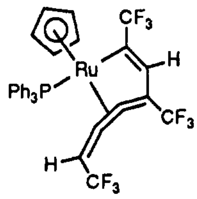
action probably occurred due to the interaction of the triphosphine with the vinylidene group, which causes the vinylidene to orient stereospecifically in space.

The compound $Ru(C{\equiv}CPh)(\eta^3\text{-}PhC_3CHPh)(Cyttp)$ formed in the reaction of excess phenylacetylene with $RuH_4(Cyttp)$ can be regarded as an intermediate in catalytic polymerization or oligomerization reactions of terminal acetylenes. Reactions between phenylacetylene and $MH(O_2CCF_3)(CO)(PPh_3)_2$ (M = Ru, Os) gave similar coupling compounds $M(C(C{\equiv}CPh){=}CHPh)(O_2CCF_3)(CO)(PPh_3)_2$ in which the C≡C triple bond is not bound to the metal centers.[8] The compound $Os(C(C{\equiv}CPh){=}CHPh)(O_2CCF_3)(CO)(PPh_3)_2$ is an active oligomerization catalyst for phenylacetylene; thus, it was suggested that it is probably an intermediate in the catalytic oligomerization of phenylacetylene by $OsH(O_2CCF_3)(CO)(PPh_3)_2$.[8] The reaction of $CF_3C{\equiv}CH$ with $CpRuMe(PPh_3)_2$ also gives a C–C coupling product (eq 7).[10c] The product could be viewed as a coupling reaction between $CF_3C{\equiv}CH$ and an intermediate such as $Ru(\eta^3\text{-}CF_3C_3CHCF_3)$, although the authors proposed an alternative mechanism for its formation. The formation of the compound $Ru(C{\equiv}CPh)(\eta^3\text{-}PhC_3CHPh)(Cyttp)$ is also related to catalytic dimerization of terminal acetylenes, for example, the head-to-tail dimerization catalyzed by $Pd(OAc)_2 + PPh_3$[34] and $Cp_2YCH(SiMe_3)_2$[35] and the head-to-head dimerization catalyzed by $Pd(PPh_3)_4$.[36]

$CpRuMe(PPh_3)_2$ + excess $CF_3C{\equiv}CH \longrightarrow$



(7)

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Organo-f-Element Thermochemistry. Actinide–Group 14 Element and Actinide–Transition-Element Bond Disruption Enthalpies and Stoichiometric/Catalytic Chemical Implications Thereof in Heterobimetallic Tris(cyclopentadienyl)uranium(IV) Compounds

Steven P. Nolan, Marina Porchia, and Tobin J. Marks*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113

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Uranium–metal bond disruption enthalpies have been determined in the series of complexes $Cp_3U{-}MPh_3$, where Cp = $\eta^5\text{-}C_5H_5$, Ph = C_6H_5, and M = Si, Ge, Sn, and in $Cp_3U{-}M'(CO)_2Cp$, where M′ = Fe, Ru. Thermochemical data were obtained by anaerobic batch-titration solution calorimetry in toluene from enthalpies of solution and iodinolysis of the aforementioned compounds. Derived U–M/U–M′ bond disruption enthalpies in toluene solution are as follows (M/M′ moiety, kcal/mol): $SiPh_3$, 37.3 (4.2); $GePh_3$, 38.9 (4.5); $SnPh_3$, 37.2 (4.0); $Fe(CO)_2Cp$, 30.9 (3.0); $Ru(CO)_2Cp$, 40.4 (4.0). These data fall in a relatively narrow range and indicate comparatively weak heterobimetallic bonding. Chemical implications of the present thermochemical results include the general favorability and marked M/M′ sensitivity of alkane, hydrogen, and amine elimination synthetic routes to these compounds, the existence of favorable pathways for hydrocarbon and olefin activation, and the observation that no steps in plausible f-element-catalyzed dehydrogenative silane polymerization and olefin hydrosilylation cycles are predicted to have major thermodynamic impediments.

Although metal–metal bonding is a ubiquitous feature of contemporary transition-metal chemistry, that involving well-characterized heterobimetallic early-transition-metal–late-transition-metal[1–3] and f-element–late-transition-metal combinations[4,5] as well as early-transition-metal–metalloid[6] and f-element–metalloid[7,8] combinations

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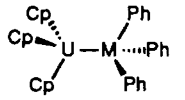
is in a relatively early stage of development. Such systems display a rich diversity of unusual bonding and reactivity patterns that are far from well-understood. Recent developments in other areas of organometallic chemistry have underscored the considerable insight into bonding and reaction chemistry afforded by measurements of absolute and relative metal–ligand bond disruption enthalpies (eq 1 for the adiabatic homolytic process of eq 2).[9,10] In the

$$D(L_n\text{-R}) = \Delta H_f^\circ(L_nM) + \Delta H_f^\circ(R^\bullet) - \Delta H_f^\circ(L_nM\text{-R}) \quad (1)$$

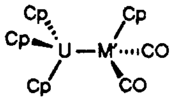
$$L_n = \text{ancillary ligands}$$

$$L_nM\text{-R} \rightarrow L_nM + R^\bullet \quad (2)$$

present contribution, we report a study by isoperibol batch titration calorimetry of metal–metal bonding energetics in the actinide–group 14 metalloid series $Cp_3U\text{-}MPh_3$ (A; Cp = $\eta^5\text{-}C_5H_5$; M = Si, Ge, Sn) and in the actinide–group 8 carbonyl series $Cp_3U\text{-}M'(CO)_2Cp$ (B; M' = Fe, Ru). Not only do these results allow an analysis of bonding/reactivity trends in metal–metal-bonded compounds involving actinides but also, with use of the well-supported observation that actinides are reasonable thermochemical models for 4f and d^0 group 4 centers,[11] significant implications can be drawn about the chemical nature of metal–metal bonding in analogous 4f and group 4 systems.



A



B

Table I. Enthalpies of Solution in Toluene, Enthalpies of Reaction of $Cp_3U\text{-}M/Cp_3U\text{-}R$ Compounds with I_2 in Toluene, and Derived Absolute U–M/U–R Bond Disruption Enthalpies

compd	ΔH_{soln}[a]	$-\Delta H_{reacn}$[a]	D(U–M)/ D(U–R)
$Cp_3U\text{—}SiPh_3$ (1)	1.7 (0.2)	63.0 (1.2)	37.3 (4.2)
$Cp^+{}_3U\text{—}I$ (2)			62.4 (0.5)[b]
$Cp_3U\text{—}GePh_3$ (3)	1.5 (0.2)	53.4 (1.0)	38.9 (4.5)
$Cp_3U\text{—}SnPh_3$ (4)	1.5 (0.2)	51.1 (1.0)	37.2 (4.0)
$Cp_3U\text{—}Fe(CO)_2Cp$ (5)	2.0 (0.2)	50.4 (1.2)	30.9 (3.0)
$Cp_3U\text{—}Ru(CO)_2Cp$ (6)	2.1 (0.2)	47.6 (0.9)	40.4 (4.0)[c]
$Cp^+{}_3U\text{—}Me$			44.8 (1.1)[b]
$Cp^+{}_3U\text{—}n\text{-}Bu$			28.9 (1.7)[b]
$Cp^+{}_3U\text{—}CH_2SiMe_3$			39.3 (2.3)[b]
$Cp^+{}_3U\text{—}CH_2Ph$			25.6 (3.1)[b]
$Cp^+{}_3U\text{—}CH{=}CH_2$			48.5 (2.2)[b]
$Cp^+{}_3U\text{—}C{\equiv}CPh$			86.7[b,d]

[a] In kcal/mol; quantities in parentheses are 95% confidence limits (3σ). [b] Taken from ref 11d. Cp$^+$ = $\eta^5\text{-}Me_3SiC_5H_4$. [c] See text for explanation of derived value of D[I–Ru(CO)$_2$Cp]. [d] See ref 11d for the derivation of this parameter.

Experimental Section

General Considerations. Manipulations of organouranium complexes were carried out under an atmosphere of purified argon with use of standard high-vacuum techniques or in a Vacuum Atmospheres glovebox under prepurified nitrogen. Solvents used were predried and distilled from appropriate drying agents. The toluene used in the calorimetric measurements was additionally stored over Na/K alloy and vacuum-transferred immediately prior to use. The iodine used to prepare the titrant solution was sublimed prior to use. ^{1}H NMR spectra were recorded on a JEOL FX-90 (FT, 90 MHz) or on a Varian XL-400 (FT, 400 MHz) spectrometer.

Synthesis and Calorimetric Measurements. The complexes $Cp_3USi(C_6H_5)_3$ (1),[8a] $Cp_3UGe(C_6H_5)_3$ (3),[8b] $Cp_3USn(C_6H_5)_3$ (4),[8c] $Cp_3UFe(CO)_2Cp$ (5),[4c] and $Cp_3URu(CO)_2Cp$ (6)[4c] were prepared and purified according to literature procedures. Calorimetric measurements were carried out with use of an extensively modified Tronac Model 450 isoperibol titration calorimeter. These modifications permit the study of highly air- and moisture-sensitive reactions. The system has been previously described.[11,12] A typical experimental procedure begins with the loading, in the glovebox, of precisely weighed amounts of the organouranium complex of interest into glass ampules. These are then sealed with Ultra Torr fittings, removed from the box, and connected to the calorimeter. The other removable parts of the calorimeter (reaction dewar, solvent bulb and titrant reservoir) are then connected. The entire system is next subjected to a series of evacuation and inert-gas (argon) back-filling cycles to ensure the exclusion of water and oxygen. The solvent is then added to the reaction dewar, the system placed under an argon blanket, stirring initiated, and the system lowered into a constant-temperature bath (25.000 ± 0.001 °C) for thermal equilibration. Once the system has reached operating temperature, a series of electrical heat calibrations is performed with a calibrated resistor. The ampules are then broken with use of a metal anvil attached to a blade of the stirring shaft, thereby allowing the organouranium complex to dissolve in the solvent. The heat of solvation is recorded, and the corresponding enthalpies of solution are calculated. After all ampules have been broken, the motor-driven buret containing the titrant solution is activated, and a series of titrations (ca. 25–30 individual titrations) are performed. At the end of the titration period, when the organouranium complex has been consumed, a series of electrical calibrations is again performed. From the average of the electrical calibration, electrically derived heat is converted to chemically derived heat. Since the titrant molarity and the buret delivery rate (calibrated) are known,

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the enthalpy of reaction can then be calculated for each individual titration. The known amount of organouranium compound present in solution and the known titrant volume employed provide an internal verification of the reaction stoichiometry. Uncertainties reported for ΔH_{soln} and ΔH_{reacn} are 95% confidence limits,[13] and uncertainties in derived D(U–M) values include these as well as reported uncertainties in literature parameters used in the D(U–M) calculations.

^{1}H NMR Titration Experiments. Prior to every calorimetric experiment, a known amount of the organouranium complex of interest is weighed into a Wilmad screw-capped NMR tube fitted with a septum and C_6D_6 is subsequently added. This solution is then titrated with standard solutions of I_2 by injecting the latter in aliquots through the septum with a microsyringe, followed by vigorous shaking. The titrations are monitored by ^{1}H NMR spectroscopy to validate the rapid and quantitative nature of each reaction, a condition necessary for accurate and meaningful calorimetric measurements. This criterion is satisfied for all organouranium reactions investigated. In each titration, the products were identified as Cp_3U–I and the appropriate M–I/M′–I complexes (M/M′ = $SiPh_3$, $GePh_3$, $Fe(CO)_2Cp$, $Ru(CO)_2Cp$) by comparison with published spectral data and/or those of authentic samples.[14]

Results

This section begins with a presentation of calorimetric results for the series Cp_3U–MPh_3 (M = Si, Ge, Sn) and Cp_3U–$M'(CO)_2Cp$ (M′ = Fe, Ru). Relevant thermodynamic data to establish absolute U–M and U–M′ bond disruption enthalpies are next offered. In the Discussion, the thermochemical results are considered in terms of trends in metal–metal bonding and are employed to analyze the driving force(s) for a number of known and hypothetical U–M,M′-centered reaction patterns.

Iodinolytic Calorimetry of $(C_5H_5)_3U$–$M(C_6H_5)_3$ and $(C_5H_5)_3U$–$M'(CO)_2(C_5H_5)$ Complexes. The Cp_3U–MPh_3 and Cp_3U–$M'(CO)_2Cp$ complexes were synthesized as described in the literature (M = Si (**1**),[8a] Ge (**3**),[8b] Sn (**4**);[8c] M′ = Fe (**5**),[4b] Ru (**6**)[4b]). As monitored by ^{1}H NMR titrations (vide supra), the reactions of **1** and **3**–**6** with I_2 in toluene proceed cleanly and rapidly under calorimetric conditions as shown in eqs 3–7. Experimental heat of solution and heat of reaction data for eqs 3–7 are compiled in Table I along with 95% confidence limits.[13]

$$\underset{\mathbf{1}}{Cp_3U\text{–}SiPh_3} + I_2 \rightarrow \underset{\mathbf{2}}{Cp_3U\text{–}I} + I\text{–}SiPh_3 \tag{3}$$

$$\underset{\mathbf{3}}{Cp_3U\text{–}GePh_3} + I_2 \rightarrow \underset{\mathbf{2}}{Cp_3U\text{–}I} + I\text{–}GePh_3 \tag{4}$$

$$\underset{\mathbf{4}}{Cp_3U\text{–}SnPh_3} + I_2 \rightarrow \underset{\mathbf{2}}{Cp_3U\text{–}I} + I\text{–}SnPh_3 \tag{5}$$

$$\underset{\mathbf{5}}{Cp_3U\text{–}Fe(CO)_2Cp} + I_2 \rightarrow \underset{\mathbf{2}}{Cp_3U\text{–}I} + I\text{–}Fe(CO)_2Cp \tag{6}$$

$$\underset{\mathbf{6}}{Cp_3U\text{–}Ru(CO)_2Cp} + I_2 \rightarrow \underset{\mathbf{2}}{Cp_3U\text{–}I} + I\text{–}Ru(CO)_2Cp \tag{7}$$

The solution-phase metal–metal bond disruption enthalpies can be related to the corresponding heats of iodinolysis via eqs 8 and 9. The value of $D(I_2)$ is taken from

$$D(Cp_3U\text{–}MPh_3) = D(Cp_3U\text{–}I) + D(Ph_3M\text{–}I) + \Delta H_{reacn} - D(I_2) \tag{8}$$

$$D(Cp_3U\text{–}M'(CO)_2Cp) = D(Cp_3U\text{–}I) + D(I\text{–}M'(CO)_2Cp) + \Delta H_{reacn} - D(I_2) \tag{9}$$

standard sources,[15] while $D(Cp_3U\text{–}I)$ is taken to be equal to the previously determined, absolute value of $D[(Me_3SiC_5H_4)_3U\text{–}I]$, 62.4 (0.5) kcal/mol.[11d] This is a reasonable approximation, since absolute D(M–halogen) values are known to be relatively insensitive to ancillary ligation for M being an f element[11a–d] and since existing Cp_3UR and $(Me_3SiC_5H_4)_3UR$ structures, reactions, and thermochemistry are closely parallel.[11d,16]

Although experimental $D(Ph_3M\text{–}I)$ data are not available for M = Si, Ge, Sn, there is an abundance of other organo-group 14 data[10a,g,17,18] (especially kinetically derived data for Si[17a–c,19a]), which readily lead to reasonable estimates. There is considerable evidence that aryl substitution has only minor weakening effects on D(Si–Cl) and D(Si–H) values in organosilanes;[17a,e,k,18] thus, we take $D(Ph_3Si\text{–}I)$ to be 3 kcal/mol less than that in Me_3SiI, 76.8 (1.9) kcal/mol.[17f,19b] Available heat of formation/sublimation data [10g,17f] yield $D(Me_3Sn\text{–}I)$ = 69 kcal/mol. A similar calculation from available data[10g,19d] suggests that $D(Ph_3Sn\text{–}Br)$ = 79 kcal/mol while $D(Me_3Sn\text{–}Br)$ = 85 kcal/mol.[17f] Adjusting $D(Me_3Sn\text{–}I)$ by this proportionality gives $D(Ph_3Sn\text{–}I)$ = 64 kcal/mol. Calculation of $D(Me_3Sn\text{–}I)$ from proportionalities involving other kinetically derived $D(Me_3M\text{–}X)$ data and bond energy contribution (E) data[17j,19a] for $D(Me_3Sn\text{–}I)/D(Me_3M\text{–}X)$ pairs or estimates from SnX_4/MX_4 data[19c] invariably give slightly lower (~2 kcal/mol) values for $D(Me_3Sn\text{–}I)$; therefore, we take $D(Ph_3Sn\text{–}I)$ = 62 kcal/mol. Less thermochemical data are available for organogermanium halides; however, the many linearities in plots of group 14

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[16] (a) ΔH_{reacn} values for iodinolysis:[11d] $Cp_3U(n\text{-}Bu)$, −47.4 (0.6) kcal/mol; $(Me_3SiC_5H_4)_3U(n\text{-}Bu)$, −46.9 (0.3) kcal/mol. (b) Cp_3U is insufficiently soluble for accurate solution calorimetry, presumably owing to a polymeric solid-state structure.[15c] (c) Marks, T. J.; Streitwieser, A., Jr. In *The Chemistry of the Actinide Elements*, 2nd ed.; Katz, J. J., Seaborg, G. T., Morss, L. R., Eds.; Chapman and Hall: London, 1986; Chapter 22.

[17] (a) Walsh, R. In ref 6a, pp 371–391. (b) Carson, A. S.; James, E. H.; Laye, P. G.; Spencer, J. A. *J. Chem. Thermodyn.* **1988**, *20*, 1223–1229 and references therein. (c) Walsh, R. *J. Chem. Soc., Faraday Trans. 1*, **1983**, *79*, 2233–2248. (d) Steele, W. V. *J. Chem. Thermodyn.* **1983**, *15*, 595–601. (e) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246–262 and references therein. (f) Jackson, R. A. *J. Organomet. Chem.* **1979**, *166*, 17–19. (g) Steele, W. V. *J. Chem. Thermodyn.* **1978**, *10*, 445–448. (h) Butler, R. S.; Carson, A. S.; Laye, P. G.; Steele, W. V. *J. Chem. Thermodyn.* **1976**, *8*, 1153–1158. (i) Carson, A. S.; Franklin, J.; Laye, P. G.; Morris, H. *J. Chem. Thermodyn.* **1975**, *7*, 763–766. (j) Baldwin, J. C.; Lappert, M. F.; Pedley, J. B.; Poland, J. S. *J. Chem. Soc., Dalton Trans.* **1972**, 1943–1947. (k) Ring, M. A.; O'Neal, H. E. O.; Kadhim, A. H.; Jappe, F. *J. Organomet. Chem.* **1966**, *5*, 124–129.

[18] D(M–H) values were taken from the following sources. (a) $D(Me_3Si\text{–}H)$ = 90.3 (2.0) kcal/mol: from ref 17a. (b) $D(Ph_3Si\text{–}H)$ = 84.2 (0.5) kcal/mol from: Dias, A. R.; Diogo, H. P.; Griller, D.; Minas de Piedade; Simoes, J. A. M. In ref 9a, pp 205–217. (c) $D(Me_3Ge\text{–}H)$ = 81.8 (2.5) kcal/mol from: Doncaster, A. M.; Walsh, R. *J. Chem. Soc., Chem. Commun.* **1977**, 446–447. Using the above Si proportionalities, we estimate $D(Ph_3Ge\text{–}H)$ = 76.2 kcal/mol. (d) $D[(n\text{-}Bu)_3Sn\text{–}H]$ = 73.7 (2.0) kcal/mol from: Burkey, T. J.; Majewski, M.; Griller, D. *J. Am. Chem. Soc.* **1986**, *108*, 2218–2221. We estimate $D(Ph_3Sn\text{–}H)$ = 68.7 kcal/mol using the above Si proportionalities. (e) From the above Si data, it is reasonable to take $D(Ph_3Si\text{–}SiPh_3)$ as ca. 6 kcal/mol less than $D(Me_3Si\text{–}SiMe_3)$.

[19] (a) For discussions of the reliability of the various measurement techniques and means of expressing bond strengths, see ref 10a,b,f–h and Chapter 1 of ref 9a. (b) Where overlapping organosilicon data exist, there is generally good agreement between kinetically derived parameters and those[17f] based heavily upon earlier, appearance potential derived $\Delta H_f^\circ(Me_3M^\bullet)$ data. However, from data trends for the corresponding MX_4 compounds,[17c,19c] the estimated[17f] $D(Me_3Ge\text{–}Cl)$ and $D(Me_3Ge\text{–}Br)$ parameters appear to be too large. (c) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, U.K., 1984; p 436. (d) We estimate $\Delta H_{sub}(Ph_3SnBr)$ from proportionalities as: $[\Delta H_{sub}(Ph_4Sn)][\Delta H_{sub}(Ph_3PbBr)]/[\Delta H_{sub}(Ph_4Pb)]$.

D(M–X/R) data versus M as well as D/E(Me_3M–X)- or MX_4-based proportionalities[17f,j,19c] suggest that an interpolated value of D(Ph_3Ge–I) = 66 kcal/mol is reasonable. We consider these D(Ph_3M–I) parameters to be reliable to ±3, ±3.5, and ±3 kcal/mol for M = Si, Ge, and Sn, respectively. As previously,[11] we make the physically reasonable assumption that these gas-phase data are readily transferred to nonpolar hydrocarbon solutions.

The D(Cp(CO)$_2$Fe–I) value needed for eq 9 (55.4 (2) kcal/mol) is calculated from the enthalpy of $[CpFe(CO)_2]_2$ (7) iodinolysis determined by Hoff and co-workers[20a] combined with estimates of the homolytic *free energy* of dissociation for 7[20b] (22 kcal/mol) corrected to an enthalpy by $T\Delta S$ = 8 kcal/mol.[21] The corresponding value of D(Cp(CO)$_2$Ru–I) is not presently available. Until this parameter is measured, we employ a tentative value estimated from the corresponding hydride disruption enthalpy data[22] (eq 10) as 62 (3) kcal/mol.[23]

$$D(\mathrm{Ru{-}I}) \approx D(\mathrm{Fe{-}I})\frac{D(\mathrm{Ru{-}H})}{D(\mathrm{Fe{-}H})} \qquad (10)$$

In Table I are compiled the D(Cp_3U–M) and D(Cp_3U–M′) parameters provided by the aforementioned treatment. Although several of the contributing D(M–I) and D(M′–I) data were necessarily arrived at by an indirect procedure, it will be seen that the resulting metal–metal bond disruption enthalpies are sufficiently accurate to discern major trends in bonding and reaction thermodynamics. *Importantly*, the transformations of greatest interest involve U–M, U–M′ → X–M, X–M′ transpositions in which many uncertainties in M/M′-based parameters should cancel. Moreover, it will be seen that overall enthalpy changes in catalytic cycles calculated from sums of reaction enthalpy changes, in turn estimated from the present bond enthalpy data, are in good agreement with reactant → product enthalpy changes calculated from standard data tabulations. For comparative purposes, D-[$(Me_3SiC_5H_4)_3U$–R] data from a previous study[11d] are also included in Table I.

Discussion

Bonding Trends. Several points are evident from the bond disruption enthalpy data in Table I. First, the uranium–group 14 metal and uranium–group 8 transition-metal bonds exhibit a surprisingly small bond enthalpy dispersion and are relatively weak, comparable to uranium–sp^3 hydrocarbyl bonds, and significantly weaker than uranium–sp, sp^2 hydrocarbyl bonds. As noted previously,[11] certain gross aspects of such metal–ligand bonding energetics can be understood in terms of Pauling-like electronegativity considerations. Certainly the relative weakness of the present bonds involving the group 14 elements are explicable in terms of these ideas, although steric interactions are probably not insignificant, judging from diffraction results.[8a,c] Further support for the relative weakness of d^0 metal–group 14 metal bonding derives from structural data indicating that M–Si distances are frequently longer than predicted on the basis of covalent radii.[6a] This is opposite to the situation for later transition metals, where significant M–element bond shortening is observed and where M→group 14 metal π back-bonding may be operative.[6a,24]

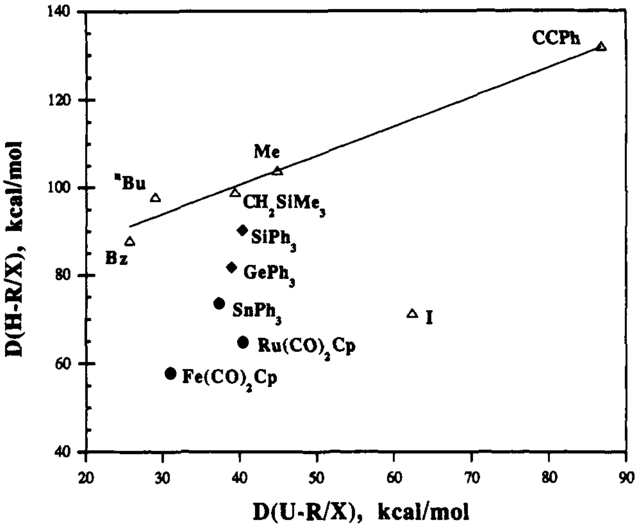

Figure 1. Correlation between measured $(Me_3SiC_5H_4)_3U$–R/X/M/M′ bond disruption enthalpies (open triangles, ref 11d; filled diamonds, this work) and the corresponding literature D(R–H)/D(X–H)/D(M–H)/D(M′–H) values.

In regard to U–M′Cp(CO)$_2$ bonding, infrared ν_{CO} spectral data indicate substantial polarity in the metal–metal bonding (C).[4] This conclusion is further supported by

$$Cp_3U{-}M'(CO)_2Cp \underset{C}{\leftrightarrow} Cp_3U^+M'^-(CO)_2Cp$$

quasirelativistic Xα–SW calculations,[5a] which also suggest that the metal carbonyl fragment in such bonds can be viewed as a "pseudohalide". While this pseudohalide analogy appears qualitatively reasonable, it should also be noted that the present U–Fe,Ru bond enthalpies are *25 or more kcal/mol weaker* than those involving U–halogen bonds.[11] Structurally, actinide–transition-metal bond lengths exhibit some shortening versus sums of plausible covalent radii.[4b,c]

Significant linearity in plots of D(M–R/X) versus D(H–R/X) data is a feature of middle-transiton-metal and late-transition-metal to ligand bonding.[25] The linearlity can be rationalized to first order in terms of electronegativity considerations,[11a–e] with the greatest deviations observed for electropositive metals (lanthanides, actinides, early transition metals) having electronegative ligands (alkoxide, thiolate, halide). Here D(M–R/X) values are stronger than otherwise anticipated (data points are displaced to the right of the hydrocarbyl/hydride line). As can be seen in Figure 1, the present D(U–M)/D(U–M′) data exhibit a different type of deviation in that the bimetallic data points fall below but also to the right of the hydrocarbyl/hydride line. Note that the deviations are far less than for the aforementioned electronegative ligands.[11a–e] Clearly, the heterobimetallic bonding is rather different from than that in the corresponding $HMPh_3$ and HM′(CO)$_2$Cp molecules.

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[20] (a) Hoff, C. D., private communication. (b) Pugh, J. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 8245–8246.

[21] (a) Smith, G. M.; Carpenter, J. D.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 6805–6807. (b) Page, M. I. In *The Chemistry of Enzyme Action*; Page, M. I., Ed.; Elsevier: New York, 1984; pp 1–54. (c) Page, M. I.; Jencks, W. F. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 1678–1683. (d) The corresponding room-temperature $T\Delta S$ value involving a more sterically congested dimer, $[CpCr(CO)_3]_2 \rightleftarrows 2CpCr(CO)_3$, is 10.6 (0.4) kcal/mol: McLain, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 643–644.

[22] Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711–6717; **1990**, *112*, 2843. D[CpFe(CO)$_2$–H] = 58 kcal/mol; D[CpRu(CO)$_2$–H] = 65 kcal/mol.

[23] (a) Alternatively, the D(M–I) value of another second-row early-transition-metal cyclopentadienyl carbonyl iodide, CpMo(CO)$_3$I, could be used. The measured quantity, 54.2 (1.5) kcal/mol,[23b] is within ca. 7 kcal/mol of that estimated via eq 10. (b) Nolan, S. P.; Lopez, de la Vega, R.; Hoff, C. D. *J. Organomet. Chem.* **1986**, *315*, 187–199.

[24] Berry, A. D.; Corey, E. R.; Hagen, A. P.; MacDiarmid, A. G.; Saalfeld, F. E.; Wayland, B. B. *J. Am. Chem. Soc.* **1970**, *92*, 1940–1945.

[25] Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444–1456.

Thermochemistry of Known and Hypothetical U–M,M′ Transformations. The bond disruption enthalpy data of Table I, combined with data derived from previous linear $D(\mathrm{M{-}R/X})/D(\mathrm{M'{-}R/X})$ correlations drawn between actinide, lanthanide, and group 4 complexes,[11a–e] allow the approximate thermodynamic analysis of a variety of transformations involving heterobimetallic linkages. For this purpose, bond enthalpies of organic[15] and organometallic[10,11,17,18] fragments are taken from standard sources, and it is assumed that metal substituent effects largely attenuate within two σ bonds. ΔH values estimated for various reactions are conservatively taken to have uncertainties on the order of ±6 kcal/mol.

The "amine-elimination" route is a common approach to the synthesis of heterobimetallic metal–metal bonds[1,2] and was employed in the synthesis of 4.[8c] From the previously noted linear relationship of $(\mathrm{Me_3SiC_5H_4})_3\mathrm{U{-}R}/\mathrm{Cp'_2Sm{-}R}$ bond enthalpy data[11b] ($\mathrm{Cp'} = \eta^5\text{-}\mathrm{Me_5C_5}$), $D(\mathrm{Cp_3U{-}NMe_2})$ can be estimated to be 45 kcal/mol. It is then seen from eqs 11–15 that the exothermicity of this synthetic pathway is strongly dependent upon $D(\mathrm{M/M'{-}H})$ of the corresponding hydride reagent, since $D(\mathrm{U{-}M/M'})$ has a far smaller energetic dispersion (Table I).

$$\mathrm{Cp_3U{-}NMe_2 + HSiPh_3 \rightarrow Cp_3U{-}SiPh_3 + HNMe_2} \quad (11)$$

$$\Delta H_{\mathrm{calcd}} \approx 0 \text{ kcal/mol}$$

$$\mathrm{Cp_3U{-}NMe_2 + HGePh_3 \rightarrow Cp_3U{-}GePh_3 + HNMe_2} \quad (12)$$

$$\Delta H_{\mathrm{calcd}} \approx -10 \text{ kcal/mol}$$

$$\mathrm{Cp_3U{-}NMe_2 + HSnPh_3 \rightarrow Cp_3U{-}SnPh_3 + HNMe_2} \quad (13)$$

$$\Delta H_{\mathrm{calcd}} \approx -15 \text{ kcal/mol}$$

$$\mathrm{Cp_3U{-}NMe_2 + HFe(CO)_2Cp \rightarrow Cp_3U{-}Fe(CO)_2Cp + HNMe_2} \quad (14)$$

$$\Delta H_{\mathrm{calcd}} \approx -20 \text{ kcal/mol}$$

$$\mathrm{Cp_3U{-}NMe_2 + HRu(CO)_2Cp \rightarrow Cp_3U{-}Ru(CO)_2Cp + HNMe_2} \quad (15)$$

$$\Delta H_{\mathrm{calcd}} \approx -22 \text{ kcal/mol}$$

Since $D(\mathrm{Cp_3U{-}NMe_2}) \approx D(\mathrm{Cp_3U{-}CH_3})$ and $D(\mathrm{CH_3{-}H})$ is ca. 13 kcal/mol greater than $D(\mathrm{Me_2N{-}H})$,[15a,b] alkane elimination syntheses (e.g., eq 16) should be thermodynamically more favorable than the corresponding reactions of the eq 11–15 series by ca. 13 kcal/mol. The estimated

$$\mathrm{Cp_3U{-}CH_3 + HMPh_3/HM'(CO)_2Cp \rightarrow Cp_3U{-}MPh_3/M'(CO)_2Cp + CH_4} \quad (16)$$

$$\Delta H_{\mathrm{calcd}}\ (\text{kcal/mol}) \approx -12\ (\mathrm{M = Si}),\ -22\ (\mathrm{M = Ge}),\ -27\ (\mathrm{M = Sn}),\ -33\ (\mathrm{M' = Fe}),\ -35\ (\mathrm{M' = Ru})$$

endothermicity of the microscopic reverse of eq 16 also indicates that uranium-containing bimetallic complexes will not, in general, be effective reagents for hydrocarbon activation. Exceptions will be cases of weak hydrocarbon C–H bonds and strong metal–hydride bonds (e.g. Si–H, eq 17),[26a,b] exceptionally strong actinide–carbon bonds (cf. eqs 18 and 19),[26c] or cases in which an exothermic follow-up

$$\mathrm{Cp_3U{-}SiPh_3 + HC{\equiv}CPh \rightarrow Cp_3U{-}C{\equiv}CPh + HSiPh_3} \quad (18)$$

$$\Delta H_{\mathrm{calcd}} \approx -4 \text{ kcal/mol}$$

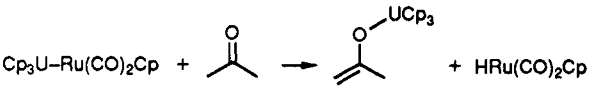
$$\mathrm{Cp_3U{-}SiPh_3 + C_6H_6 \rightarrow Cp_3U{-}C_6H_5 + HSiPh_3} \quad (19)$$

$$\Delta H_{\mathrm{calcd}} \approx +8 \text{ kcal/mol}$$

process (U–O bond formation) is involved (e.g., eq 20).[4d,27] The relatively small endothermicity of eq 19 can be compared to the recent $\mathrm{Ta^{III}{-}Si}$ arene activation results of Berry et al.[26c]

(17)

$\Delta H_{\mathrm{calcd}} \approx -1$ kcal/mol



(20)

$\Delta H_{\mathrm{calcd}} \approx -3$ kcal/mol

Closely related to eq 16 is the formation of U–M/M′ bonds by dihydrogen elimination and the microscopic reverse, U–M/M′ hydrogenolysis (eq 21). Although $\mathrm{Cp_3UH}$

$$\mathrm{Cp_3UH + HMPh_3/HM'(CO)_2Cp \rightarrow Cp_3U{-}MPh_3/M'(CO)_2Cp + H_2} \quad (21)$$

$$\Delta H_{\mathrm{calcd}}\ (\text{kcal/mol}) \approx -7\ (\mathrm{M' = Si})\ -17\ (\mathrm{M = Ge}),\ -22\ (\mathrm{M = Sn}),\ -27\ (\mathrm{M' = Fe}),\ -29\ (\mathrm{M' = Ru})$$

is not a known compound,[11d,28] these results illustrate a qualitative trend that should obtain for other actinide, lanthanide, and early-transition-metal centers and that will be seen to be of catalytic relevance (vide infra). As for many other reaction patterns analyzed in this study, dihydrogen elimination and addition thermodynamics involving these heterobimetallic complexes are largely dictated by the disruption enthalpy of the corresponding group 14 or transition-metal to hydrogen bond created or broken.

An intriguing alternative to the metal–metal bond-forming process of eq 16 is an exchange process in which alkyl and hydride groups are transposed to form a new M/M′–alkyl bond (eq 22). For the analysis shown, tab-

$$\mathrm{Cp_3U{-}CH_3 + HMPh_3/HM'(CO)_2Cp \rightarrow Cp_3U{-}H + CH_3{-}MPh_3/CH_3{-}M'(CO)_2Cp} \quad (22)$$

$$\Delta H_{\mathrm{calcd}}\ (\text{kcal/mol}) \approx -10\ (\mathrm{M = Si}),\ -5\ (\mathrm{M = Ge}),\ -1\ (\mathrm{M = Sn}),\ +13\ (\mathrm{M' = Ru})$$

ulated group 14–methyl bond enthalpies[17a,c,f] are employed. Since $D(\mathrm{CpRu(CO)_2{-}CH_3})$ is presently unavailable, it is reasonable for illustrative purposes to substitute that of $\mathrm{CpMo(CO)_3CH_3}$, 47 kcal/mol.[29] It can be seen from the results in eq 22 that the exothermicity of this exchange process declines as $D(\mathrm{M/M'{-}CH_3}) - D(\mathrm{M/M'{-}H})$ declines. This process will be seen to be of catalytic interest (vide infra).

Certain early transition metal and actinide complexes are reported to be active homogeneous catalysts for the dehydrogenative oligomerization/polymerization of silanes (eq 23).[30–32] Among the plausible reaction mechanisms

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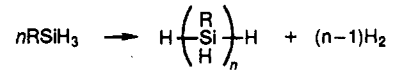
(26) (a) $D(\mathrm{Cp_3U{-}allyl})$ is estimated to be ca. 40 kcal/mol from $(\mathrm{Me_3SiC_5H_4})_3\mathrm{UR}/\mathrm{Cp'_2SmR}$ correlations.[11a,b] However, since $\mathrm{Cp_3U(allyl)}$ is actually an η^1-allyl, presumably because of steric crowding,[26b] this analysis is more relevant to less sterically sensitive transpositions of the type $\mathrm{Cp'_2SmSiPh_3} \rightarrow \mathrm{Cp'_2Sm}(\eta^3\text{-allyl})$. (b) Marks, T. J.; Seyam, A. M.; Kolb, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 5529–5539. (c) Berry, D. H.; Jiang, Z. *J. Am. Chem. Soc.* **1989**, *111*, 8049–8051.

(27) (a) All indications are that C–H activation is followed by sigmatropic U–C → U–O rearrangement in this reaction.[4d] The heat of reaction is estimated by using $\Delta H \approx +12$ kcal/mol for the keto → enol tautomerization of acetone.[27b] (b) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 2nd ed.; Plenum Press: New York, 1984; Part A, pp 390–395.

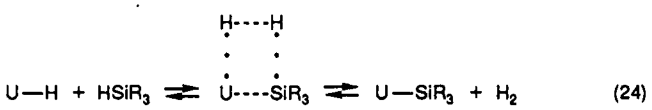
(28) Marks, T. J. In ref 16c, Chapter 23.

(29) Nolan, S. P.; Lopez de la Vega, R.; Mukerjee, S. I.; Gonzalez, A. A.; Zhang, K.; Hoff, C. D. In ref 9b, pp 1491–1498.



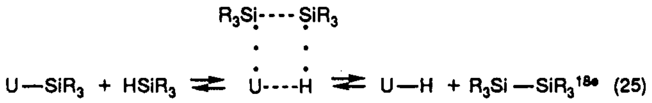
$$n\mathrm{RSiH_3} \longrightarrow \mathrm{H}\left(\begin{array}{c}\mathrm{R}\\ \mathrm{Si}\\ \mathrm{H}\end{array}\right)_n\mathrm{H} + (n-1)\mathrm{H_2} \qquad (23)$$

proposed is a heterolytic "four-center" process not involving silylene complexes or formal changes in metal oxidation state (Scheme I).[32] The strongest support for this mechanism derives from the characterization of several group 4 centered model reactions by Tilley et al.[32b] and the recent observation that highly electrophilic organolanthanides of the type $\mathrm{Cp'_2LnR/Me_2Si(Me_4C_5)_2LnR}$ (Ln = La,[33a,b] Nd,[33a,b] Sm,[33a,b] Lu;[33a,b] R = alkyl, H), which effectively mediate a number of other four-center processes (e.g., Ln–C hydrogenolysis, C–H activation, olefin insertion),[34a–f] are also exceedingly active catalysts for eq 23. In this case, there can be little doubt that formal changes in metal oxidation state are not important in the catalytic cycle. The present thermochemical data allow analysis of the thermodynamic favorability (and generality) of the types of transformations operative in Scheme I (eqs 24–26).



$$\mathrm{U{-}H + HSiR_3} \rightleftarrows \begin{array}{c}\mathrm{H{\cdots}H}\\ \vdots\quad\vdots\\ \mathrm{U{\cdots}SiR_3}\end{array} \rightleftarrows \mathrm{U{-}SiR_3 + H_2} \qquad (24)$$

$\Delta H_{\mathrm{calcd}} \approx -7$ kcal/mol (see eq 21)



$$\mathrm{U{-}SiR_3 + HSiR_3} \rightleftarrows \begin{array}{c}\mathrm{R_3Si{\cdots}SiR_3}\\ \vdots\quad\vdots\\ \mathrm{U{\cdots}H}\end{array} \rightleftarrows \mathrm{U{-}H + R_3Si{-}SiR_3}^{18a} \qquad (25)$$

$\Delta H_{\mathrm{calcd}} \approx -4$ kcal/mol

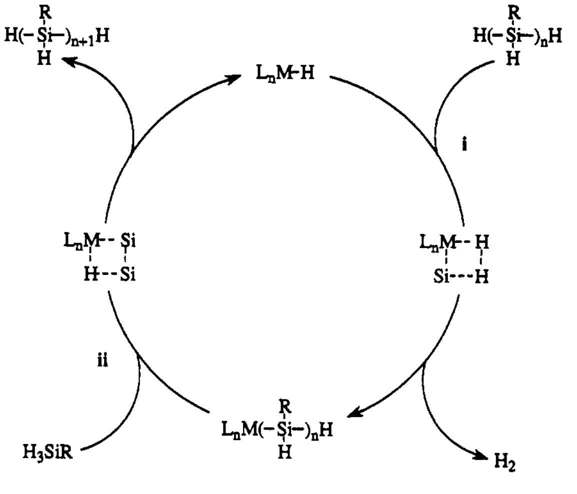
overall:

$$\mathrm{2HSiR_3 \xrightarrow{Cp_3UH} R_3Si{-}SiR_3 + H_2} \qquad (26)$$

$\Delta H_{\mathrm{calcd}} \approx -11$ kcal/mol of $\mathrm{H_2}$

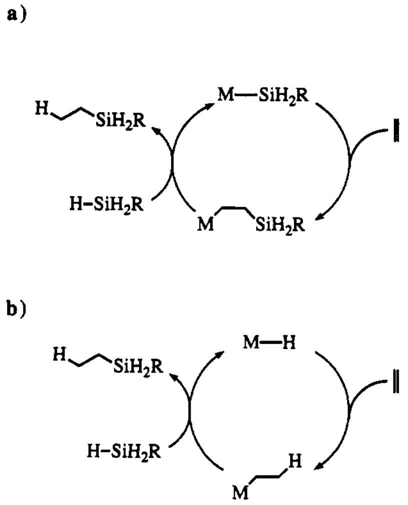
It can be seen that the dihydrogen elimination step ((i) in Scheme I) is predicted to be exothermic while the (presumably) sterically more demanding Si–Si bond-forming process ((ii) in Scheme I) is probably less so. Hence, there are no major thermodynamic impediments in Scheme I. From tabulated $\mathrm{HSiR_3}$ and $\mathrm{(R_3Si)_2}$ $\Delta H_f°$ data (R = Me),[10g,17a] we estimate $\Delta H \approx -8$ kcal/mol for eq 26, in reasonable agreement with that calculated from the steps represented by eqs 24 and 25 for R = Ph.

Scheme I



$\mathrm{L_n}$ = ancillary ligation

Scheme II



With respect to catalysis of analogues of Scheme I and eq 26, the corresponding catalytic Ge and Sn dehydrogenations are estimated to be comparably exothermic ($\Delta H_{\mathrm{calcd}} \approx -11$ and -11 kcal/mol, respectively), while those of the Fe and Ru analogues should be even more exothermic ($\Delta H_{\mathrm{calcd}} \approx -18$ and -14 kcal/mol,[29,35] respectively).

The very favorable kinetics for olefin insertion processes within organo-f-element coordination spheres[34a–f] prompts an examination of the thermodynamics of such reactions for the present bimetallic complexes with ethylene as a model olefin (eqs 27–29).[34g] The trend from exothermic

$$\mathrm{Cp_3U{-}SiPh_3} + \| \rightarrow \mathrm{Cp_3\overline{U\ Si}Ph_3} \qquad (27)$$

$\Delta H_{\mathrm{calcd}} \approx -15$ kcal/mol

$$\mathrm{Cp_3U{-}GePh_3} + \| \rightarrow \mathrm{Cp_3\overline{U\ Ge}Ph_3} \qquad (28)$$

$\Delta H_{\mathrm{calcd}} \approx 0$ kcal/mol

$$\mathrm{Cp_3U{-}SnPh_3} + \| \rightarrow \mathrm{Cp_3\overline{U\ Sn}Ph_3} \qquad (29)$$

$\Delta H_{\mathrm{calcd}} \approx +11$ kcal/mol

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[30] (a) Aitken, C. T.; Harrod, J. F.; Gill, U. S. *Can. J. Chem.* **1987**, *65*, 1804–1809. (b) Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059–4066. (c) Aitken, C. T.; Harrod, J. F.; Samuel, E. *Can. J. Chem.* **1986**, *64*, 1677–1679. (d) Harrod, J. F. In *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988; pp 89–100.

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[35] We make the reasonable approximation that $D(\mathrm{Ru{-}Ru}) \approx D(\mathrm{Fe{-}Fe}) + 10$ kcal/mol in the $\mathrm{[CpM(CO)_2]_2}$ products. In the sterically more crowded $\mathrm{[CpM(CO)_3]_2}$ series (M = Cr, Mo), this difference is ca. 17 kcal/mol.[21d,29]

to endothermic in eqs 27–29 largely reflects the declining strength of the group 14 metal–carbon bond enthalpy in the products. Equation 27 is in agreement with recent group 4–silyl olefin insertion results of Tilley.[6a] Since $D[\mathrm{CpM(CO)_2{-}Et}]$ is unavailable, it is reasonable for illustrative purposes to substitute $D[\mathrm{CpMo(CO)_3{-}Et}]$[29] for the Ru–alkyl bond enthalpy. In eq 30, the ethylene in-

$$\mathrm{Cp_3U{-}Ru(CO)_2Cp} + \parallel \rightarrow \mathrm{Cp_3\overbrace{U\ Ru}(CO)_2Cp} \qquad (30)$$

$$\Delta H_{\mathrm{calcd}} \approx +13\ \mathrm{kcal/mol}$$

sertion process is also rather endothermic. In all cases, subsequent ethylene insertions should be almost equally exothermic, since this is effectively the propagation step of a standard coordinative polymerization. Interestingly, coupling eq 27 to eq 16 (M = Si) affords a thermodynamically plausible organoactinide-mediated catalytic cycle for the homogeneous hydrosilylation[36] of olefins (eq 31;

$$\mathrm{Ph_3SiH} + \parallel \xrightarrow{\mathrm{Cp_3UH}} \mathrm{Ph_3\overbrace{Si\ H}} \qquad (31)$$

$$\Delta H_{\mathrm{calcd}} \approx -27\ \mathrm{kcal/mol}\ (\text{eq 16 + eq 27})$$
$$\approx -29\ \mathrm{kcal/mol}\ (\text{eq 22 for U/Si–Et + eq 32})$$

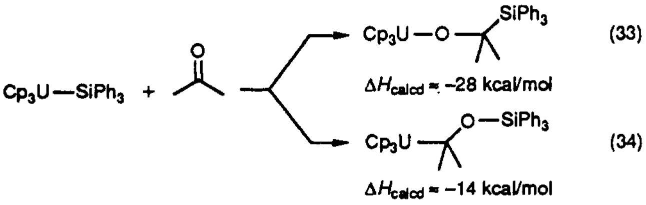
Scheme IIa). Note that such a cycle does not involve conventional oxidative-addition or reductive-elimination sequences.[36] Equally interesting is the possibility of coupling the exothermic insertion of olefins into actinide hydride bonds[11f-h] (eq 32) with the alkyl-hydride tran-

$$\mathrm{Cp_3UH} + \parallel \rightarrow \mathrm{Cp_3\overbrace{U\ H}} \qquad (32)$$

$$\Delta H_{\mathrm{calcd}} \approx -20\ \mathrm{kcal/mol}$$

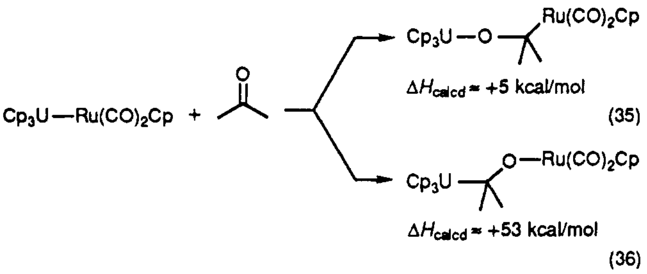
sposition process of eq 22 to effect olefin hydrolysilylation by an alternative, to our knowledge previously unrecognized,[36] reaction sequence (eq 31; Scheme IIb; $\Delta H_{\mathrm{calcd}} \approx -30$ kcal/mol). Evidence for this latter pathway has recently been presented by Watson.[33c,d] The only proviso in both components of Scheme II is the possibility that the most kinetically labile f-element catalysts may also effect, in competing processes, the efficient oligomerization or polymerization of unhindered olefins.[34a-f] Using tabulated thermochemical data,[10f,15d] we calculate $\Delta H \approx -29$ kcal/mol for $\mathrm{Et_3SiH} + \parallel \rightarrow \mathrm{Et_4Si}$, in reasonable agreement with the estimates of eqs 16 + 27, or eqs 22 + 32.

The present thermochemical data also allow an examination of the thermodynamics and regiochemistry of ketone insertion reactions. For eqs 33 and 34, the thermodynamically preferred regiochemistry is that observed for Ta–Si bonds,[37] with both regiochemistries predicted to be exothermic. Since $D(\mathrm{Si{-}OR})$[10a,17a-e] is predicted to be greater than $D(\mathrm{U{-}OR})$,[11a,d,f] the preferred pathway among eqs 33 and 34 is strongly influenced by the strength of the Si–C bond[17a-e,34g] formed in eq 33 and the relative anticipated weakness of the U–C(tertiary) bond[11d] formed in eq 34. For other $\mathrm{Cp_3UM/M'}$ reagents, the ketone insertion thermochemistry is expected to evolve according to two important factors. First, product $D(\mathrm{M/M'{-}C})$ and $D(\mathrm{M/M'{-}O})$ values are expected to be less than for silicon; hence, all insertion reactions will be less exothermic. Second, product $D(\mathrm{M/M'{-}O}) - D(\mathrm{M/M'{-}C})$ differences are likely to decline on descending group 14[10a,g,17j,38] and are expected to be less for Fe and Ru[25] than for Si. Thus, the bias toward formation of U–O bond is enhanced as illustrated in eqs 35 and 36.[39] Of course, eq 35 would be more favorable if coupled to an exothermic follow-up β-H elimination (eq 20).



(33) $\Delta H_{\mathrm{calcd}} \approx -28$ kcal/mol

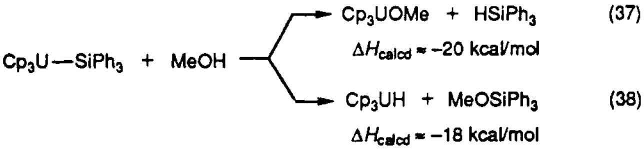
(34) $\Delta H_{\mathrm{calcd}} \approx -14$ kcal/mol



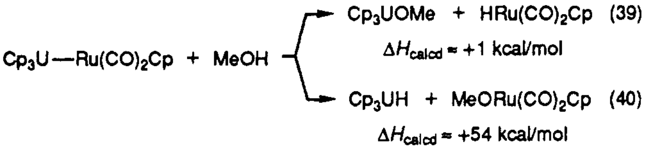
(35) $\Delta H_{\mathrm{calcd}} \approx +5$ kcal/mol

(36) $\Delta H_{\mathrm{calcd}} \approx +53$ kcal/mol

The thermochemistry and regiochemistry of alcohol addition to the present heterobimetallic bonds was investigated for a U–Si and a U–Ru compound (eqs 37–40).



$$\mathrm{Cp_3U{-}SiPh_3} + \mathrm{MeOH} \rightarrow \mathrm{Cp_3UOMe} + \mathrm{HSiPh_3} \qquad (37)$$
$$\Delta H_{\mathrm{calcd}} \approx -20\ \mathrm{kcal/mol}$$
$$\rightarrow \mathrm{Cp_3UH} + \mathrm{MeOSiPh_3} \qquad (38)$$
$$\Delta H_{\mathrm{calcd}} \approx -18\ \mathrm{kcal/mol}$$



$$\mathrm{Cp_3U{-}Ru(CO)_2Cp} + \mathrm{MeOH} \rightarrow \mathrm{Cp_3UOMe} + \mathrm{HRu(CO)_2Cp} \qquad (39)$$
$$\Delta H_{\mathrm{calcd}} \approx +1\ \mathrm{kcal/mol}$$
$$\rightarrow \mathrm{Cp_3UH} + \mathrm{MeORu(CO)_2Cp} \qquad (40)$$
$$\Delta H_{\mathrm{calcd}} \approx +54\ \mathrm{kcal/mol}$$

While both U–Si reactions are predicted to be exothermic, the formation of the stronger Si–O bond in eq 38 is essentially balanced by the strong Si–H bond formed in eq 37. Hence, the former regiochemistry is predicted to be slightly more exothermic. Indeed, the pathway of eq 37 is the sense of addition observed for early-transition-metal silyl complexes,[6a] while eq 38 regiochemistries predominate for later transition metal silyl derivatives.[6a] Heavier group 14 derivatives and the metal carbonyl fragments are less oxophilic, and the pathway exemplified by eq 39 should predominate in these cases. Indeed, eq 39 is the alcoholysis regiochemistry observed experimentally.[4b,c]

The present data also allow an assessment of metathesis thermodynamics between group 14 hydrides and compounds 1, 3, and 4 (eqs 41–43). It can be seen that

$$\mathrm{Cp_3USiPh_3} + \mathrm{HSnPh_3} \rightarrow \mathrm{Cp_3USnPh_3} + \mathrm{HSiPh_3} \qquad (41)$$
$$\Delta H_{\mathrm{calcd}} \approx -15\ \mathrm{kcal/mol}$$

$$\mathrm{Cp_3USiPh_3} + \mathrm{HGePh_3} \rightarrow \mathrm{Cp_3UGePh_3} + \mathrm{HSiPh_3} \qquad (42)$$
$$\Delta H_{\mathrm{calcd}} \approx -10\ \mathrm{kcal/mol}$$

$$\mathrm{Cp_3UGePh_3} + \mathrm{HSnPh_3} \rightarrow \mathrm{Cp_3USnPh_3} + \mathrm{HGePh_3} \qquad (43)$$
$$\Delta H_{\mathrm{calcd}} \approx -5\ \mathrm{kcal/mol}$$

transpositions in which weaker group 14–hydride bonds

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are replaced by stronger ones are predicted to be thermodynamically favorable. Indeed, just such an ordering of metathesis patterns has been observed experimentally.[8a,b]

Finally, the present data provide information, with use of $D(Cp_3U{-}R)/D(Cp'_2Sm{-}R)$ parallels,[11b] on the viability of divalent samarium-mediated oxidative-addition routes to heterobimetallic compounds (eq 44). It is evident that

$$2Cp'_2Sm + HMPh_3/HM'(CO)_2Cp \rightarrow Cp'_2Sm{-}MPh_3/M'(CO)_2Cp + \tfrac{1}{2}(Cp'_2SmH)_2 \quad (44)$$

$$\Delta H_{calcd}\ (kcal/mol) \approx -11\ (Si), -19\ (Ge), -23\ (Sn), -31\ (Fe), -33\ (Ru)$$

such transformations are favorable,[40] with the predicted exothermicity increasing as $D(M/M'{-}H)$ falls. Experimental evidence supporting this analysis comes from the observation that Cp'_2Sm and $Cp'_2Sm(THF)_2$ are effective precatalysts for the dehydrogenative polymerization of silanes (see Scheme I) and that trivalent samarium complexes are rapidly formed upon mixing of the reagents.[35a]

Conclusions

This study provides the first detailed information on absolute metal–metal bonding energetics for an archetypical series of heterobimetallic complexes—uranium–group 14 element and uranium–transition-metal carbonyl. The bond enthalpies are found to be rather modest and to span a relatively narrow range compared to $D(U{-}X)$ values for X = a first-row or more electronegative element. A major chemical consequence of these trends is that relative reaction thermodynamics are far more sensitive to bond enthalpies in other reactants and in products than in the heterobimetallic complex. Nevertheless, these linkages can access a rich diversity of known or thermodynamically plausible stoichiometric and catalytic reaction patterns.

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[40] This analysis assumes Sm–Fe and Sm–Ru bond formation rather than isocarbonyl (e.g., Sm–OC–M′) bond formation, which could be more exothermic. For relevant examples of the latter compounds, see: Boncella, J. M.; Andersen, R. A. *Inorg. Chem.* 1984, *23*, 432–437 and references therein.

Poly(vinylsilane): A Precursor to Silicon Carbide. 1.[1] Preparation and Characterization

Bruno Boury, Robert J. P. Corriu,* Dominique Leclercq, P. Hubert Mutin, Jean-Marc Planeix, and André Vioux

UM 44, CNRS/Rhône-Poulenc/USTL, Place E. Bataillon, F34095 Montpellier Cedex 05, France

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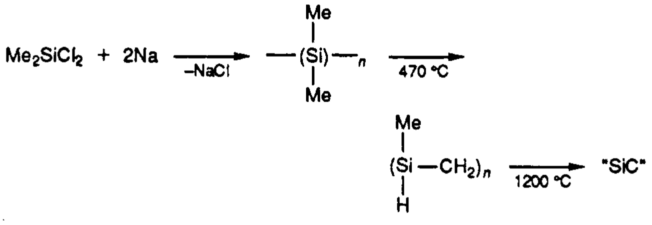
Poly(vinylsilane), $(H_2SiC_2H_4)_n$, has been synthesized by a hydrosilylation route. Depending on the experimental conditions, the average molecular weight varies from 640 to 5500. The structure of these polymers, which was investigated by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy, is explained on the basis of the two possible modes of addition in the hydrosilylation reaction. Pyrolysis of either low or high molecular weight polymers gives similar ceramic yields (32–40%), which are higher than for non-cross-linked poly(silapropylene), $(CH_3SiHCH_2)_n$. This result emphasizes the role of the latent SiH functions in the pyrolysis step.

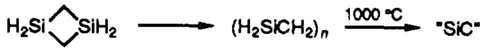
Introduction

Since the pioneering work of Yajima demonstrated that polycarbosilanes were convenient precursors to silicon carbide fibers,[2] there has been considerable interest focused on polysilanes and polycarbosilanes as polymeric precursors. The Yajima process (Scheme I) implies preparation of insoluble poly(dimethylsilane) and its thermal rearrangement to a soluble, functional poly(silapropylene). The poly(silapropylene) is melt, spun, and cured by heating in air to obtain infusible fibers, which are then pyrolyzed in argon to give silicon carbide fibers.[2] However, the polycarbosilane obtained by the thermal rearrangement[3] is not perfectly linear due to a certain degree of cross-linking.[4]

Scheme I



Scheme II



In order to correlate the structure of the preceramic polymer and its thermal behavior, it is necessay to synthesize polycarbosilanes of well-defined structure. To this end, linear poly(silapropylene), $(CH_3SiHCH_2)_n$, has been prepared by Dunoguès[5] and Interrante[6] using the ring-opening polymerization of substituted 1,3-disilacyclobu-

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