Hz, ³ J _{CH} = 5 Hz
	C ₅ (CH ₃) ₅	1.66 s	11.31 q, ¹ J _{CH} = 128 Hz
	C ₅ (CH ₃) ₅		118.99 s
	Ta(CH ₃) ₃	0.67 s	76.3 br q, ¹ J _{CH} = 120 Hz
	Ta(CH ₂ C ₆ H ₅)	1.63 s	96.25 t, ¹ J _{CH} = 120 Hz
	Ta(CH ₂ C ₆ H ₅)	7.3 m	148.50 s
			127.51 dd, ¹ J _{CH} = 157 Hz, ² J _{CH} = 6 Hz
			122.89 d, ¹ J _{CH} = 157 Hz
			101.58 d ^c
Cp*Ta(η ³ -CH ₂ CMeCH ₂)Me ₃ (15) ^f	C ₅ (CH ₃) ₅	1.64 s	
	Ta(CH ₃) ₃	0.73 s	
	Ta(CH ₂ CMeCH ₂)	2.84 s	
Cp*Ta[η ⁴ -C(CH ₂) ₃]Me ₂ (16) ^g	Ta[CH ₂ C(CH ₃)CH ₂]	2.00 s	
	C ₅ (CH ₃) ₅	1.52 s	11.0
	C ₅ (CH ₃) ₅		115.8
	Ta(CH ₃) ₂	-0.04 s	41.0
		4.10 d, ² J _{HH} = 5 Hz	64.5
	Ta[(CHH ^h) ₂ CCH ₂] ^h	0.50 d, ² J _{HH} = 5 Hz	
	Ta[(CH ₂) ₂ CCH ₂] ^h		133.8
	Ta[(CH ₂) ₂ CCH ₂] ^h	1.35 s	91.4
	Ta[C(CH ₂) ₃] ^g		134.1
	Ta[C(CH ₂) ₃] ^g	1.71 s	74.9
Cp*Ta(NCMe ₃)H ₂ (PMe ₃) (17)	C ₅ (CH ₃) ₅	2.18 s	12.71 q, ¹ J _{CH} = 126 Hz
	C ₅ (CH ₃) ₅		110.10 s
	TaH ₂	6.00 d, ² J _{PH} = 61 Hz	
	Ta[P(CH ₃) ₃]	1.25 d, ² J _{PH} = 6 Hz	21.28 qd, ¹ J _{CH} = 128 Hz, ¹ J _{PC} = 24 Hz
	Ta(NCMe ₃)		64.34 s
Cp*Ta(NCMe ₃)H ₂ (PMe ₂ C ₆ H ₅) (18)	Ta[NC(CH ₃) ₃]	1.22 s	34.73 q-sept, ¹ J _{CH} = 125 Hz, ³ J _{CH} = 4 Hz
	C ₅ (CH ₃) ₅	2.06 s	12.46 q, ¹ J _{CH} = 126 Hz
	C ₅ (CH ₃) ₅		110.32 s
	TaH ₂	6.38 d, ² J _{PH} = 59 Hz	
	Ta[P(CH ₃) ₂ C ₆ H ₅]	1.63 d, ² J _{PH} = 7 Hz	21.78 qd, ¹ J _{CH} = 130 Hz, ¹ J _{PC} = 25 Hz
	Ta(PMe ₂ C ₆ H ₅)	7.51 m	138.53 d, ¹ J _{PC} = 29 Hz
		7.05 m	131.08 dd, ^c ¹ J _{PC} = 10 Hz
			128.78 ^c
			128.1 ^c
			64.47 s
			34.65 qd, ¹ J _{CH} = 126 Hz, ⁴ J _{PC} = 2 Hz
Cp*Ta(NCH ₂ CMe ₃)H ₂ (PMe ₃) (19) ^f	Ta[NC(CH ₃) ₃]	1.30 s	
	C ₅ (CH ₃) ₅	2.17 s	
	TaH ₂	6.37 d, ² J _{PH} = 59 Hz	
	Ta[P(CH ₃) ₃]	1.23 d, ² J _{PH} = 7 Hz	
	Ta(NCH ₂ CMe ₃)	3.43 d, ⁴ J _{PH} = 5 Hz	
Cp*Ta(NCH ₂ CMe ₃)H ₂ (PMe ₂ C ₆ H ₅) (20)	Ta[NCH ₂ C(CH ₃) ₃]	0.99 s	
	C ₅ (CH ₃) ₅	2.02 s	11.90 q, ¹ J _{CH} = 127 Hz
	C ₅ (CH ₃) ₅		109.84 s
	TaH ₂	6.62 d, ² J _{PH} = 58 Hz	
	Ta[P(CH ₃) ₂ C ₆ H ₅]	1.63 d, ² J _{PH} = 7 Hz	21.06 qd, ¹ J _{CH} = 130 Hz, ¹ J _{CP} = 24 Hz
	Ta(PMe ₂ C ₆ H ₅)	7.48 m	138.40 d, ¹ J _{CP} = 29 Hz
		7.03 m	131.11 dd, ¹ J _{CH} = 155 Hz, ¹ J _{CP} = 9 Hz
			128.83 dd, ^c ¹ J _{CP} = 2 Hz
			128.2 d, ¹ J _{CH} = 160 Hz

Table I (Continued)

compd	assignt	chemical shift, multiplicity, coupling const	
		¹ H NMR	¹³ C NMR
20 (continued)	Ta(NCH ₂ CMe ₃)	3.10 d, ⁴ J _{PH} = 5 Hz	72.14 td, ¹ J _{CH} = 131 Hz, ³ J _{CP} = 2 Hz
	Ta(NCH ₂ CMe ₃)		32.70 s
	Ta[NCH ₂ C(CH ₃) ₃]	1.02 s	27.63 q-sept, ¹ J _{CH} = 124 Hz, ³ J _{CH} = 4 Hz
Cp*Ta(NCMe ₃)(OCHMe ₂) ₂ (21) ^f	C ₅ (CH ₃) ₅	2.05 s	
	Ta(OCHMe ₂) ₂	4.87 sept, ³ J _{HH} = 6 Hz	
	Ta[OCH(CH ₃) ₂] ₂	1.30 d, ³ J _{HH} = 6 Hz	
	Ta[NC(CH ₃) ₃]	1.29 s	
	C ₅ (CH ₃) ₅	2.00 s	10.75 q, ¹ J _{CH} = 127 Hz
Cp*Ta(NCH ₂ CMe ₃)(OCHMe ₂) ₂ (22)	C ₅ (CH ₃) ₅		116.11 s
	Ta(OCHMe ₂) ₂	4.86 sept, ³ J _{HH} = 6 Hz	76.37 dm, ¹ J _{CH} = 142 Hz, ² J _{CH} = 4 Hz
	Ta[OCH(CH ₃)(CH ₃)'] ₂	1.30 d, ³ J _{HH} = 6 Hz	27.61 qm, ¹ J _{CH} = 125 Hz, ² J _{CH} = 5 Hz
	Ta[OCH(CH ₃)(CH ₃)'] ₂	1.27 d, ³ J _{HH} = 6 Hz	27.17 q, ¹ J _{CH} = 125 Hz
	Ta(NCH ₂ CMe ₃)	3.93 s	69.91 t, ¹ J _{CH} = 129 Hz
	Ta(NCH ₂ CMe ₃)		33.59 s
	Ta[NCH ₂ C(CH ₃) ₃]	1.02 s	27.61 qm, ¹ J _{CH} = 125 Hz, ² J _{CH} = 5 Hz
	C ₅ (CH ₃) ₅	1.93 s	11.66 q, ¹ J _{CH} = 127 Hz
	C ₅ (CH ₃) ₅		111.00 s
	Ta(CH ₃)	-0.41 dd, ³ J _{PH} = 15 Hz, ³ J _{HH} = 5 Hz	18.66 qd, ^c ² J _{CP} = 11 Hz
Cp*Ta(CH ₂ NMe)Me(PMe ₃)H (23) ⁱ	Ta[P(CH ₃) ₃]	1.16 d, ² J _{PH} = 7 Hz	17.92 qdm, ¹ J _{CH} = 128 Hz, ¹ J _{CP} = 22 Hz, ³ J _{CH} = 4 Hz
	TaH	5.75 dq, ² J _{PH} = 60 Hz, ³ J _{HH} = 5 Hz	
	Ta(CHH'NMe)	2.28 m	46.35 td, ¹ J _{CH} = 152 Hz, ² J _{CP} = 17 Hz
	Ta(CH ₂ NCH ₃)	1.42 m	
	Ta(CH ₂ NCH ₃)	3.62 s	46.60 qd, ¹ J _{CH} = 134 Hz, ³ J _{CP} = 4 Hz
	C ₅ (CH ₃) ₅	1.84 s	10.68 q, ¹ J _{CH} = 127 Hz
	C ₅ (CH ₃) ₅		114.82 s
	Ta(CH ₃)	0.57 s	24.11 q, ¹ J _{CH} = 119 Hz
	Ta(OCHMe ₂)	4.23 sept, ³ J _{HH} = 6 Hz	74.79 d-sept, ¹ J _{CH} = 144 Hz, ² J _{CH} = 4 Hz
	Ta[OCH(CH ₃)(CH ₃)']	0.93 ^j d, ³ J _{HH} = 6 Hz	26.06 dq, ¹ J _{CH} = 126 Hz, ³ J _{CH} = 5 Hz
Cp*Ta(CH ₂ NMe)Me(OCHMe ₂) (24)	Ta[OCH(CH ₃)(CH ₃)']	0.93 ^j d, ³ J _{HH} = 6 Hz	25.89 dq, ¹ J _{CH} = 126 Hz, ³ J _{CH} = 5 Hz
	Ta(CHH'NMe)	1.02 d, ² J _{HH} = 4 Hz	37.12 t, ¹ J _{CH} = 153 Hz
	Ta(CHH'NMe)	1.44 d, ² J _{HH} = 4 Hz	
	Ta(CH ₂ NCH ₃)	3.80 s	42.66 q, ¹ J _{CH} = 133 Hz

^a NMR spectra taken in benzene-*d*₆ solvent at 34 °C unless otherwise noted. Chemical shifts in δ measured from internal Me₄Si. Long-range ¹³C-¹H coupling is reported only when a coupling constant could be determined from the pattern. ^b For data on compounds 9 and 10, see ref 19 and 39. ^c Spectra obtained at -40 °C in toluene-*d*₈. ^d Chemical shift determined from a proton-decoupled spectrum. Coupling constant(s) could not be determined due to overlapping resonances or insufficient signal to noise in the gated decoupled spectrum. ^e Spectra obtained at 3 °C. ^f ¹³C NMR spectrum obtained at 0 °C. The three tantalum-bound methyl groups are involved in a fluxional process with a coalescence temperature of 40 °C in the ¹³C NMR. ^g A ¹³C NMR spectrum was not obtained for this compound. ^h High-temperature limits. ⁱ Low-temperature limit. ^j The ³¹P NMR spectrum with selective proton decoupling at δ 1.16 (P(CH₃)₃) is a doublet of quartets. ^k Resonances separated by 0.003 ppm; resolved only at 500 MHz.

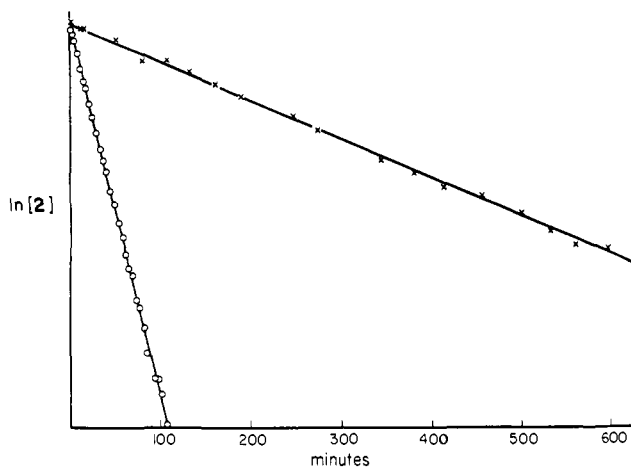
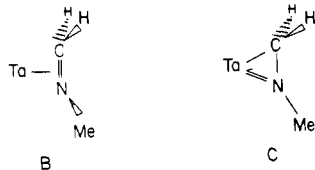


Figure 1. ln (concentration) vs. time plots for the decomposition of Cp*Ta(NMe₃)Me₃, **2** (circles), and Cp*Ta[N(CD₃)₂]Me₃, **2-d₆** (crosses), at 34 °C.

complex, Cp*Ta(OCMe₂)Me₂, is also thought to be bonded through both the carbon and oxygen atoms.¹⁹

Two limiting structures can be used to describe the η² bonding of the imine ligand (B and C). Whereas these resemble the



resonance structures drawn for olefin binding to a transition-metal center,²⁰ the presence of the nitrogen lone pair and its involvement in M–N bonding lead one to expect a distinct structural difference between the π-bonded form B and the metallacyclic form C: a coplanarity of Ta, N, the methylene carbon atom, and methyl carbon atom only for C.²¹ This distinction can be made by observing the proton NMR spectrum, since the two methylene hydrogen atoms are expected to be inequivalent in the π-bonded form B, as they are in uncoordinated methylenimines (RN=CH₂),²² whereas they may be equivalent for C. The ¹H NMR spectrum for **3** shows a single resonance for these two hydrogen atoms, even at –80 °C and 500 MHz. Hence, **3** is best described not as a π complex, but as in C, the metallacycle or metalated dimethylamide form. The NMR data further indicate that this metallacycle is oriented, as shown in the projection below, “perpendicular” to the plane of the Cp* ring (similar to an analogous benzyne complex²³) and not in the “parallel” geometry found for related ethylene,²⁴ acetylene,²⁵ and metallacyclopentane²⁶ derivatives.

(19) Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5421–2. The ¹H and ¹³C NMR spectra of **9** are not given in this paper; the spectral data (C₆D₆, 34 °C) are as follows: ¹H NMR δ 1.69 (s, Cp*), 0.63 (s, Ta(CH₃)₄); ¹³C NMR δ 114.78 (s, C₅(CH₃)₅), 11.28 (q, ¹J_{CH} = 128 Hz, C₅(CH₃)₅), 73.69 (q, ¹J_{CH} = 118 Hz, Ta(CH₃)₄).

(20) (a) Green, M. L. H. “Organometallic Compounds”; Chapman and Hall: London, 1968; Vol. 11, pp 13–19. (b) Reference 4a, pp 106–108.

(21) (a) Transition-metal dialkylamide complexes almost invariably have planar geometry about the nitrogen atom.^{19b,c} (b) Bradley, D. C.; Chisholm, M. H. *Acc. Chem. Res.* **1976**, *9*, 273–280. (c) Chisholm, M. H.; Haitko, D. A.; Foltz, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4046–53.

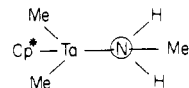
(22) (a) Sastry, K. V. L. N.; Curl, R. F. *J. Chem. Phys.* **1964**, *41*, 77. (b) Shapiro, B. L.; Ebersole, S. S.; Karabatsos, G. J.; Vane, F. M.; Manatt, S. L. *J. Am. Chem. Soc.* **1963**, *85*, 4041. (c) Patai, S., Ed. “The Chemistry of the Carbon-Nitrogen Double Bond”; Interscience: New York, 1970.

(23) (a) McLain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263. (b) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1697–1702.

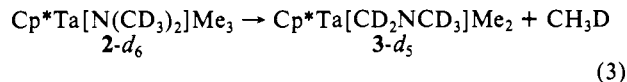
(24) Mentioned in ref 23b.

(25) Smith, G.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 387–93.

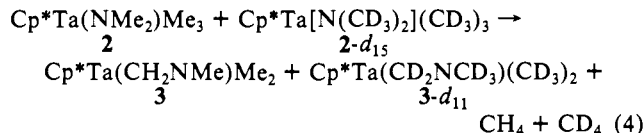
(26) Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 6462–3.



The decomposition of **2** to **3** (eq 2) obeys first-order kinetics for greater than 3 half-lives (Figure 1), with $k = 5.6 \times 10^{-4} \text{ s}^{-1}$ at 34 °C. **2-d₆** forms only CH₃D (eq 3), and a mixture of **2** and

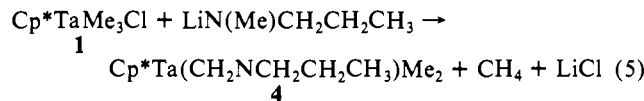


2-d₁₅ produces CH₄ and CD₄ with no observable crossover product (<5% CH₃D and CD₃H by NMR and IR spectroscopies, eq 4).

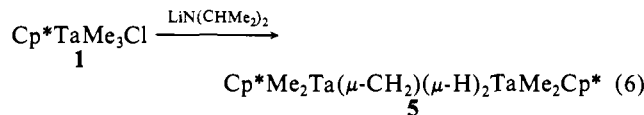


The conversion of **2** to **3** therefore appears to be a unimolecular process. The decay of **2-d₆** (eq 3) is much slower than the perprotio material (Figure 1): the kinetic isotope effect ($k_{\text{H}}/k_{\text{D}}$) is 9.7 (±1).

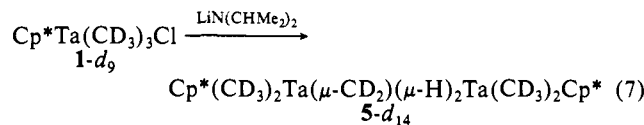
The *N*-propylmethylenimine derivative **4** has been prepared analogously (eq 5), but this reaction does not proceed cleanly, and a number of other (as yet unidentified) products are formed. An intermediate amide complex analogous to **2** has not been observed.



The reaction of **1** with lithium diisopropylamide (LDA) also gives a number of products; however, the expected imine derivative does not appear to be formed. One complex (**5**) can be cleanly isolated, albeit in only 10% yield, because of its limited solubility in petroleum ether (eq 6). Compound **5** is stable in solution for



only a few hours at ambient temperatures but is sufficiently robust in the solid state to enable satisfactory elemental analyses to be obtained (see Experimental Section). The ¹³C NMR spectrum of **5** indicates the presence of a methylene group (δ 135.76 (t, ¹J_{CH} = 123 Hz)) in addition to tantalum methyl groups and the Cp* ligand. The proton NMR spectrum has two triplets coupled to each other (δ 0.54 and 9.72 ($J_{\text{HH}} = 6 \text{ Hz}$)), integrating as one hydrogen each (to Cp* = 15). These triplets are assigned to a bridging methylene and two bridging hydride ligands.²⁷ The reaction of **1-d₉** with LDA produces **5** deuterated at the methyl and methylene positions but not at the hydride ligands (eq 7). The

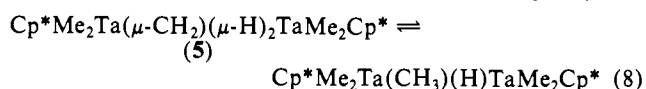


hydride resonance in the ¹H NMR spectrum of **5-d₁₄** is a singlet, and the methylene signal at δ 0.54 is absent.²⁸ This result also

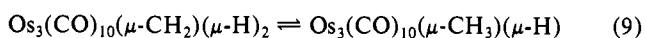
(27) Coupling between bridging methylene and bridging hydride ligands has also been observed in osmium and platinum cluster compounds. (a) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225–6. (b) Green, M.; Hankey, D. R.; Murray, M.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1981**, 698–699.

(28) **5** is unusual because it does not appear to contain a Ta–Ta bond, while most bridging methylene groups span metal–metal bonds. This may account for the unusually high-field resonances for the methylene ligand in the ¹³C and ¹H NMR spectra of **5**. One other example of an unsupported bridging methylene is reported in: Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 5922–3. For the more common type of μ-CH₂ complexes, see: Herrmann, W. A.; Plank, J.; Riedel, D.; Ziegler, M. L.; Widenhammer, K.; Guggolz, E.; Balbach, B.; *J. Am. Chem. Soc.* **1981**, *103*, 63 and references therein.

shows that the hydride ligands do not reversibly migrate to the μ -CH₂ groups (eq 8), in contrast to the rapid scrambling of hydride



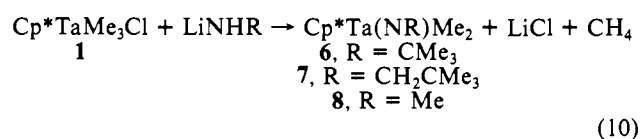
and methylene protons observed for a triosmium cluster (eq 9).^{27a}



Compound **5** does not appear to react with dihydrogen or ethylene before it decomposes; reactions with carbon monoxide and methyl iodide are rapid but yield intractable mixtures.

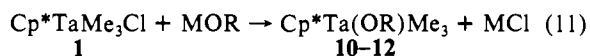
The mechanism of formation of **5** is not at all clear, but various labeling experiments do suggest that the diisopropylamide is the source of the hydride ligands. When **5** is prepared in toluene-*d*₈ or when the synthesis is carried out in glassware preirradiated with D₂O, no deuterium incorporation is noted. The synthesis using **1-d**₉ (eq 7) shows that the hydride ligands are not derived from the tantalum methyl groups. Bulky lithium dialkylamides are known to donate hydride from the α -carbon to certain organic substrates, for example, in the reduction of *o*-bromoanisole to anisole.²⁹ It is conceivable that due to the steric bulk of the diisopropylamide group the formation of a tantalum–nitrogen bond is prevented and hydride donation becomes competitive.

Compound **1** reacts with lithium monoalkylamides to give tantalum alkylimido complexes, not the expected amide compounds (eq 10). A formal α abstraction occurs with the formation



of methane, a product that has been quantitatively collected and identified. These compounds are extremely soluble in petroleum ether and sublime readily at 40 °C (10⁻⁴ torr). Compound **6** melts at 30 °C; when slightly impure it is a viscous liquid. Compounds **2–8** are all plagued with a persistent impurity, Cp*TaMe₄ (**9**),¹⁹ that is difficult to remove by either recrystallization or sublimation. Fortunately the amount of **9** formed is reduced in more dilute solutions. The problem is most severe in the synthesis of **8**, which has not been obtained in pure form.

Alkali-metal alkoxides react with **1** to give the corresponding tantalum alkoxide complexes (eq 11).³⁰ Compounds **10–12** are



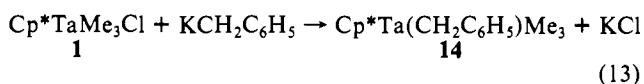
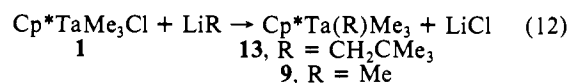
10, R = CMe₃, M = K; **11**, R = CHMe₂, M = Na; **12**, R = Me, M = Li

very soluble in hydrocarbon solvents and sublime readily. **10** melts at 40 °C and is conveniently isolated by short-path distillation as a slightly impure liquid. Unlike the isoelectronic amide complexes, the alkoxide compounds are very stable: **12** decomposes only at 120 °C and **10** and **11** are unchanged after a day at that temperature.

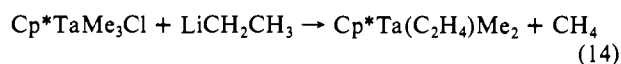
The ¹³C NMR spectra of **10–12** indicate that the methyl groups bound to the tantalum are not all equivalent at ambient temperatures, although the proton spectra show one broad resonance for the methyl ligands. Cp*Ta(X)Me₃ compounds most likely have “four-legged, piano-stool” geometries in which the methyl groups are inequivalent if the molecule is not fluxional.³¹ The ¹H and ¹³C NMR spectra of Cp*Ta(NMe₂)Me₃ (**2**) show inequivalent methyl groups at ambient temperature, while the alkyl

complexes Cp*Ta(R)Me₃ (see below) have equivalent methyl groups. The alkoxide complexes are in an intermediate range: the methyl resonances for **12** in the ¹³C NMR spectrum coalesce at 45 °C, indicating approximately a 16.1 (±1) kcal/mol barrier to rearrangement.³² For Cp*TaMe₃Cl (**1**), a ΔG^\ddagger of 13.6 (±1.4) kcal/mol has been derived for this fluxional process.¹² The different behavior of these compounds may be related to the π -donor ability of the unique ligand since the barrier seems to decrease in the same order (NR₂ > OR > Cl > R).³³

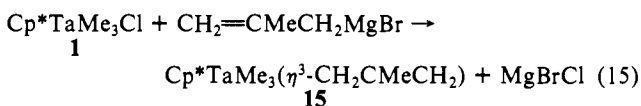
Alkyl complexes with the [Cp*TaMe₃] unit have also been prepared (eq 12, 13); **9** has been previously reported.¹⁹ These



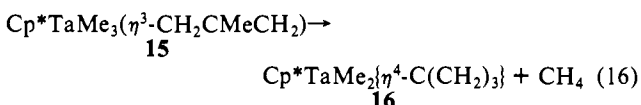
compounds are thermally stable, decomposing only over a period of weeks at 80 °C. Complexes containing alkyl groups with β -hydrogen atoms appear to be unstable; however, since treatment of **1** with ethyllithium is reported to give an ethylene complex (eq 14),³⁴ presumably by β elimination from an intermediate ethyl



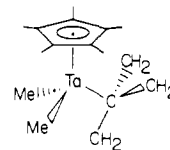
derivative. The (apparently η^3) 2-methylallyl complex **15** has been prepared (eq 15), but it is unstable, decomposing in a few hours



at ambient temperatures to a trimethylenemethane complex **16** (eq 16).³⁵ The production of CD₃H from **15-d**₉ suggests that



a facile hydrogen abstraction process is occurring in this case also.³⁶ The ¹H and ¹³C NMR spectra of **16** indicate that the trimethylenemethane ligand is rotating on the NMR timescale at ambient temperatures. At -80 °C this process is effectively frozen out, with the observation of a static structure, most likely that



shown below possessing a mirror plane that bisects the tri-

(33) The π -donor ability of the unique ligand affects not only the size of the activation barrier of the fluxional process but also the chemical shift difference between inequivalent methyl groups in the low-temperature limit. For example, the resonances for the inequivalent methyl groups in the ¹³C NMR spectrum of Cp*Ta(NMe₂)Me₃ (**2**) are separated by 5.6 ppm while the separation in Cp*Ta(OMe)Me₃ (**12**) is only 2.5 ppm. Other effects are also important, since the analogous separation in Cp*Ta(OCMe₃)Me₃ (**10**) is 4.9 ppm.

(34) (a) McLain, S. J., personal communication, 1982. (b) McLain, S. J. Ph.D. Thesis, Massachusetts Institute of Technology, 1979.

(35) For other trimethylenemethane complexes, see: (a) Barnes, S. G.; Green, M. J. *Chem. Soc., Chem. Commun.* **1980**, 267. (b) Pinhas, A. R.; Samuelson, A. G.; Arnold, E. V.; Clardy, J.; Carpenter, B. K. *J. Am. Chem. Soc.* **1981**, *103*, 1668 and references therein.

(36) “ β -H elimination” from the (η^3 -CH₂CMeCH₂) group may be viewed as analogous to H abstraction from a methyl group of (η^5 -C₅Me₅) ligands. (a) Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087–5095. (b) Bercaw, J. E. *Adv. Chem. Ser.* **1978**, No. **167**, 136–148. (c) McAlister, D. R.; Erwin, D. K.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 5966–8.

(29) (a) Mosher, H. S.; Blanz, E. J., Jr. *J. Org. Chem.* **1957**, *22*, 445–6.

(b) Benkeser, R. A.; DeBoer, C. E. *Ibid.* **1956**, *21*, 281–284.

(30) Compound **10** has been previously described. See ref 39.

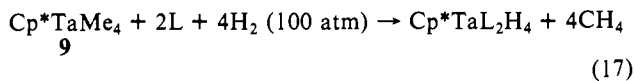
(31) Kubáček, P.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180–188.

(32) (a) Shanan-Atidi, H.; Bar-Eli, K. H. *J. Phys. Chem.* **1970**, *74*, 961–3.

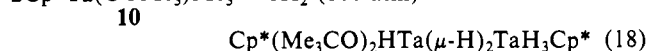
(b) Martin, J. L.; Martin, G. J.; Delpuech, J. J. “Practical NMR Spectroscopy”; Heyden, London, 1980; pp 295–297.

methylenemethane ligand.³⁷ A rotational barrier of 10.6 (±1) kcal/mol is calculated from the -36 °C coalescence temperature in the ¹³C{¹H} NMR (22.5 MHz) spectra.^{32,37}

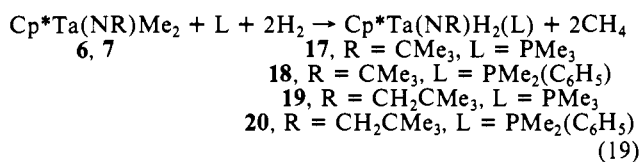
The reactions of the compounds described above with dihydrogen have also been examined. We have reported that hydrogenation of tantalum alkyl compounds is a good synthetic route to hydride complexes.³⁸ Thus **9** reacts with hydrogen in the presence of phosphine ligands to give tetrahydride complexes (eq 17),³⁸ and the hydrogenation of **10** produces an unusual asym-



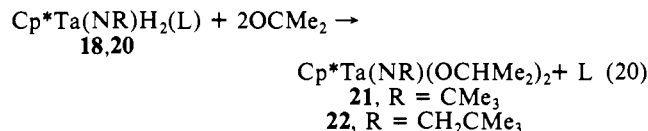
metric dimer (eq 18).³⁹ Similarly, the imido compounds reported



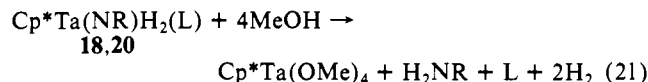
here (**6** and **7**) react cleanly with hydrogen in the presence of phosphine ligands to afford the expected dihydride complexes **17**–**20** (eq 19). It is of interest that these hydrogenation reactions



afford the imido hydride, not the analogous amide complexes even in the presence of excess phosphine. These are among the few reported imido hydride compounds.⁴⁰ Unlike reactions 17 and 18 high pressures of H₂ are not required for clean conversions, although the reactions are slow, requiring two weeks at 80 °C under 3 atm of hydrogen. The trimethylphosphine complexes **17** and **19** are difficult to isolate because of their solubility in hydrocarbon solvents, so the dimethylphenylphosphine derivatives have been examined in more detail. The hydrogen ligands in these compounds are "hydridic".⁴¹ They reduce acetone to isopropoxide complexes (eq 20) and react with methanol to produce H₂.



Methanol also removes the imido ligand as the amine (eq 21),



even if less than a stoichiometric amount of MeOH is used.³⁸ The reactions of **18** and **20** with carbon monoxide and ethylene give intractable mixtures of products.

(37) This structure has been calculated as the most stable geometry. A significant barrier to rotation was also calculated. Goddard, R.; Hoffmann, R., personal communication, Cornell University, 1979.

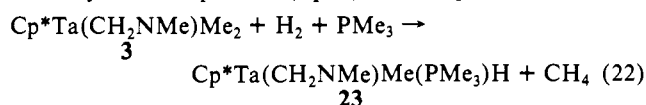
(38) Mayer, J. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 2157–2165.

(39) Mayer, J. M.; Wolczanski, P. T.; Santarsiero, B. D.; Olson, W. A.; Bercaw, J. E. *Inorg. Chem.*, in press.

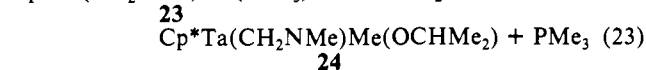
(40) A recent report describes a series of rhenium(V) compounds of the forms ReH(NR)Cl₂(PPh₃)₂ and ReH(NR)(OR')Cl(PPh₃)₂ that are the only other examples of mononuclear transition-metal imido hydride complexes.^{42a} The trimetal clusters M₃(μ-H)₂(CO)₅(μ₃-NR) (M = Fe, Os) are also known.^{42b-d} (a) La Monica, G.; Cenini, S.; Porta, F. *Inorg. Chim. Acta* **1981**, *48*, 91. (b) Lin, Y. C.; Knobler, C. B.; Kaesz, H. D. *J. Organomet. Chem.* **1981**, *213*, C41. (c) Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7255. (d) Burgess, K.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Organomet. Chem.* **1982**, *224*, C40.

(41) The reactions of hydride complexes with acetone and methanol have been previously discussed, and it was concluded that the rate of reaction with methanol is an indication of the hydridic character of the hydride ligands.³⁸ Following this definition, **18** and **20** are roughly as "hydridic" as Cp*Ta(Me₂PCH₂CH₂PMe₂)H₄.

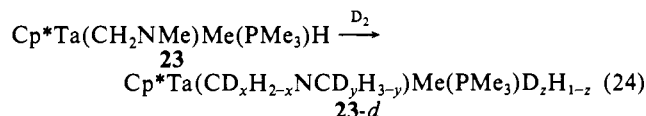
Complex **3** reacts with hydrogen in the presence of trimethylphosphine to lose (only) 1 equiv of methane and form an imine hydride complex, **23** (eq 22).⁴² Compound **23** has been



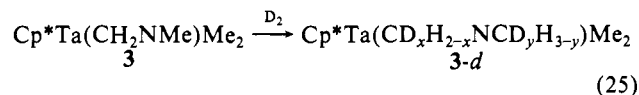
characterized by elemental analysis, molecular weight measurement (calcd. 451, found, 478), and IR (ν(TaH) 1680 cm⁻¹) and NMR spectroscopies. To our knowledge, **23** is the first isolable mononuclear tantalum alkyl hydride complex. The NMR spectra are particularly informative due to the distinctive P–H and H–H couplings (Table I). The reaction of **23** with 1 equiv of acetone proceeds with loss of PMe₃ to give an isopropoxide complex **24** (eq 23), which does *not* readily rearrange to a dimethylamide



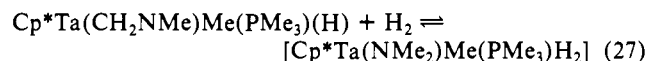
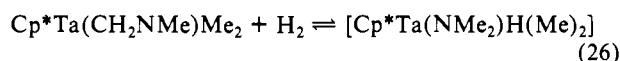
acetone complex. Compound **23** decomposes slowly (to unidentified product(s)) under hydrogen, and the reaction appears to be inhibited by excess PMe₃. If **23** is stirred under D₂, H–D exchange is observed prior to decomposition, with deuterium incorporation not only in the hydride position but also in the methylene and methyl groups of the imine ligand (eq 24). The



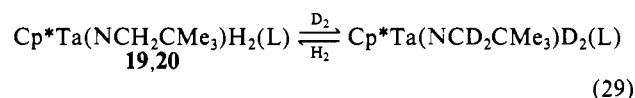
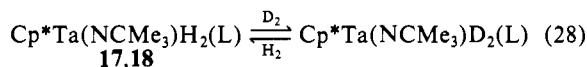
protons of the imine ligand in **3** also exchange with D₂ (eq 25),



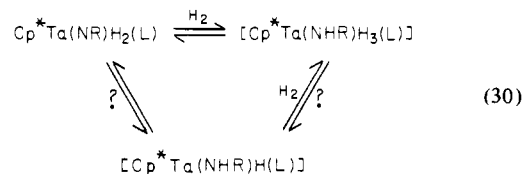
although decomposition does occur slowly under these conditions. The H–D exchange for **3** and **23** preceding hydrogenolysis of the Ta–CH₃ bonds forces one to conclude equilibria such as eq 26 and 27 exist.



The hydride ligands of the imido hydride complexes (**17**–**20**) exchange very slowly with D₂, requiring weeks at 80 °C (eq 28, 29). The high temperature required for these reactions suggests



that an amide complex like D or E is not easily accessible (eq 30).



Finally, it is interesting to note that in the reactions of the neo-

(42) It is interesting that **23** contains a phosphine ligand while **3** binds PMe₃ only weakly: the resonances in the ¹H NMR spectrum of **3** are shifted up to 1 ppm on addition of 1 or 2 equiv of PMe₃, but the PMe₃ resonance is unshifted from free PMe₃. Evaporation of the PMe₃ regenerates the spectrum of **3**.

pentyl derivatives, H-D exchange is also observed with the methylene hydrogens of the neopentyl group (eq 29).⁴³

Discussion

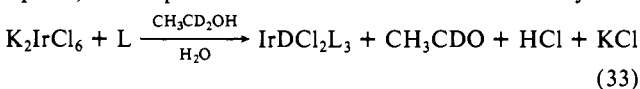
The decomposition of Cp*Ta(NMe₂)Me₃ (**2**) to Cp*Ta(CH₂NMe)Me₂ (**3**) may be viewed as a unimolecular β-hydrogen abstraction or elimination reaction, as evidenced by the kinetic and labeling experiments discussed above. Although not a common reaction of dialkylamide ligands,^{21b,c} an analogous decomposition of tantalum pentakis(diethylamide) to an "imine" complex has been observed (eq 31, Et = CH₂CH₃).¹⁵ There are two Ta(NEt₂)₅ → Ta[CH(CH₃)NEt](NEt₂)₃ + HNEt₂ (31)

reasonable mechanisms for this transformation, (i) a direct hydrogen abstraction process and (ii) a β-hydrogen elimination pathway involving a tantalum hydride intermediate. Mechanisms in between these two extremes can also be imagined.⁴⁴ The large kinetic isotope effect ($k(\mathbf{2})/k(\mathbf{2-d}_6) = 9.7 \pm 1$) does not directly distinguish between the mechanisms, but it does suggest that the migrating hydrogen atom is very loosely bound in the transition state. A comparable deuterium kinetic isotope effect has been measured: abstraction of a hydrogen atom from CH₄ by a chlorine atom is 10 times faster than deuterium abstraction from CD₄.⁴⁵ The relationship of these two processes to each other is not clear, however.

In complexes with hydrocarbon ligands, β-hydrogen elimination processes appear to be even more facile. Methane loss occurs readily by H abstraction (or elimination) even from phenyl²³ or 2-methylallyl, leading to the remarkable benzyne (eq 32) or Cp*Ta(C₆H₅)Me₃ → Cp*Ta(C₆H₄)Me₂ + CH₄ (32)

trimethylenemethane (eq 16) species. Whereas these processes are not, strictly speaking, "true β-H eliminations", they may be considered closely related.³⁶

In view of the facile β-hydrogen migrations from amide and alkyl ligands, the high thermal stability of the alkoxide compounds **10-12** is surprising. Whereas there are no unambiguous examples of alkoxide complexes that decompose in β-hydrogen transfer, this step is strongly suggested by the synthesis of middle and later transition-metal hydride complexes in alcoholic solvents⁴⁶ (e.g., eq 33⁴⁷). This process does not occur in this tantalum system.



β-Hydrogen transfer from the isopropoxide ligand of **11** would yield the η²-acetone complex **25** (eq 34), a stable compound Cp*Ta(OCHMe₂)Me₃ ⇌ Cp*Ta(OCMe₂)Me₂ + CH₄ (34)

prepared by another route.¹⁹ Furthermore, decomposition of **12** would give an η²-formaldehyde complex,⁴⁸ completely analogous to the formation of the η²-imine complex **3**. However, the formal reverse of a β-H migration reaction appears facile, since hydrogenation of tantalum acetone complex **25** has been reported to

(43) (a) Although the mechanism of this reaction is not understood, it should be noted that hydrogen atoms α to the nitrogen seem to be very reactive in most alkylimido compounds.^{43b} For example, deprotonation of alkylimido ligands to methyleneamido groups (isoelectronic with NO) has been observed (eq 38, L = a phosphine ligand, py = pyridine): Chatt, J.; Dossier, R. J.; King, ReCl₃(NCH₂R)L₂ + 2py → ReCl₂(NCHR)L₂(py) + (py)HCl (38)

F.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2435-2440. (b) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123-175.

(44) A theoretical analysis of an analogous process, α elimination to form an alkylidene, has been presented: Goddard, R. J.; Hoffmann, R.; Jemmis, E. D. *J. Am. Chem. Soc.* **1980**, *102*, 7667-7676.

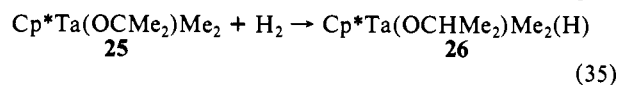
(45) (a) Wiberg, K. B.; Motell, E. L. *Tetrahedron* **1963**, *19*, 2009. (b) Chiltz, G.; Eckling, R.; Goldfinger, P.; Huybrechts, G.; Johnston, H. S.; Meyers, L.; Verbeke, G. *J. Chem. Phys.* **1963**, *38*, 1053.

(46) (a) Schunn, R. A. In "Transition Metal Hydrides"; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1981; pp 203-269. (b) Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231.

(47) Vaska, L.; DiLuzio, J. W. *J. Am. Chem. Soc.* **1962**, *84*, 4989-4990.

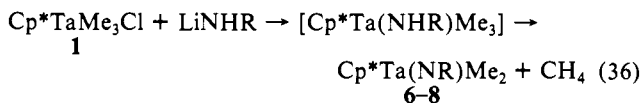
(48) (a) Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503-5. (b) Thorn, D. L. *Organometallics* **1982**, *1*, 197-204.

yield an isopropoxide derivative **26** (eq 35).¹⁹ (Complete spec-



troscopic data for **26** are given in ref 49.) In addition, tantalum hydride complexes react with acetone to form isopropoxide compounds (eq 20 and 23 and ref 38).

When **1** is treated with monoalkyl amides, α-hydrogen-transfer processes appear to be more facile than β-hydrogen migrations. These reactions probably involve an intermediate amide complex analogous to **2**, which is not observed due to rapid elimination of methane (eq 36).⁵⁰ The second step in eq 36 is best described



as a hydrogen abstraction reaction and not an α elimination, because the elimination mechanism would involve an unreasonable tantalum hydride intermediate.^{44,51,52}

The rates of the hydrogen-transfer processes correlate with the nature of the atom bound to the tantalum. For reactions involving a β-hydrogen, the observed order is C > N > O; α-abstraction reactions appear to vary in reverse order, N > C, since the alkyl complexes are stable and imido compounds are rapidly generated from monoalkyl amide complexes. The reaction of **1** with LiOH gives methane and what appears to be an insoluble polymeric oxo complex,⁵³ so α abstraction from oxygen ligands appears to be facile for this system also. Given a choice, complexes with alkyl amide ligands undergo α-H-transfer reactions, while those with hydrocarbon ligands undergo β-H transfer. It should be emphasized that these comparisons are based on the reactivity of complexes of the [Cp*TaMe₃] fragment, and it is not clear that they will be valid for other metals or even tantalum complexes with different ligand arrays.⁵⁴

A number of observations described above leave little doubt that the kinetic barriers to hydrogen-transfer processes are small, so that the reactivities in this series of compounds reflect the thermodynamic preferences. For example, decomposition of the alkoxide compounds by β-H transfer appears to be thermodynamically unfavorable. It will be interesting to explore the reasons why the facility of the β-hydrogen-transfer reactions correlates inversely with the strength of the metal ligand bond (Ta-O > Ta-N > Ta-C),⁵⁵ while the ease of α-hydrogen-transfer reactions correlates directly with the strength of the multiple bond formed (Ta=NR > Ta=CR₂).

Experimental Section

All manipulations were carried out using either high vacuum line or glovebox techniques, as previously described.³⁸ IR spectra were obtained on Nujol mulls unless indicated otherwise and are reported in cm⁻¹. Molecular weights were determined either by osmometry (by Alfred Bernhardt Analytische Laboratorien) or by isothermal distillation using the Singer method.⁵⁶ In several cases the two results do not agree.

(49) The ¹H NMR spectrum of **26** is reported in ref 17 except for the hydride resonance (δ 16.77 (br s): ¹³C NMR (C₆D₆, 34 °C): δ 11.46 (q, ¹J_{CH} = 127 Hz, C₅(CH₃)₅), 113.52 (s, C₅Me₂), 38.20 (qd, ¹J_{CH} = 119 Hz, ²J_{CH} = 10 Hz, Ta(CH₃)₂), 75.04 (d, ¹J_{CH} = 144 Hz, TaOCHMe₂), 25.37 (dq, ¹J_{CH} = 125 Hz, ³J_{CH} = 5 Hz, TaOCH(CH₃)₂); IR 1720 (ν(Ta-H)), 1260, 1130, 1020, 1000, 850 cm⁻¹. We have been unable to isolate **26** as anything but an oil due to its very high solubility in hydrocarbon solvents.

(50) Alternative mechanisms that do not involve initial metathesis of chloride and amide groups are unlikely since the reactions of primary amines (RNH₂) with Cp*TaMe₃Cl (**1**) and Cp*TaMe₄ (**9**) are very slow at 25 °C.

(51) The decomposition of tantalum(V) alkyls to alkylidene complexes is also described as an α-elimination process.⁹

(52) Since the α abstraction reactions are facile, it is tempting to view the β-hydrogen transfer reactions (e.g., eq 2) as proceeding by a similar mechanism.

(53) Rocklage, S. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 7808-9.

(54) A tantalum complex has recently been reported in which α- and β-hydrogen elimination reactions are competitive: Fellmann, J. D.; Schrock, R. R.; Traficante, D. D. *Organometallics* **1982**, *1*, 481.

(55) Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71.

While we do not understand these disparities, we see no compelling reason to favor these very high values for **5–7** received from Bernhardt. Methanol, 2-propanol, acetone, dimethylamine (Eastman Kodak), methyl-*n*-propylamine (Pfaltz and Bauer), *tert*-butylamine, and neopentylamine were stored over 4-Å molecular sieves and vacuum transferred prior to use. Methylamine (Matheson) and bis(methyl-*d*₂)-amine (Merck) were used without further purification. NaOCHMe₂ was prepared from sodium and 2-propanol; lithium alkoxides and amides were prepared by the following procedure, described for LiNHMe. *n*-Butyllithium (1.55 M in hexane, 90 mL, 0.14 mol) was transferred via syringe to a frit apparatus and filtered. The solution was cooled to -80 °C, 30 mL of petroleum ether added, and H₂NMe (7 mL at -80 °C, ~0.16 mol) added. After the mixture was warmed to 25 °C, the white solid (LiNHMe) was isolated by filtration, washed once with petroleum ether/hexane, and dried in vacuo for 16 h, 5.25 g (0.14 mol, 100%). Neopentyllithium was prepared from neopentylchloride and lithium and was recrystallized from heptane. Benzylpotassium was prepared from toluene, butyllithium, and potassium *tert*-butoxide. Cp*TaMe₃Cl (**1**) was prepared by a published procedure.¹² Many of the syntheses reported proceed quantitatively (by NMR), but the isolated yields are often low because the compounds are extremely soluble in hydrocarbon solvents.

Cp*Ta(NMe₂)Me₃ (**2**). Cp*TaMe₃Cl (**1**, 0.50 g) and LiNMe₂ (0.065 g) were stirred in 20 mL of diethyl ether (Et₂O) at -80 °C for 1 h, the solution warmed to 0 °C for 5 min, and the solvent removed. Recrystallization from petroleum ether, keeping the solution as cold as possible at all times, gave 0.275 g (50%) of a bright yellow solid, 90% **2** and 10% **3** by NMR spectroscopy. **2** is completely decomposed after 24 h in the solid state at 25 °C: IR 1310, 1290, 1020, 950, 715, 685, 495, 420 cm⁻¹.

Kinetic Measurements. The kinetics of decomposition of **2** and **2-d**₆ were followed by ¹H NMR spectroscopy, monitoring the disappearance of the N(CH₃)₂ and/or Ta(CH₃)₂(CH₃)' resonances. All of the kinetic runs obeyed first-order kinetics for >3 half-lives (see Figure 1). The probe temperature was measured before and after each run using both MeOH and HOCH₂CH₂OH; values were 33.5 °C (±1). Two runs on samples from the same batch of **2-d**₆ yielded rate constants of 5.57 and 5.65 × 10⁻⁴ s⁻¹, and two runs on samples from different preparations of **2-d**₆ gave *k* = 5.84 and 5.70 × 10⁻⁵ s⁻¹.

Cp*Ta(CH₂NMe)Me₂ (**3**). Cp*TaMe₃Cl (**1**, 2.0 g) and LiNMe₂ (0.28 g) were stirred in 80 mL of Et₂O at 25 °C for 2 h, the solvent removed, and recrystallization from petroleum ether gave yellow-orange **3** (1.37 g, 70%): IR 1265 (st, ν(CN)), 1150, 1030, 910, 490 cm⁻¹. Anal. Calcd for C₁₄H₂₆TaN: C, 43.19; H, 6.73; Ta, 46.48; N, 3.60 (mol wt 389). Found: C, 43.02; H, 6.57; Ta, 46.67; N, 3.75 (C₆H₆, Bernhardt, mol wt 406).

Cp*Ta(CH₂NCH₂CH₂CH₃)Me₂ (**4**). Cp*TaMe₃Cl (**1**, 0.50 g) and LiN(Me)CH₂CH₂CH₃ (0.11 g) were stirred in 10 mL of benzene for a day. The solvent was removed, petroleum ether added, the solution filtered, and the petroleum ether removed, leaving an orange oil containing **4** (70% pure by NMR): IR (C₆D₆) 1245 (st, ν(CN)), 1155, 1030, 965, 920, 860 cm⁻¹.

Cp*Me₂Ta(μ-CH₂)(μ-H)₂TaMe₂Cp* (**5**). Cp*TaMe₃Cl (**1**, 0.50 g) and LiN(CHMe₂)₂ (0.14 g) were stirred in 20 mL of toluene for 2.5 h at 0 °C and 10 min at 25 °C. After removal of the solvent, recrystallization from petroleum ether gave rust-colored **5**, 45 mg (10%). Methane (0.22 mmol, 0.17 equiv) was evolved in this reaction (by Toepler pump): IR 1260, 1145, 1025, 800, 770, 480, 440 cm⁻¹. Anal. Calcd for C₂₂H₄₅Ta₂: C, 42.38; H, 6.54; Ta, 51.08 (mol wt 709). Found: C, 42.21; H, 6.36; Ta, 51.30 (mol wt 1390, 1420 (C₆H₆, Bernhardt)); in view of the instability of **5**, this value may be questionable.

Cp*Ta(NCMe₃)Me₂ (**6**). Cp*TaMe₃Cl (**1**, 1.00 g) and LiNHCM₂ (0.22 g) were stirred in 80 mL of Et₂O for 15 min. The volatiles were removed, petroleum ether was added, the solution was filtered, and the solid obtained on removal of the petroleum ether was sublimed (25 °C (10⁻⁴ torr)) to give light yellow **6** (0.85 g, 81%): mp 30 °C; IR 1280 (st, ν(TaNC)), 1215, 1150, 1025, 800, 725, 525, 500 cm⁻¹. Anal. Calcd for C₁₆H₃₀N₂Ta: C, 46.04; H, 7.25; N, 3.36 (mol wt (C₆H₆) 417). Found: C, 45.94; H, 7.01; N, 3.22 (mol wt 1300 (Bernhardt), 520 (Singer method)).

Cp*Ta(NCH₂CMe₃)Me₂ (**7**). Cp*TaMe₃Cl (**1**, 0.50 g) and LiN(H)CH₂CMe₃ (0.13 g) were stirred in 30 mL of Et₂O at 25 °C for 30 min. After the volatiles were removed, recrystallization from petroleum ether yielded yellow **7** (0.20 g, 37%): sublimes at 40 °C (10⁻⁴ torr): IR 1290 (st, ν(TaNC)), 1210, 1155, 1025, 800, 725, 525, 500 cm⁻¹. Anal. Calcd for C₁₇H₃₂N₂Ta: C, 47.33; H, 7.48; N, 3.25 (mol wt (C₁₇H₆) 431). Found: C, 47.08; H, 7.30; N, 3.18 (mol wt 1377 (C₆H₆, Bernhardt)).

Cp*Ta(NMe)Me₂ (**8**). Cp*TaMe₃Cl (**1**, 170 mg) and LiNHMe (23 mg) were stirred in 20 mL of Et₂O at 25 °C for 10 min. The volatiles

were removed, benzene was added, and the suspension was filtered to give a yellow solution containing 70% **8** and 30% **9** (by NMR): IR (C₆D₆) 1295 (st, ν(TaNC)), 1160, 1030, 790 cm⁻¹.

Cp*Ta(OCMe₃)Me₃ (**10**) has been previously reported.³⁹

Cp*Ta(OCHMe₂)Me₃ (**11**). Cp*TaMe₃Cl (**1**, 0.50 g) and NaOCHMe₂ (0.12 g) were stirred in 40 mL of Et₂O for 3 h. After the solvent was removed, recrystallization from petroleum ether gave 0.22 g of yellow **11** (42%). An additional 0.1 g of slightly impure **11** was obtained by sublimation of the recrystallization residue (50 °C (10⁻⁴ torr)): IR 1190, 1120 (st), 1015 (st), 850, 580, 465 cm⁻¹. Anal. Calcd for C₁₆H₃₁O₂Ta: C, 45.72; H, 7.43. Found: C, 45.64; H, 7.24.

Cp*Ta(OMe)Me₃ (**12**). Cp*TaMe₃Cl (**1**, 215 mg) and LiOMe (30 mg) were stirred in 70 mL of Et₂O for 2 h at 25 °C. The solvent was removed, benzene was added, and after filtration removal of the benzene left **12**: >90% pure by NMR; IR (C₆D₆) 1190, 1120 (st), 1030, 790, 650 cm⁻¹.

Cp*Ta(CH₂CMe₃)Me₃ (**13**). Cp*TaMe₃Cl (**1**, 0.50 g) and LiCH₂CMe₃ (0.10 g) were stirred for 1.5 h in petroleum ether. After filtration, 0.07 g of yellow **13** (13%) was crystallized from this solution: IR (C₆D₆) 1250, 1160, 1025, 860, 680 cm⁻¹.

Cp*Ta(CH₂C₆H₅)Me₃ (**14**). A solution of Cp*TaMe₃Cl (**1**, 0.25 g) and KCH₂C₆H₅ (0.10 g) in 15 mL of toluene was stirred at -80 °C for 1 h and at 0 °C for 1 h. After filtration, red-brown **14** (0.13 g, 43%) was crystallized from petroleum ether/toluene. **14** sublimes with decomposition (80 °C (10⁻⁴ torr)): IR 1600, 1200, 1170, 1160, 1055, 1030, 800, 765, 750, 700 cm⁻¹.

Cp*Ta(η³-CH₂CMeCH₂)Me₃ (**15**). A suspension of Cp*TaMe₃Cl (**1**) (2.00 g, 5.01 mmol) in THF (50 mL) at -80 °C was treated with (2-methylallyl)magnesium chloride (11.5 mL of 0.44 M solution in THF, 5.06 mmol) to yield a clear orange solution. The solution was warmed to 0 °C and the solvent was removed while the temperature was maintained at 0 °C. The resulting orange solid was extracted with petroleum ether (20 mL) and filtered. The orange filtrate was then cooled to -80 °C to give orange crystalline product, which was collected and dried at low temperature (1.08 g, 52%). This complex decomposes with loss of CH₄ in the solid state at room temperature so no microanalysis was attempted. It is stable as a solid at -40 °C for months.

Cp*Ta[η⁴-C(CH₂)₃]Me₂ (**16**). A solution of Cp*Ta(η³-CH₂CMeCH₂)Me₃ (**15**) in THF (125 mL) was prepared as above from Cp*TaMe₃Cl (**1**) (4.58 g, 11.5 mmol) and (2-methylallyl)magnesium chloride (11.9 mmol). The THF was then removed in vacuo and replaced with hexane (100 mL), and the resulting suspension was filtered. The orange filtrate was stirred at room temperature for 2 days, during which time the color changed to dark brown. The solvent was then removed, the resulting brown residue dissolved in petroleum ether (60 mL), the solution filtered, and the volume reduced to 25 mL. Cooling to -80 °C yielded small yellow needles (2.3 g, 50%). In another experiment, Cp*Ta(η³-CH₂CMeCH₂)Me₃ (**15**, 0.230 g, 0.553 mmol) in petroleum ether (40 mL) was allowed to decompose in vacuum, and the volatile products were collected by Toepler pump. The only volatile product was CH₄ (0.386 mmol, 0.70 equiv/Ta). Anal. Calcd for C₁₆H₂₇Ta: C, 48.00; H, 6.80; Ta, 45.20. Found: C, 47.73; H, 6.90; Ta, 44.91.

Cp*Ta(NCMe₃)H₂(PMe₃) (**17**). A thick-walled glass reaction vessel with Teflon needle valve, charged with Cp*Ta(NCMe₃)Me₂ (**6**, 0.523 g, 1.25 mmol), PMe₃ (310 torr in 104.8 mL, 1.75 mmol), 10 mL of benzene, and 4 atm of H₂, was stirred at 80 °C for 11 days. The volatiles were removed, and recrystallization from petroleum ether gave 0.17 g of white solid, **17** (29%): IR 1700–1650 (ν(TaH)), 1270 (st, ν(TaNC)), 1210, 1030, 955, 935, 720 cm⁻¹.

Cp*Ta(NCMe₃)H₂(PMe₂C₆H₅) (**18**). A high-pressure reactor, charged with 1.8 g of Cp*Ta(NCMe₃)Me₂ (**6**), 0.8 mL of PMe₂C₆H₅, 40 mL of benzene, and 700 psi of H₂, was stirred for 4 days at 85 °C. The solution was transferred to a fritted apparatus, filtered, and dried in vacuo for 24 h. The residue was treated with 5 mL of hexamethyldisiloxane (Me₂SiOSiMe₂) and filtered to give 0.84 g of white **18** (37%). **18** can be recrystallized from benzene/petroleum ether: IR 1715, 1660 (ν(TaH)), 1270 (st, ν(TaNC)), 1210, 1030, 950, 930, 900, 795, 710, 690, 490 cm⁻¹. Anal. Calcd for C₂₂H₃₇N₂P₂Ta: C, 50.10; H, 7.07; Ta, 34.30. Found: C, 49.95; H, 6.97; Ta, 34.52.

Cp*Ta(NCH₂CMe₃)H₂(PMe₃) (**19**). An NMR tube sealed to a ground-glass joint was loaded with Cp*Ta(NCH₂CMe₃)Me₂ (**7**, 15 mg, 0.035 mmol), PMe₃ (43 torr in 19.8 mL, 0.046 mmol), and 0.3 mL of benzene-*d*₆. The tube was cooled to 77 K, 1 atm of H₂ introduced, and the tube sealed with a torch. After 2 weeks at 80 °C, the volatiles were removed leaving **19**.

Cp*Ta(NCH₂CMe₃)H₂(PMe₂C₆H₅) (**20**). A high-pressure reactor, charged with 2.1 g of Cp*Ta(NCH₂CMe₃)Me₂ (**7**), 0.99 mL of PMe₂C₆H₅, 50 mL of benzene, and 1200 psi of H₂, was stirred at 80 °C for 5 days. After the volatiles were removed and the solution was dried in vacuo for 36 h, recrystallization of the residue yielded 1.20 g of white

(56) (a) Singer, R. *Justus Liebigs Ann. Chem.* **1930**, 478, 246. (b) Clark, E. P. *Ind. Eng. Chem., Anal. Ed.* **1941**, 13, 820.

solid, **20** (46%): IR 1720-1650 ($\nu(\text{TaH})$), 1275, 1205, 1025, 940, 900, 835, 740, 715, 695, 490 cm^{-1} . Anal. Calcd for $\text{C}_{23}\text{H}_{39}\text{NPTa}$: C, 51.02; H, 7.26; Ta, 33.42 (mol wt 542). Found: C, 50.94; H, 7.08; Ta, 33.41 (C_6H_6 , Singer method) mol wt 550).

Cp*Ta(NCMe₃)(OCHMe₂)₂ (21). An NMR tube sealed to a ground-glass joint was loaded with **Cp*Ta(NCMe₃)H₂(PMe₂C₆H₅) (17, 75 mg, 0.038 mmol), acetone (59 torr in 25.3 mL, 0.080 mmol), and 0.3 mL of benzene-*d*₆, and sealed with a torch. After 3 days at 25 °C and 1 h at 80 °C, the volatiles were removed leaving **21**: IR (C_6H_6) 1275 (st, $\nu(\text{TaNC})$), 1215, 1120, 1030, 995, 980, 845, 740 cm^{-1} .**

Cp*Ta(NCH₂CMe₃)(OCHMe₂)₂ (22). **22** was prepared from **Cp*Ta(NCH₂CMe₃)H₂(PMe₂C₆H₅) (20, 75 mg, 0.14 mmol) and acetone (150 torr in 33 mL, 0.27 mmol) by a procedure analogous to the synthesis of **21**: IR (C_6H_6) 1280 (st, $\nu(\text{TaNC})$), 1120, 995, 980, 860, 840, 585 cm^{-1} .**

Cp*Ta(CH₂NMe)Me(PMe₃)H (23). A thick-walled glass reaction vessel with Teflon needle valve, charged with 1.86 g of **Cp*Ta(CH₂NMe)Me₂ (3, 4.78 mmol)**, 5 mL of benzene, **PMe₃ (1100 torr in 104 mL, 6.15 mmol)**, and 4 atm of **H₂**, was stirred at 25 °C for 24 h. After the volatiles were removed, recrystallization from petroleum ether gave 1.01 g of red **23 (39%)**: IR 1680 ($\nu(\text{TaH})$), 1490, 1280, 1240 (st), 1025, 955 (st), 935, 900, 720, 665, 480, 450. Anal. Calcd for $\text{C}_{16}\text{H}_{33}\text{NPTa}$: C, 42.58; H, 7.37; N, 3.10 (mol wt 451). Found: C, 42.35; H, 7.15; N, 2.91 (C_6H_6 , Bernhardt) mol wt 478).

Cp*Ta(CH₂NMe)Me(OCHMe₂) (24). A solution of **Cp*Ta(CH₂NMe)Me(PMe₃)H (23, 25 mg, 0.046 mmol)** and acetone (41 torr in 25.3 mL, 0.056 mmol) in 10 mL of petroleum ether was stirred at -80 °C for 30 min and at 25 °C for 30 min. Removal of the volatiles left **24, 70% pure (by NMR)**: **24** is extremely soluble in hydrocarbon solvents: IR (C_6D_6) 1270, 1160, 1130 (st), 1000 (st), 970, 905, 850, 620 cm^{-1} .

Acknowledgment. This work has been supported by the National Science Foundation (Grant No. CHE8024869). We also acknowledge use of the Southern California Regional NMR Facility and the support of NSF Grant No. 7916324A1.

Registry No. **1**, 69302-75-6; **2**, 84876-02-8; **2-d₆**, 84876-20-0; **3**, 84894-72-4; **4**, 84876-03-9; **5**, 84894-73-5; **6**, 84876-04-0; **7**, 84894-74-6; **8**, 84876-05-1; **9**, 71763-35-4; **10**, 84849-50-3; **11**, 84876-06-2; **12**, 84876-07-3; **13**, 84876-08-4; **14**, 84876-09-5; **15**, 84876-10-8; **16**, 84876-11-9; **17**, 84876-12-0; **18**, 84876-13-1; **19**, 84876-14-2; **20**, 84876-15-3; **21**, 84876-16-4; **22**, 84876-17-5; **23**, 84876-18-6; **24**, 84876-19-7; **LiNMe₂**, 3585-33-9; **LiN(Me)CH₂CH₂CH₃**, 84876-21-1; **LiN(CHMe₂)₂**, 4111-54-0; **LiN(H)CH₂CMe₃**, 84876-22-2; **LiNHMe**, 37123-26-5; **NaOCHMe₂**, 683-60-3; **LiOMe**, 865-34-9; **LiCH₂CMe₃**, 3710-27-8; **KCH₂C₆H₅**, 2785-29-7; (2-methylallyl)magnesium chloride, 563-47-3.

Relationship between More O'Ferrall Plots and Marcus Rate Theory. Overriding Orbital Symmetry Constraints on Chemical Reactions

Joseph R. Murdoch

Contribution from the Department of Chemistry and Biochemistry,
University of California, Los Angeles, California 90024. Received March 22, 1982

Abstract: "More O'Ferrall" plots have seen increasing use in recent years for qualitatively interpreting substituent effects on rates of a wide variety of reactions, including nucleophilic substitution, elimination reactions, proton transfers, carbonyl additions, sigmatropic shifts, and Diels-Alder reactions. In the present paper it is shown that the main idea behind the More O'Ferrall plot (geometric distortions along the reaction coordinate ("parallel" effects) and geometric distortions along orthogonal coordinates ("perpendicular" effects)) can be used to derive a quantitative expression for the reaction barrier that is very similar to the Marcus equation, now being applied to electron and proton transfer reactions, as well as nucleophilic substitutions. It is found that the perpendicular effects of the More O'Ferrall approach enter into the intrinsic barrier term of Marcus' equation. Application of this Marcus-like equation to cycloadditions and sigmatropic shifts shows that intrinsic barriers are a function of orbital symmetry constraints and are highly dependent on substituents. This large dependence can provide a mechanism for dramatic reductions in the barriers of both symmetry-allowed and symmetry-disallowed processes.

I. Introduction

The use of More O'Ferrall plots¹ and Marcus rate theory² for interpreting substituent effects on reaction rates has been widespread in recent years.^{3,4} Both approaches have lent considerable

insight into the nature of chemical reactions, and it would be worthwhile to explore the consequences of certain assumptions behind the More O'Ferrall plot. These assumptions can be shown to lead to a quantitative equation similar in many respects to the Marcus equation.

(1) R. A. More O'Ferrall, *J. Chem. Soc. B*, 274 (1970).
(2) R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956).
(3) (a) E. R. Thornton, *J. Am. Chem. Soc.*, **89**, 2915 (1967); (b) J. C. Harris and J. L. Kurz, *ibid.*, **92**, 309 (1970); (c) W. P. Jencks, *Chem. Rev.*, **72**, 705 (1972); (d) D. A. Winey and E. A. Thornton, *J. Am. Chem. Soc.*, **97**, 3102 (1975); (e) T. C. Bruice, *Annu. Rev. Biochem.*, **45**, 331 (1976); (f) D. A. Jencks and W. P. Jencks, *J. Am. Chem. Soc.*, **99**, 7948 (1977); (g) W. J. Albery and M. M. Kreevoy, *Adv. Phys. Org. Chem.*, **16**, 87 (1978); (h) J. M. Harris, S. G. Shafer, J. R. Moffatt, and A. R. Becker, *J. Am. Chem. Soc.*, **101**, 3295 (1979); (i) J. J. Gajewski, *ibid.*, **101**, 4393 (1979); (j) E. Buncl and H. Wilson, *J. Chem. Educ.*, **57**, 629 (1980); (k) J. P. Guthrie, *J. Am. Chem. Soc.*, **102**, 5286 (1980).

(4) (a) A. O. Cohen and R. A. Marcus, *J. Phys. Chem.*, **72**, 4249 (1968); (b) M. M. Kreevoy and D. E. Konasewich, *ibid.*, **74**, 4464 (1970); (c) J. R. Murdoch, *J. Am. Chem. Soc.*, **94**, 4410 (1972); (d) M. M. Kreevoy and Sea-Wha Oh, *ibid.*, **95**, 4805 (1973); (e) A. J. Kresge, *Acc. Chem. Res.*, **8**, 354 (1975); (f) J. R. Murdoch, *J. Am. Chem. Soc.*, **102**, 77 (1980); (g) E. S. Lewis, S. Kukes, and C. D. Slater, *ibid.*, **102**, 1619 (1980); (h) M. J. Pellerite and J. I. Brauman, *ibid.*, **102**, 5993 (1980); (i) M. M. Kreevoy, personal communication. (j) D. E. Magnoli and J. R. Murdoch, *J. Am. Chem. Soc.*, **103**, 7465 (1981); (k) J. R. Murdoch, J. A. Bryson, D. F. McMillen, and J. I. Brauman, *ibid.*, **104**, 600 (1982); (l) J. R. Murdoch and D. E. Magnoli, *ibid.*, **104**, 3792 (1982); (m) S. Wolfe, D. J. Mitchell, H. B. Schlegel, *ibid.*, **103**, 7694 (1981).