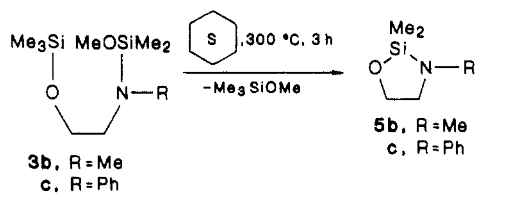
Table I. Vacuum Sealed Tube Thermolysis Experiments of $Me_3SiOCH_2CH_2NRSiMe_2(OMe)$

reactant R	conditions: temp, °C	conditions: time, h	% decomp	product	yield, %
H (**3a**)	250	3	100		
	300	3	100		
Me (**3b**)	300	3	100	**5b**	65
Ph (**3c**)	300	3	100	**5c**	95
$SiMe_3$ (**3d**)	300	3	85	**5d**	85
	300	8	100	**5d**	95
	350	3	100	**5d**	95

of the expected heterocyclic compounds 2,2,3-trimethyl-2-siloxazolidine (**5b**)[9] and trimethylmethoxysilane as



(4)

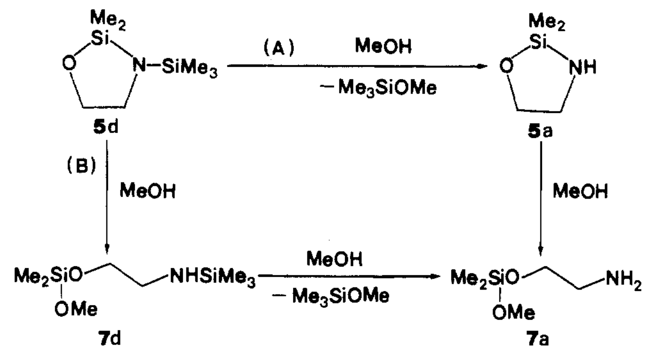
transalkoxylation products along with some other minor products. And when **3c** was also subjected to VSTT at the same condition as above, almost all of the starting material was pyrolyzed to give quantitatively the heterocyclic compound 2,2-dimethyl-3-phenyl-2-siloxazolidine (**5c**),[10] which was a colorless liquid at 0 °C (eq 4).

The VSTT of precursor **3d** was carried out at 350 °C for 3 h to increase the percent decomposition of starting material (85% decomposition at 300 °C). In this condition compound **3d** was completely pyrolyzed to give quantitatively the heterocyclic compound 2,2-dimethyl-3-(trimethylsilyl)-2-siloxazolidine (**5d**).[11] Interestingly we have not observed cyclodisilazane (**6**) which was expected as a silanimine dimer product as shown in Scheme I. This result indicates that the 1,5-elimination of trimethylmethoxysilane is favored over the 1,2-elimination[12] under this condition. The results of the experiments for **3a–d** are summarized in Table I.

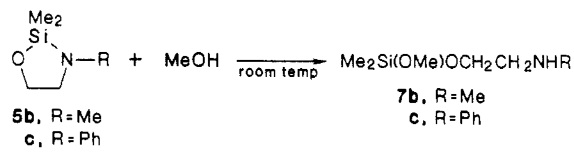
When 3a was treated similarly at 250 and 300 °C, respectively, for 3 h, almost all of **3a** was consumed, giving various unidentified products without any formation of the expected ring-closure product 2,2-dimethyl-2-siloxazolidine (**5a**). This indicates that **5a** might be thermally unstable, although compounds **5b–d** were stable under these thermolysis conditions. The thermostability of compounds **5b–d** were observed in the control experiments carried out under this thermolysis conditions.

The silicon–nitrogen bond in the 2-siloxazolidine could be readily cleaved with alcohols to give ring-cleavage products.[2] We have observed that both **5b** and **5c** were readily reacted with equimolar amount of absolute methanol in dry cyclohexane at room temperature to give the

Scheme II



expected ring-cleavage products dimethylmethoxy(2-(*N*-methylamino)ethoxy)silane (**7b**) and dimethylmethoxy(2-anilinoethoxy)silane (**7c**), respectively (eq 5).



(5)

However, the alcoholysis of **5d** in the presence of an equimolar amount of methanol gave the products dimethylmethoxy(2-aminoethoxy)silane (**7a**) and trimethylmethoxysilane with unreacted **5d** instead of **5a** and **7d** as shown in Scheme II. These products were believed to arise from the desilylation reaction of **5d** and followed by ring cleavage (pathway A) or reverse order (pathway B). Scheme II illustrates the possible reaction pathway proposed for formation of product **7a**. More work is now in progress to clarify the mechanism of this interesting methanolysis reaction.

Acknowledgment. Financial support from the Korea Science and Engineering Foundation is gratefully acknowledged. We also wish to thank Prof. Wan Chul Joo of Sungkyunkwan University for help in obtaining ^{13}C NMR spectra.

Registry No. **1a**, 5804-92-2; **1b**, 98156-23-1; **1c**, 16403-21-7; **1d**, 17165-52-5; **2**, 1825-68-9; **3a**, 105857-32-7; **3b**, 105694-22-2; **3c**, 105694-23-3; **3d**, 105694-24-4; **5b**, 86426-95-1; **5c**, 105694-25-5; **5d**, 105694-26-6; **7a**, 105694-28-8; **7b**, 105694-27-7; **7c**, 27247-86-5.

(9) Compound **5b**: mp 73–75 °C; ^1H NMR (CCl_4) δ 0.15 (s, 6 H), 2.61 (s, 3 H), 2.91 (t, $^3J_{HH}$ = 4.2 Hz, 2 H), 3.63 (t, $^3J_{HH}$ = 4.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ −3.35, 36.11, 53.92, 60.03; mass spectrum, *m/e* 131 (M^+), 130 ($M^+ - H$), 116 ($M^+ - CH_3$). Anal. Calcd for $C_5H_{13}ONSi$: C, 45.75; H, 9.98; N, 10.67. Found: C, 45.06; H, 10.00; N, 10.37.

(10) Compound **5c**: ^1H NMR (CCl_4) δ 0.36 (s, 6 H), 3.26 (t, $^3J_{HH}$ = 6.3 Hz, 2 H), 4.05 (t, $^3J_{HH}$ = 6.3 Hz, 2 H), 6.4–7.2 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 0.11, 46.92, 64.04, 114.87, 118.26, 129.97, 147.64; mass spectrum, *m/e* 193 (M^+), 178 ($M^+ - CH_3$). Anal. Calcd for $C_{10}H_{15}ONSi$: C, 62.12; H, 7.82; N, 7.25. Found: C, 61.20; H, 7.83; N, 7.17.

(11) Compound **5d**: ^1H NMR (CCl_4) δ 0.01 (s, 9 H), 0.12 (s, 6 H), 3.00 (t, $^3J_{HH}$ = 6.0 Hz, 2 H), 3.86 (t, $^3J_{HH}$ = 6.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 0.25, 2.36, 46.97, 65.56; mass spectrum, *m/e* 189 (M^+), 174 ($M^+ - CH_3$). Anal. Calcd for $C_7H_{19}ONSi_2$: C, 44.39; H, 10.11; N, 7.39. Found: C, 43.55; H, 9.89; N, 7.14.

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Coordinatively Unsaturated Clusters: The Rapid Reversible Addition of Two Carbonyl Ligands to a Trinuclear Platinum Cluster

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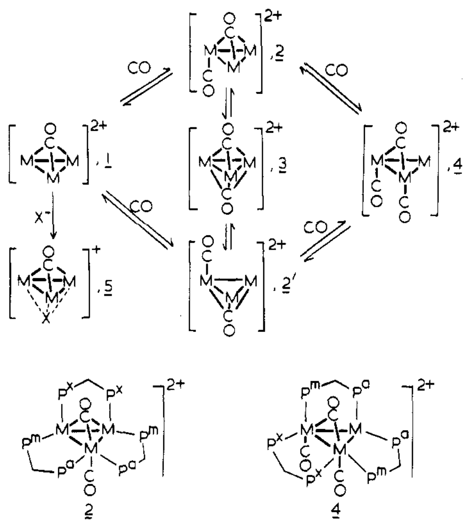
Summary: The complexes $[M_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$ (M = Pt or Pd; dppm = $Ph_2PCH_2PPh_2$) add CO rapidly and reversibly at room temperature to give $[M_3(\mu_3\text{-CO})(CO)(\mu\text{-dppm})_3]^{2+}$ and, when M = Pt, $[M_3(\mu\text{-CO})(CO)_2(\mu\text{-dppm})_3]^{2+}$, but the halide adducts $[M_3(\mu_3\text{-X})(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{+}$ (X = Cl, Br, or I) do not add extra CO ligands; this reversible addition of two ligands to a coordinatively unsaturated cluster without cluster breakdown is a novel feature and allows a closer cluster–surface analogy than in earlier model systems.

Scheme I



It has been argued that clusters in which each metal atom is coordinatively unsaturated should be able to mimic reactions occurring at a metal surface.[1] Trinuclear clusters with a 42-electron count fulfill this requirement and examples include $[M_3(\mu\text{-}CO)_3L_3]$ (M = Pd or Pt; L = tertiary phosphine ligand) and $[Rh_3(\mu\text{-}H)_3L_6]$.[1-6] However, these complexes easily break down to mononuclear fragments, and hence the addition of ligand to two adjacent metal centers without cluster breakdown has not been achieved. Such *double* addition is a prerequisite if catalysis by cluster complexes by fundamentally different pathways from those found for mononuclear catalysts is to be proved.[1] We therefore report studies of the rapid reversible coordination of one or two carbonyl ligands to the 42e complex cations $[M_3(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ (**1a**, M = Pt; **1b**, M = Pd; dppm = $Ph_2PCH_2PPh_2$) whose syntheses have been described earlier.[7]

Relevant work includes the reversible addition of one or two ligands, including CO, to coordinatively saturated clusters, which usually occurs with cleavage of metal–metal bonds. If the cluster is large enough or if there is a capping ligand to prevent fragmentation, the nuclearity of the cluster can be maintained in such reactions.[8] The reactions described below differ significantly because no metal–metal bonds are broken in the CO addition reactions. There are precedents for addition of one CO ligand to coordinatively unsaturated clusters, but we know of no precedents for double CO addition.[9]

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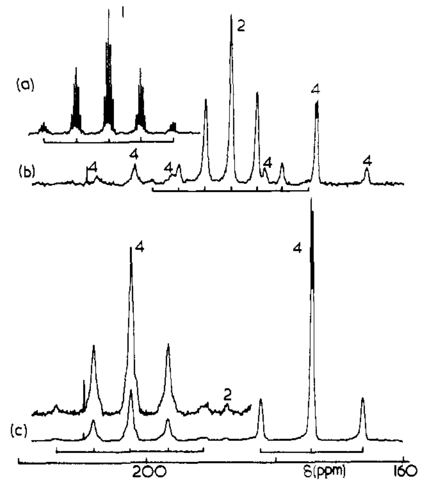

Figure 1. $^{13}C\{^1H\}$ NMR spectra (75 MHz) in the carbonyl region for complexes **1a**–**4a**, prepared from 99.5% ^{13}CO: (a) complex **1a**; (b) complex **2a** at −90 °C, resonances due to equilibrium amount of **4a** are indicated above; (c) complex **4a** at −90 °C, a minor resonance due to **2a** is indicated in the expansion of the μ-CO resonance. In all cases, the centers of the multiplets due to $^1J(^{195}Pt^{13}C)$ coupling are shown below. Note that the resonance for **2** (spectrum b) has a chemical shift intermediate between the bridging and terminal carbonyl regions.[11]

Results. The principal results are shown in Scheme I, from which the μ-dppm ligands either have been omitted or are represented as P͡P. The exchange between free CO and **1a** to give **2a** and **4a** (M = Pt) was fast on the NMR time scale ($t_{1/2} < 0.1$ s) at room temperature, and evaporation of solutions gave only **1a**. This was demonstrated by the observation of only a broad carbonyl resonance (δ 186.0) in the ^{13}C NMR with no coupling to ^{195}Pt, a broad resonance in the ^{31}P NMR with ^{195}Pt satellites [δ −15.3 ($^1J(PtP)$ = 3410 Hz)] and a single CH_2P_2 resonance in the ^1H NMR. Note that the CH_2P_2 resonance for **1** appears as an "AB" quartet due to nonequivalent $CH^aH^bP_2$ protons.[7] The fluxional process leads to an effective plane of symmetry containing the Pt_3P_6 atoms, which we interpret in terms of the rapid equilibration of the species **2**, **3**, and **2′** (Scheme I). Because of these exchange reactions, the carbonyl adducts were characterized by multinuclear NMR studies of CD_2Cl_2 solutions under CO or ^{13}CO in sealed tubes at −90 °C, at which temperature most of the exchange processes were frozen out.

At high p(CO) (ca. 2 atm at room temperature) the only complex present was **4a**, which was not fluxional at −90 °C. Complex **4a** is characterized by having three equal intensity ^{31}P resonances due to the phosphorus atoms P^a, P^m, and P^x (Scheme I) and, in samples prepared by using ^{13}CO, by the presence of both doubly bridging [δ 201.7 ($^1J(PtC)$ = 860 Hz)] and terminal [δ 174.0 ($^1J(PtC)$ = 1170 Hz)] carbonyl resonances in the ^{13}C NMR spectrum (Figure 1, spectrum c). These signals had relative integrals of 1:2.0 in a series of spectra recorded by using pulse delays from 2 to 10 s, and, since nuclear Overhauser effects and related complications are not expected, this indicates the presence of two terminal and one bridging carbonyl. The doubly bridging carbonyl is identified by the ^{13}C chemical shift, by the intensities of the lines due to ^{195}PtC coupling, which are in agreement with the calculated values of 1:8:18:8:1 (Figure 1, spectrum c), with shoulders due to a long-range $^2J(PtC)$ coupling of 110 Hz. In contrast, a

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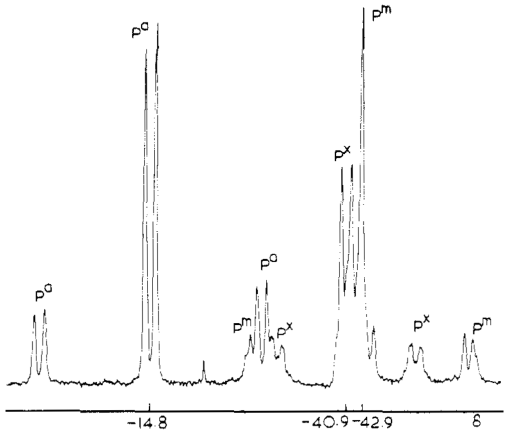

Figure 2. $^{31}P\{^1H\}$ NMR spectrum (121.5 MHz) of complex **4a** at −90 °C.

$Pt_3(\mu_3\text{-}CO)$ group gives a septet with the inner five lines having intensities 1:4:7:4:1 (Figure 1, spectrum a). Complex **4a** is isoelectronic with the 46e cluster $[Pt_3(\mu\text{-}CO)(\mu\text{-}dmpm)_4]^{2+}$ (**6**, dmpm = $Me_2PCH_2PMe_2$) which has a μ-dmpm in place of the two additional carbonyls and which has been characterized crystallographically.[10] No evidence for a complex analogous to **4a** was found on reaction of **1b** (M = Pd) with excess CO.

The presence of three Pt–Pt bonds in **4a** was expected by analogy with **6** and was supported by the ^{31}P NMR parameters. These show large couplings $^3J(PPtPtP)$ through the Pt–Pt bonds, which would not be expected if these bonds were not present.[7] The couplings $^3J(P^aP^x)$ = 165 Hz for **4a** were observed in the resonances due to the isotopomers containing no ^{195}Pt, but the coupling $^3J(P^mP^m)$ = 170 Hz was observed only in the ^{195}Pt satellite spectra as expected[7,10] (Figure 2).

At lower pressure of CO, a second complex was formed from **1a** and was characterized by a single ^{31}P resonance [δ −14.2, ($^1J(PtP)$ = 3400 Hz)] and, in a ^{13}CO-enriched sample, by a single ^{13}CO resonance (Figure 1, spectrum b) showing equal coupling to three ^{195}Pt atoms [δ 186.0 ($^1J(PtC)$ = 590 Hz, $^2J(PC)$ not resolved)]. These data are most easily rationalized in terms of the symmetrical structure **3**. However, IR spectra of solutions under a partial CO atmosphere, such that no **4a** is expected to be present, show bands at 1760 (μ_3-CO) and 2075 cm^{-1} (terminal CO). Therefore, we suggest that the ground-state structure is **2a** but that the species **2a**, **3a**, and **2a′** are in rapid equilibrium even at −90 °C and so the structure appears to be **3** on the NMR time scale (Scheme I). Support for this interpretation is obtained from the ^{13}C NMR parameters for the carbonyl ligands. If the terminal and μ_3-CO ligands for **2** had the same ^{13}CO NMR parameters as for **4** and **1**, respectively, the average parameters would be δ 0.5(205 + 174) = 189.5 ppm ($^1J(PtC)$ = 0.5(777 + $^1/_3$1170) = 584 Hz), in good agreement with the observed parameters: δ(CO) 186 ppm ($^1J(PtC)$ = 590 Hz). We note also that **2a** is isoelectronic with $[Pt_3(\mu_3\text{-}CO)(SCN)(\mu\text{-}dppm)_3]^+$, which has a SCN^- in place of the terminal CO ligand of **2a**.[11] The similar palladium complex **2b** is characterized in the ^{31}P and ^{13}C NMR by $\delta(^{31}P)$ −7.4 and $\delta(^{13}CO)$ 188.2 ($^2J(PC)$ = 8 Hz) and in the IR by peaks at 1827 cm^{-1} (μ_3-CO) and 2021 and 1995 cm^{-1} (terminal CO), and we propose that it undergoes a similar fluxional process. The coordination of extra CO atoms is not observed for the halide complexes **5** (X = Cl, Br, or I). Evidently the halide ligands, though weakly bound,[7] prevent access of CO to the metal centers.

Discussion. There are several significant aspects of the above chemistry. The results show clearly the mechanism of ligand substitution that occurs very rapidly for the complexes **1**. Addition of CO to **1** gives **2**, which then gives **2′** (probably via **3**) and then loss of CO gives back **1** (Scheme I). The overall reaction is then just CO for CO exchange. The slow steps are the addition and loss of CO, and the exchange of **2** $\rightleftharpoons$ **2′** (Scheme I) is fast on the NMR time scale even at −90 °C. Similar ligand substitution mechanisms have been found in some other cluster complexes, and the most interesting aspect in the present case is the great rapidity of the exchange reaction.[8,9]

We have suggested previously that the coordinatively unsaturated clusters **1** act as models for the triangles of platinum atoms on a platinum(111) surface.[7,12] The coordination of one or two carbonyl ligands to **1** to give **2** or **4** can be compared to chemisorption on platinum(111), which gives terminal CO groups at low CO coverage and mostly μ_2-CO with some μ_3-CO groups at higher coverage.[13] The energy difference between the terminal μ_2- and μ_3-CO groups on platinum(111) is very low, and CO migrates over the surface by interconversions between these bonding modes. Clearly, the interconversions between **1**, **2**, **3**, and **4** model several important features of the chemisorption of CO, including the rapidity of addition and the easy interconversion between the bonding modes of CO.[13]

Finally, for catalysis by clusters it is desirable to design coordinatively unsaturated clusters that are stable to fragmentation. The clusters **1**, which are stabilized by μ-dppm ligands, fall into this category. The stability is demonstrated by the addition of two carbonyl ligands without fragmentation. The related platinum clusters $[Pt_3(\mu\text{-}CO)_3L_3]$ add one extra ligand to give $[Pt_3(\mu\text{-}CO)_3L_4]$, but they fragment on further ligand addition. The μ-dppm ligands of **1** are clearly more effective than μ-CO ligands for maintaining cluster nuclearity. To obtain useful catalysis by clusters analogous to complexes **1**, it is desirable that two ligands (which may or may not be different) add to adjacent metal centers, then combine, and dissociate to give the product and regenerate the catalyst.[1] The double addition of CO to complex **1a** to give **4a** (Scheme I) shows that the first step in this sequence is possible. The second and third steps have yet to be demonstrated. We suggest that this is most likely to be achieved by using coordinatively unsaturated complexes which, like **1**, are strongly anchored by bridging ligands.[9]

Experimental Section. NMR spectra were recorded by using a Varian XL200 (^1H) or Varian XL300 (^{13}C, ^{31}P) NMR spectrometer. The cluster complexes **1** and **5** were prepared as described previously.[7]

^{13}CO-Labeled Complexes. A sample of $[Pt_3(\mu_3\text{-}^{13}CO)(\mu\text{-}dppm)_3][PF_6]_2$ was prepared by reaction of the ^{12}CO derivative (0.1 g) with excess ^{13}CO in CH_2Cl_2 solution, followed by evaporation of the solvent. The purity was established by the ^{31}P NMR, which gave only a doublet due to $^2J(^{31}P^{13}C)$ coupling. NMR in CD_2Cl_2: δ −6.7 [d, $^1J(PtP)$ = 3710, $^3J(PP)$ = 140, $^2J(PC)$ = 26 Hz, ^{31}P], 209 [septet, $^1J(PtC)$ = 777, $^2J(PC)$ = 26 Hz ^{13}CO]. The Pd analogue **1b**-^{13}*CO* was prepared in the same way: δ 9.4 [d, $^2J(PC)$ = 20 Hz, ^{31}P], 204.8 [septet, $^2J(PC)$ = 20 Hz, ^{13}CO].

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Study of CO Adducts. A sample of **1a**-^{13}CO (25 mg) in CD_2Cl_2 (0.5 mL) was placed in an NMR tube (5 mm) fitted with a Teflon tap. Excess ^{13}CO was condensed into the liquid-nitrogen-cooled tube via a vacuum line, and the tap was closed. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded at variable temperatures between room temperature and −90 °C, the lowest temperature possible using CD_2Cl_2 solvent. Spectral parameters are given in the text, except for the ^{31}P NMR spectrum of **4a** at −90 °C. **4a**: δ −14.8 [d, $^1J(PtP^a)$ = 3595, $^3J(P^aP^c)$ = 165, $^2J(P^aC) \approx 20$ Hz, P^a], −42.9 [s, $^1J(PtP^m)$ = 3440, $^3J(P^mP^m)$ = 160, $^2J(PtP^m)$ = 170 Hz, P^m], −40.9 [d, $^1J(PtP^x)$ = 2246, $^3J(P^aP^x)$ = 165 Hz, P^x]. ^{31}P NMR spectra were also obtained on samples prepared from ^{12}CO in the same way.

Acknowledgment. We thank NSERC (Canada) for financial support.

Registry No. **1a**, 99583-74-1; **1b**, 89189-79-7; **2a**, 106213-08-5; **2b**, 106213-09-6; **3a**, 106230-79-9; **4a**, 106230-78-8; **5a** (X = Cl), 106213-10-9; **5a** (X = Br), 106213-11-0; **5a** (X = I), 106213-07-4; **5b** (X = Cl), 106213-12-1; **5b** (X = Br), 106213-13-2; **5b** (X = I), 106213-14-3; CO, 630-08-0.

Unusual Th–C–C Angles in Bis(cyclopentadienyl)–Dialkyl Complexes of Thorium

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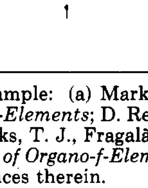
Summary: Some $Cp^*_2Th(alkyl)_2$ complexes display an interesting structural deformation in which a Th–C–C(alkyl) angle opens up considerably. A molecular orbital analysis of $Cp_2Th(C_2H_5)_2$ traces the deformation to the characteristic shape of the d_σ fragment orbital of $Cp_2Th(C_2H_5)^+$. The potential energy curve for the ethyl pivoting was found to be very soft, with a shallow minimum at $\alpha \simeq 160°$. Nonrigidity of the ethyl orientation indicates that either an α-hydrogen or a β-hydrogen can come close to Th without a loss of Th–C bond strength.

In the rapidly growing area of organoactinide chemistry,[1] it remains a major challenge to construct logical frameworks that aid us to understand factors determining the properties characteristic of 5f-transition-metal complexes. The immediate impetus for this theoretical study was provided by the neutron-derived accurate structure of $Cp^*_2Th(CH_2CMe_3)_2$ (**1**),[2,3] where one Th–C–C(neopentyl)



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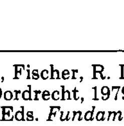

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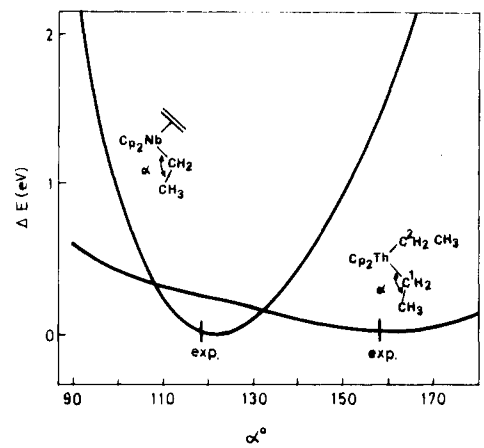

Figure 1. Potential energy curves of $Cp_2Th(C_2H_5)_2$ and $Cp_2Nb(H_2C{=}CH_2)(C_2H_5)$ as a function of M–C–C(ethyl) angle α. The experimentally observed angle α for $Cp^*_2Th(CH_2CMe_3)_2$ or $Cp_2Nb(H_2C{=}CH_2)(C_2H_5)$ is located by a mark "exp." in each corresponding curve.

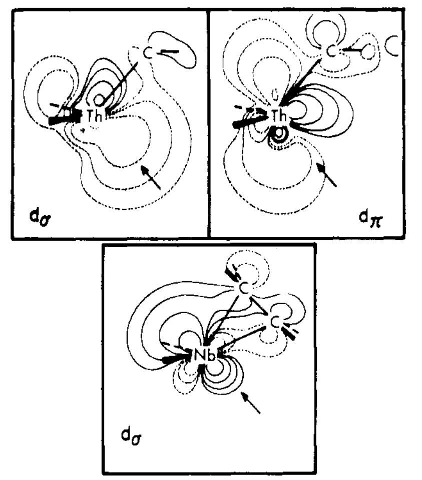

Figure 2. Contour plots of the two frontier orbitals d_σ and d_π of a $Cp_2Th(C^2H_2CH_3)^+$ fragment (top), and the frontier d_σ orbital of $Cp_2Nb(H_2C{=}CH_2)^+$ (bottom). The orbitals are shown in the *xy* plane. The contour levels of each diagram are ±0.025, ±0.05, ±0.1, and ±0.2. The arrows indicate the direction from which the incoming ligand $C_2H_5^-$ approaches.

angle, at C^1 in **1**, is remarkably obtuse while coordination of the other neopentyl ligand is slightly distorted as well. The steric congestion around Th may have something to do with the distortion. However, what we find impressive about **1**, and what we wish to understand in terms of its electronic origin, is that the Th atom is capable of holding *tightly* the extensively distorted neopentyl ligand. The observed Th–C^1 bond is short, even shorter than the Th–C^2 distance.

The model compound for **1** is $Cp_2Th(C_2H_5)_2$ in our extended Hückel calculations.[4,5] Figure 1 presents the po-

(1) See for example: (a) Marks, T. J., Fischer, R. D., Eds. *Organometallics of the f-Elements*; D. Reidel: Dordrecht, 1979; and references therein. (b) Marks, T. J., Fragalà, I. L., Eds. *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; D. Reidel: Dordrecht, 1985, and references therein.

(2) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650–6667. (b) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *Ibid.* **1986**, *108*, 40–56.

(3) There are three homologues of **1**: $Cp^*_2Th(CH_2CMe_3)(CH_2SiMe_3)$, $Cp^*_2Th(CH_2SiMe_3)_2$, and $(CH_3)_2Si\{(CH_3)_4C_5\}_2Th(CH_2SiMe_3)_2$. Each molecule is also characterized by one large Th–C–Si angle (~150°) and simultaneous Th–C bond shortening (2.46–2.48 Å). See ref 2b and: (a) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Organomet. Chem.* **1983**, *250*, 237–246. (b) Fendrick, C. M.; Mintz, E. A.; Schertz, L. D.; Marks, T. J.; Day, V. W. *Organometallics* **1984**, *3*, 819–821.

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