Energetics of Metal−Ligand Multiple Bonds. Thermochemistry of Tantalum(V) Alkylidene Formation
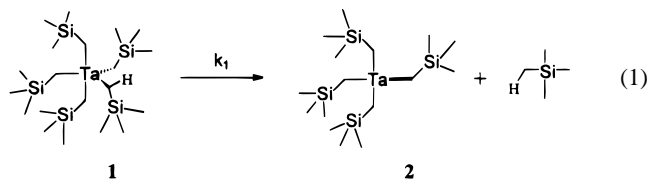
Lubin Luo, Liting Li, and Tobin J. Marks*

Department of Chemistry
Northwestern University
Evanston, Illinois 60208-3113

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Alkylidene complexes of early transition metals[1] display a rich and diverse chemistry which includes a central catalytic role in olefin metathesis processes.[1,2] However, despite the broad existing synthetic/structural/reactivity information base, little is known about the energetics of the formal M=C bonding or of the driving forces for the transformations such complexes undergo. We report here the first experimental analysis of metal alkylidene bonding energetics in a Ta(V), complex which reveals a *very large Ta=C bond enthalpy* as well as thermochemical insight into several important alkylidene reaction patterns.[3]

α-Elimination processes represent a common route to transition metal alkylidenes,[1] and Xue recently showed in a detailed mechanistic study that eq 1 proceeds cleanly and unimolecularly to afford alkylidene complex **2**.[4] The driving force for alky-

lidene formation is not immediately obvious since C−H bonds are both made and broken, and the formation of the Ta=C bond requires the breaking of two Ta−C single bonds. Under first-order kinetics, the heat evolved in eq 1 per solution volume in time interval $t_i - t_{i+1}$ can be expressed in terms of the change of [**1**],

$$C_i = C_o e^{-k_1 t_i} \tag{2}$$

$$H_i - H_{i+1} = \Delta H^{\mathrm{rxn}}(C_i - C_{i+1}) = \Delta H^{\mathrm{rxn}} C_o (e^{-k_1 t_i} - e^{-k_1 t_{i+1}}) \tag{3}$$

$$\Delta H^{\mathrm{rxn}} = (H_i - H_{i+1})[C_o(e^{-k_1 t_i} - e^{-k_1 t_{i+1}})]^{-1} \tag{4}$$

$C_i - C_{i+1}$, where k_1 is known[4] (eqs 2−4). Monitoring the **1** → **2** conversion (which begins upon dissolution of solid samples of **1**) at 25.000 ± 0.001 °C in a rigorously anaerobic, isoperibol

solution calorimeter[5] under conditions[4] in which **2** undergoes negligible dimerization, yields $\Delta H^{\mathrm{rxn}} = -15.8(4)$ kcal/mol.[6] Clearly, the **1** → **2** + SiMe$_4$ conversion is significantly exothermic and eq 1 is not driven by entropic factors alone (1 particle → 2 particles).[7]

More detailed examination of the bonding energetic changes in eq 1 can be achieved via a stepwise analysis (eqs 5−8) invoking several reasonable assumptions. It is assumed that

$$(RCH_2)_3Ta(CH_2R)_2 \rightarrow (RCH_2)_3Ta + 2 \bullet CH_2R$$
$$2D(Ta-C) \quad (5)$$

$$2 \bullet CH_2R \rightarrow CH_3R + :CHR$$
$$D(H-\bullet CHR) - D(H-CH_2R) \quad (6)$$

$$(RCH_2)_3Ta + :CHR \rightarrow (RCH_2)_3Ta=CHR \quad -D(Ta=C) \quad (7)$$

$$(RCH_2)_3Ta(CH_2R)_2 \rightarrow (RCH_2)_3Ta=CHR + CH_3R \quad \Delta H^{\mathrm{rxn}} \tag{8}$$

reorganization of the $(RCH_2)_3Ta$ framework makes a minor contribution to the energetics over and above what is incorporated in the derived D(Ta−C) parameters (vide infra). Second, it is assumed that $D(H-\bullet CHR) \approx D(H-CH_2R)$, which is supported by data for :CH$_2$ and $\bullet$CH$_3$.[8,9] Estimation of $\bar{D}[Ta(CH_2SiMe_3)_5]$ and, to assess possible destabilizing interligand repulsions in driving eq 1, of $D_1[Ta(CH_2SiMe_3)_5]$ was achieved by iodinolytic solution titration calorimetry in toluene (eqs 9 and 10) in which TaI$_5$ (soluble in toluene) was identified after isolation by X-ray diffraction, $(Me_3SiCH_2)_4TaI$ by ^{1}H and ^{13}C NMR, and Me$_3$SiCH$_2$I by ^{1}H and ^{13}C NMR and by GC-MS.[5,6] Using $\bar{D}(TaI_5)$[10] as an anchor point, using standard

$$Ta(CH_2R)_5 + 5I_2 \rightarrow TaI_5 + 5ICH_2R \tag{9}$$

$$Ta(CH_2R)_5 + I_2 \rightarrow (RCH_2)_4TaI + ICH_2R \tag{10}$$

tabulated thermochemical data,[11] and reasonably assuming[5d,12] that $D_1(TaI_5) \approx \bar{D}_1(TaI_5)$ yields $D_1[Ta(CH_2SiMe_3)_5] = 44(1)$ kcal/mol and $\bar{D}[Ta(CH_2SiMe_3)_5] = 67(1)$ kcal/mol. The former result suggests non-negligible crowding in **1** while the latter is

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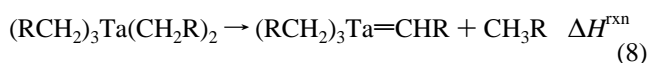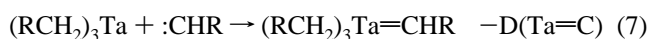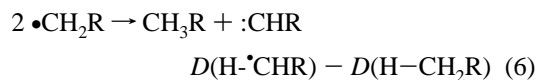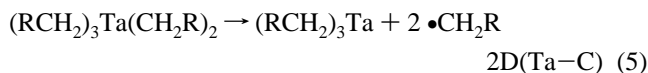
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(8) (a) From tabulated ΔH_f^o values for :CH$_2$[8b,c] and $\bullet$CH$_3$,[8d] D(H−CH$_3$) and D(H−$\bullet$CH$_2$), are estimated to be 104 and 103.7 kcal/mol, respectively. (b) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; John Wiley and Sons: New York, 1976; Appendix Tables A.11 and A.12. (c) Isaacs, N. S. *Physical Organic Chemistry*; Longmans: Essex, U.K., 1987; pp 37−39. (d) Griller, D.; Kanabus-Kaminska, J. M.; Maccoll, A. *J. Mol. Struct.* **1988**, *163*, 125−131.

(9) (a) This assumption is invalid in cases where the carbene has a singlet ground state.[9b,c] Calculations on H$_3$SiCH at the 6-31G**/MP2 and DZP/MP2 levels indicate that the triplet state lies below the singlet by 27.9 and 26.3 kcal/mol, respectively. At the AUG-cc-TVZ level with an MP4 level of correlation, the difference is 19.5 kcal/mol. (b) Chen, P. *Acc. Chem. Res.* **1992**, *25*, 385−391. (c) Clauberg, H.; Minsek, D.; Chen, P. *J. Am. Chem. Soc.* **1992**, *114*, 99−107.

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Table 1.   Experimental Thermochemical Data

eq	ΔH^{rxn} (kcal/mol)	$D(I-I)$ (kcal/mol)[a]	$D(C-I)$ (kcal/mol)[b]	$\bar{D}$ (Ta$-$I) (kcal/mol)	$D($Ta$-$C) or $D($Ta$=$C) (kcal/mol)
1	$-15.8(4)$				$D($Ta$=$C$) = 126(4)$
9	$-75.1(6)$	36.5	55	62.9	$\bar{D}($Ta$-$C$) = 67(1)$
10	$-38(1)$	36.5	55	62.9	$D_1($Ta$-$C$) = 44(1)$

[a] From ref 10d. [b] From refs 10a$-$c.

in favorable agreement with the reported $\bar{D}(\text{TaMe}_5) = 62(2)$ kcal/mol.[13]   Using $2D($Ta$-$C$) \approx D_1[\text{Ta(CH}_2\text{SiMe}_3)_5] + \bar{D}[\text{Ta(CH}_2\text{SiMe}_3)_5]$ in eq 5[14] then yields $D($Ta$=$C$) = 126(4)$ kcal/mol, which is very large and implicitly incorporates any α-CH agostic interaction[1,15] (apparent in the NMR spectroscopic data for **2**[4,15c]).   Thermochemical data are compiled in Table 1.

Although the presently observed stability of Ta alkylidene bonding might at first appear incompatible with reaction patterns such as metallacyclobutane formation in metathesis/ROMP/ADMET processes,[1,2] thermochemical analysis[16] (incorporating ring strain[17]) reveals that for ethylene and acetylene addition, Ta$=$C bond breaking is almost exactly compensated by Ta$-$C and C$-$C bond formation (eqs 11 and 12).   That complex **2** is

$$\Delta H_{calcd} \approx +1 \text{ kcal/mol} \quad (11)$$

$$\Delta H_{calcd} \approx +4 \text{ kcal/mol} \quad (12)$$

not an anomalous alkylidene complex and that eq 11 is doubtless more exothermic for strained olefins is confirmed by our observation that **2** mediates the rapid ROMP polymerization of norbornene (*trans*:*cis* product linkage ratio = 1:2).[18]   The present data also implicate metal oxo/oxide ligand formation as the principal driving force for metathesis termination by carbonyl reagents (eqs 13 and 14).[1,2,19]

$$\Delta H_{calcd} \approx 0 \text{ kcal/mol} \quad (13)$$

$$\Delta H_{calcd} \approx -15 \text{ kcal/mol} \quad (14)$$

These results demonstrate not only that early transition metal alkylidene-forming α-elimination and other processes are driven by the strong metal$-$alkylidene bonds that are formed but also that the metal$-$ligand bonding energetics are ideally poised for alkylidene $\rightleftharpoons$ metallacycle catalytic cycles with minimal enthalpic excursions.

Supporting Information Available: Experimental details of calorimetry and product characterization (2 pages) See any current masthead page for ordering and Internet access instructions.

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(11) (a) Since $D(\text{CH}_3\text{CH}_2-\text{H}) \approx D(\text{Me}_3\text{SiCH}_2-\text{H})$,[11b,c] we take $D(\text{Me}_3\text{SiCH}_2-\text{I}) \approx D(\text{CH}_3\text{CH}_2-\text{I})$.[8d,11b] (b) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493$-$532. (c) Walsh, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; Chapter 5. (d) *Landolt-Börnstein*; Hellwege, K. H., Ed. in Chief; Springer-Verlag: Berlin 1976; Vol. 2, Chapter 3.2, Group IV.
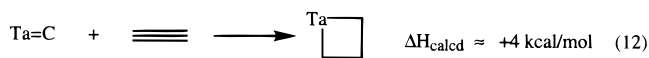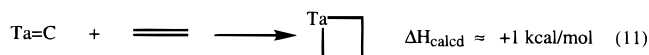
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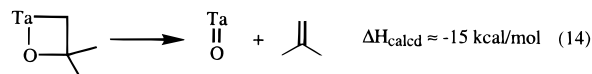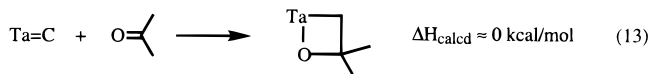(13) Adedeji, F. A.; Connor, J. A.; Skinner, H. A. *J. Chem. Soc., Chem. Commun.* **1976**, 159$-$160.

(14) Assuming $2D($Ta$-$C$) = 2\bar{D}[\text{Ta(CH}_2\text{SiMe}_3)_5]$ yields a slightly larger $D($Ta$=$C$)$, but fails to account fully for the apparent weakness of the first Ta$-$C σ bond.

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