

# Supported Organoactinides. High-Resolution Solid-State $^{13}\text{C}$ NMR Studies of Catalytically Active, Alumina-Bound (Pentamethylcyclopentadienyl)thorium Methyl and Hydride Complexes

Paul J. Toscano and Tobin J. Marks\*

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. Received July 10, 1984

**Abstract:** This contribution reports a high-resolution solid-state  $^{13}\text{C}$  NMR study of the organoactinides  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2$ ,  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2$ , and  $[\text{Cp}'_2\text{Th}(\mu\text{-H})\text{H}]_2$  ( $\text{Cp}' = \eta^5\text{-(CH}_3)_5\text{C}_5$ ) adsorbed on partially dehydroxylated (PDA) or dehydroxylated (DA)  $\gamma$ -alumina. Cross-polarization (CP) combined with magic angle spinning (MAS) and high-power  $^1\text{H}$  decoupling produces adsorbate  $^{13}\text{C}$  NMR spectra of sufficient resolution and sensitivity to obtain significant structural information. On the basis of the observed  $^{13}\text{C}$  chemical shifts, line widths, and field dependence thereof as well as comparison to a number of model systems and dipolar dephasing experiments, methyl transfer from Th to Al on the surface of the support is proposed for the reaction of  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2$  with DA. Several types of experiments (Bloch decay, cessation of dipole decoupling, variable contact time) suggest that the adsorbed species are not highly mobile. On the other hand, adsorption of  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2$  on PDA results in protonolysis of the Th- $\text{CH}_3$  units and the formation of surface Th-O-Al aluminoy species. Useful correlations with the companion surface and catalysis study are presented. The utility of  $^{13}\text{C}$  CPMAS NMR spectroscopy in probing surface-bound metal alkyls (especially in proximity to quadrupolar support nuclei) is emphasized.

Recently there has been a burgeoning interest in the fate of transition-metal organometallic complexes adsorbed on the surfaces of high-area metal oxide supports such as  $\gamma$ -alumina, silica, zeolites, etc.<sup>1</sup> With but a few exceptions the structural, chemical, and mechanistic properties of the adsorbed species have not been established, although such knowledge is highly desirable since the supported complexes frequently display unique and enhanced catalytic activity relative to the precursor molecules in homogeneous solution. In the accompanying paper,<sup>1</sup> we report a detailed investigation of the surface chemistry and catalytic properties of selected organoactinides adsorbed on alumina and silica surfaces. The surface chemical studies with partially dehydroxylated (PDA) and dehydroxylated (DA)  $\gamma$ -alumina supports reveal that methane-evolving surface reaction pathways for  $\text{Cp}'_2\text{M}(\text{CH}_3)_2$  ( $\text{M} = \text{Th, U; Cp}' = \eta^5\text{-(CH}_3)_5\text{C}_5$ ) include M- $\text{CH}_3$  protonolysis via surface hydroxyl (OH) groups (dominant on PDA), Cp' ring H atom abstraction, and intramolecular elimination of methane within  $\text{M}(\text{CH}_3)_2$  units.<sup>1</sup> On DA (but not on PDA), these complexes exhibit high activity for propylene hydrogenation and ethylene polymerization. However, in the case of DA, well over half (depending upon the exact activation conditions) of the methyl groups originally bound to the actinide ion remain on the surface and, curiously, are not completely accessible to hydrogenolysis at 100 °C. In order to further elucidate the structure of surface-adsorbed species, we turned to high-resolution solid-state  $^{13}\text{C}$  NMR spectroscopy utilizing cross-polarization (CP)<sup>2</sup> and magic angle spinning (MAS).<sup>3</sup>

CPMAS NMR<sup>4</sup> is a relatively recent addition to the arsenal of instrumental methods available for the study of chemically modified surfaces. Investigations utilizing conventional Fourier transform (FT) NMR methods<sup>5</sup> in general yield well-resolved signals only for relatively mobile species (useful information may

still be obtained<sup>6</sup>). Surface CPMAS studies have included  $^{13}\text{C}$ ,  $^{29}\text{Si}$ ,  $^{15}\text{N}$ , and  $^{31}\text{P}$  investigations of structure and dynamics for chemically functionalized silicas,<sup>7</sup> the interaction of metal ions and complexes thereof with functionalized silicas, polymers, and glasses,<sup>8</sup> chemisorbed and physisorbed organic molecules,<sup>9</sup> occluded guest molecules in zeolites,<sup>10</sup> carbonaceous residues from zeolite-catalyzed reactions,<sup>11</sup> and the low-temperature oligomerization of small olefins on zeolite H-ZSM-5.<sup>12</sup> In addition,  $^{27}\text{Al}$ ,<sup>13</sup>  $^{17}\text{O}$ ,<sup>14</sup>

(6) (a) Duncan, T. M.; Winslow, P.; Bell, A. T. *Chem. Phys. Lett.* **1983**, *102*, 163-167. (b) Stokes, H. T.; Makowa, C. D.; Wang, P.-K.; Rudaz, S. L.; Slichter, C. P.; Sinfelt, J. H. *J. Mol. Catal.* **1983**, *20*, 321-325.

(7) (a) Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 3767-3776. (b) Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 1848-1851. (c) Shinoda, S.; Nakamura, K.; Saito, Y. *Chem. Lett.* **1983**, 1449-1452. (d) Bayer, E.; Albert, K.; Reiners, J.; Nieder, M.; Müller, D. *J. Chromatogr.* **1983**, *264*, 197-213. (e) Sindorf, D. W.; Maciel, G. E. *J. Phys. Chem.* **1982**, *86*, 5208-5219. (f) Hays, G. R.; Clague, A. D. H.; Huis, R.; van der Velden, G. *Appl. Surf. Sci.* **1982**, *10*, 247-263. (g) Leyden, D. E.; Kendall, D. S.; Waddell, T. G. *Anal. Chim. Acta* **1981**, *126*, 207-212. (h) Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1981**, *103*, 4263-4265. (i) Maciel, G. E.; Sindorf, D. W.; Bartuska, V. J. *J. Chromatogr.* **1981**, *205*, 438-443. (j) Maciel, G. E.; Sindorf, D. W.; Bartuska, V. J. *J. Am. Chem. Soc.* **1980**, *102*, 7606-7607.

(8) (a) Liu, D. K.; Wrighton, M. S.; McKay, D. R.; Maciel, G. E. *Inorg. Chem.* **1984**, *23*, 212-220. (b) Fyfe, C. A.; Clark, H. C.; Davies, J. A.; Hayes, P. J.; Wasylishen, R. E. *J. Am. Chem. Soc.* **1983**, *105*, 6577-6584. (c) Clark, H. C.; Davies, J. A.; Fyfe, C. A.; Hayes, P. J.; Wasylishen, R. E. *Organometallics* **1983**, *2*, 177-180. (d) Fischer, A. B.; Bruce, J. A.; McKay, D. R.; Maciel, G. E.; Wrighton, M. S. *Inorg. Chem.* **1982**, *21*, 1766-1771. (e) Beml, L.; Clark, H. C.; Davies, J. A.; Fyfe, C. A.; Wasylishen, R. E. *J. Am. Chem. Soc.* **1982**, *104*, 438-445. (f) Beml, L.; Clark, H. C.; Davies, J. A.; Drexler, D.; Fyfe, C. A.; Wasylishen, R. *J. Organomet. Chem.* **1982**, *224*, C5-C9. (g) Shinoda, S.; Saito, Y. *Inorg. Chim. Acta* **1982**, *63*, 23-26.

(9) (a) Rothwell, W. P.; Shen, W. X.; Lunsford, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 2452-2453. (b) Maciel, G. E.; Haw, J. F.; Chuang, I.-S.; Hawkins, B. L.; Early, T. A.; McKay, D. R.; Petrakis, L. *J. Am. Chem. Soc.* **1983**, *105*, 5529-5535. (c) Haw, J. F.; Chuang, I.-S.; Hawkins, B. L.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 7206-7207. (d) Ripmeester, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 2925-2927. (e) Juenger, I.; Meiler, W.; Pfeiffer, H. *Zeolites* **1982**, *2*, 310-312. (f) Dawson, W. H.; Kaiser, S. W.; Ellis, P. D.; Inners, R. *J. Am. Chem. Soc.* **1981**, *103*, 6780-6781.

(10) (a) Jarman, R. H.; Melchior, M. T. *J. Chem. Soc., Chem. Commun.* **1984**, 414-416. (b) Groenen, E. J. J.; Alma, N. C. M.; Bastein, A. G. T. M.; Hays, G. R.; Huis, R.; Kortbeek, A. G. T. *J. Chem. Soc. Chem. Commun.* **1983**, 1360-1362. (c) Gabelica, Z.; Nagy, J. B.; Debras, G. *J. Catal.* **1983**, *84*, 256-260. (d) Nagy, J. B.; Gabelica, Z.; Derouane, E. G. *Zeolites* **1983**, *3*, 43-49. (e) Gabelica, Z.; Derouane, E. G.; Blom, N. *Appl. Catal.* **1983**, *5*, 109-117. (f) Boxhoorn, G.; van Santen, R. A.; van Erp, W. A.; Hays, G. R.; Huis, R.; Clague, D. J. *J. Chem. Soc., Chem. Commun.* **1982**, 264-265.

(11) Derouane, E. G.; Gilson, J. P.; Nagy, J. B. *Zeolites* **1982**, *2*, 42-46. (12) van den Berg, J. P.; Wolthuisen, J. P.; Clague, A. D. H.; Hays, G. R.; Huis, R.; van Hooff, J. H. C. *J. Catal.* **1983**, *80*, 130-138.

(1) He, M.-Y.; Xiong, G.; Toscano, P. J.; Burwell, R. L., Jr.; Marks, T. J., preceding paper in this issue and references therein.

(2) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569-590.

(3) (a) Andrew, E. R. *Prog. Nucl. Magn. Reson. Spectrosc.* **1971**, *8*, 1-39. (b) Schaefer, J.; Stejskal, E. O. *J. Am. Chem. Soc.* **1976**, *98*, 1031-1032.

(4) (a) Wasylishen, R. E.; Fyfe, C. E. *Annu. Rep. NMR Spectrosc.* **1982**, *12*, 1-80. (b) Yannoni, C. S. *Acc. Chem. Res.* **1982**, *15*, 201-208. (c) Gerstein, B. C. *Anal. Chem.* **1983**, *55*, 781A-790A. (d) Gerstein, B. C. *Anal. Chem.* **1983**, *55*, 899A-907A. (e) Fyfe, C. A. "Solid State NMR for Chemists"; CFC Press: Guelph, 1983. (f) Maciel, G. E. *Science (Washington, D.C.)* **1984**, *226*, 282-288.

(5) (a) Duncan, T. M.; Dybowski, C. *Surface Sci. Rep.* **1981**, *1*, 157-250. (b) Pfeifer, H.; Meiler, W.; Deininger, D. *Annu. Rep. NMR Spectrosc.* **1983**, *15*, 291-356.

and  $^1\text{H}^{15}$  MAS NMR spectroscopy has been utilized to probe the bulk and surface structures of several metal oxide supports. However, there has been very little application of  $^{13}\text{C}$  CPMAS NMR to the study of catalysts derived from organometallic molecules and high surface area metal oxides (the few examples involve metal carbonyls<sup>16</sup>).

In this contribution we present a high-resolution  $^{13}\text{C}$  CPMAS NMR study of  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2$  and  $[\text{Cp}'_2\text{Th}(\mu\text{-H})\text{H}]_2$  adsorbed on DA and PDA. The complexes have been deposited in the same manner and at the same loading levels ( $<0.5 \text{ Cp}'_2\text{Th}(\text{CH}_3)_2/100 \text{ \AA}^2$ ) as employed in our companion surface chemical and catalytic studies.<sup>1</sup> To our knowledge, this study represents the first CPMAS NMR investigation of a metal alkyl/metal oxide catalyst system. It will be seen that the derivation of significant structural and dynamic information benefits greatly from the high surface areas of DA and PDA<sup>1</sup> (ca.  $160 \text{ m}^2/\text{g}$ —high concentrations of organometallic molecules are possible), the availability of  $^{13}\text{C}$ -enriched analogues ( $\text{Cp}'_2\text{Th}(^{13}\text{CH}_3)_2$ ), the availability of a number of  $\text{Cp}'_2\text{Th}(\text{CH}_3)\text{X}$  model compounds, and the unique quadrupolar characteristics of the  $^{27}\text{Al}$  nucleus. Perhaps the most interesting and broadly applicable result of this study is the direct evidence that alkyl groups on precatalyst molecules can be transferred to the surface metal ions of the oxide support.

## Experimental Section

**Materials and Methods.** All procedures were performed in Schlenk-type glassware interfaced to a high-vacuum ( $10^{-4}$ – $10^{-5}$  torr) line or in a nitrogen-filled Vacuum Atmospheres glovebox equipped with an efficient, recirculating atmosphere purification system. Argon (Matheson, prepurified), nitrogen (Matheson, prepurified), and hydrogen (Linde) were purified further by passage through a supported MnO oxygen removal column and a Davison 4-Å molecular sieve column. Pentane ( $\text{H}_2\text{SO}_4$  washed), heptane ( $\text{H}_2\text{SO}_4$  washed), toluene, and diethyl ether (all previously distilled from Na/K/benzophenone) were condensed and stored in vacuo in bulbs on the vacuum line.

$^{13}\text{CH}_3\text{I}$  (99%  $^{13}\text{C}$ , Cambridge Isotope Laboratories) was degassed by freeze-pump-thaw cycles on a high vacuum line and dried by condensing in vacuo onto  $\text{P}_2\text{O}_5$  and stirring overnight.  $^{13}\text{CH}_3\text{Li}\cdot\text{LiI}$  (99%  $^{13}\text{C}$ ) was prepared in the conventional fashion by reaction with washed Li sand (1% sodium, 30% dispersion in mineral oil, Alfa) in diethyl ether.<sup>17a</sup>  $[(\text{C}-\text{H}_3)\text{AlCl}_2]_2$  was prepared by methyl exchange between equimolar amounts of  $\text{AlCl}_3$  (Fisher) and  $(\text{CH}_3)_3\text{Al}_2\text{Cl}_3$  (1 M solution in toluene, Aldrich) at  $100^\circ\text{C}$  by a modification of the method of Adkins and Scanley.<sup>17b</sup> The complexes  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2$ ,<sup>18</sup>  $[\text{Cp}'_2\text{Th}(\mu\text{-H})\text{H}]_2$ ,<sup>18</sup> and  $\text{Cp}'_2\text{Th}(\text{CH}_3)\text{X}$ , where  $\text{X} = \text{CH}_2\text{CMe}_3$ ,<sup>19a</sup>  $\text{Cl}$ ,<sup>18</sup>  $\text{OCH}(t\text{-Bu})_2$ ,<sup>19b</sup> and  $\text{OCMe}_3$ <sup>18</sup> were prepared according to our procedures. The complex  $\text{Cp}'_2\text{Th}(^{13}\text{CH}_3)_2$  (99%  $^{13}\text{C}$ ) was prepared analogously to  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2$ , employing  $^{13}\text{CH}_3\text{Li}\cdot\text{LiI}$  (99%  $^{13}\text{C}$ ). The poly(methylaluminoxane)  $[-(\text{OAl}(\text{CH}_3)-)_n]$  sample was prepared by the method of Kaminsky et al.<sup>20</sup>

Partially dehydroxylated alumina (PDA) and dehydroxylated alumina

(DA) were prepared in the following manner. Approximately 1.0 g of American Cyanamid PHF  $\gamma$ -alumina, 99.99% pure, which had been treated as previously described,<sup>21</sup> was spread in a thin layer ( $<1 \text{ mm}$  thick) in a quartz tube. The quartz tube was attached to a high vacuum line in a manner such that the main axis was horizontal (in order to maintain the alumina in a thin layer), evacuated, and placed in a tube furnace, the temperature of which could be monitored continuously with a chromel/alumel thermocouple. The alumina was heated for 2 h under dynamic vacuum ( $10^{-4}$ – $10^{-5}$  torr) at  $475$  or  $950^\circ\text{C}$  for PDA or DA, respectively. The alumina was then cooled and brought into the glovebox for storage and experiments. PDA has ca. 4 surface OH groups/ $100 \text{ \AA}^2$ , while DA has ca.  $0.12/100 \text{ \AA}^2$ .<sup>1</sup>

**Reaction of Alumina with Organoactinides.** On a high vacuum line, a solution of approximately  $50 \mu\text{mol}$  of organoactinide complex in pentane (8–10 mL) was poured onto 0.50 g of either DA or PDA. This loading is comparable to typical loadings employed in the surface chemical studies. The slurry was vigorously stirred under Ar for 1 h at ambient temperature while covered by Al foil to exclude light. At the end of this time, the suspension was filtered; the impregnated alumina was then back-washed once by condensing a small portion of pentane from the filtrate into the upper portion of the filtration apparatus. The pentane was removed in vacuo and the alumina dried well and brought into the glovebox for NMR experiments.

**High-Resolution  $^{13}\text{C}$  NMR Experiments.**  $^{13}\text{C}$  CPMAS NMR spectra were measured at a carbon frequency of 15.0 MHz on a JEOL FX-60QS spectrometer with Chemagnetics solid-state accessories. High-power  $^1\text{H}$  decoupling and magic angle spinning were employed for the routine experiments. Bullet rotors machined to close tolerances from Kel-F were used at a spinning speed of 2.2–2.6 kHz. Since the samples are extremely air sensitive, rotors were loaded with material inside the glovebox under an anaerobic nitrogen atmosphere. The insert of the rotor was coated with a light layer of high vacuum silicone grease (Dow Corning) before being pressed into the outer part. No  $^{13}\text{C}$  resonance was ever observed for the grease. No air-induced discoloration of the organoactinide-treated alumina samples from white to yellow or brown was observed for any of the organothorium samples during the course of an NMR experiment. Several other experiments were performed to check the integrity of the rotors toward exclusion of air. A solid sample of the oxygen indicator  $[\text{Cp}_2\text{Ti}(\mu\text{-Cl})_2]_2\text{Zn}$  was placed in a rotor; no change from green (starting Ti(III) complex) to yellow (oxidized Ti(IV) complex) was observed over a 2-day spinning period. Repeated  $^{13}\text{C}$  CPMAS NMR spectra of the same sample of  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2/\text{DA}$  over a period of time were identical. Finally, a sample of  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2/\text{DA}$  was deliberately exposed to air. The sample immediately turned bright yellow, then gradually became light yellowish brown. A  $^{13}\text{C}$  CPMAS NMR spectrum of the air-exposed sample contained many very weak signals and was entirely different from the relatively simple spectrum obtained from anaerobically manipulated samples. In addition, the  $^{13}\text{C}$  NMR spectra obtained from five independently prepared samples of the  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2/\text{DA}$  system were identical. The magic angle was set for each spectrum by observing the  $^{79}\text{Br}$  line of a small amount of dry  $\text{KBr}$ <sup>22</sup> which was partitioned from the sample in the rotor by a thin Teflon-brand disk. All solid-state  $^{13}\text{C}$  NMR spectra were externally referenced to liquid  $\text{Me}_4\text{Si}$  on the basis of substitution of hexamethylbenzene (HMB) as secondary reference and assigning 132.3 ppm to the shift of the aromatic carbons of HMB relative to liquid  $\text{Me}_4\text{Si}$ . The proton  $90^\circ$  pulse width was  $5 \mu\text{s}$ . For  $^{13}\text{C}$ , the routinely employed contact time for cross-polarization was 3 ms and the repetition time was 4 s. In general, 1000–2000 scans were required to obtain satisfactory spectra of the neat organothorium complexes, while 10 000–50 000 scans were required for the thorium complexes adsorbed on alumina and for the organoaluminum samples.

Several  $^{13}\text{C}$  NMR experiments were performed for  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2/\text{DA}$  in order to probe adsorbate mobility. One set of experiments involved obtaining  $^{13}\text{C}$  CPMAS NMR spectra under varying cross-polarization contact times (0.8, 3.0, and 10.0 ms). This experiment can yield information on motions which average  $^{13}\text{C}$ – $^1\text{H}$  dipolar coupling.<sup>9b</sup> Interrupted decoupling experiments were performed by inserting a 40- or 125- $\mu\text{s}$  delay during which the decoupler is turned off before data acquisition. These experiments give information on the number of protons coupled to the carbon atoms.<sup>23</sup> Finally, two experiments were performed which would yield signals only for surface species having significant mobility. In the first experiment, a  $^{13}\text{C}$  CPMAS NMR spectrum of  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2/\text{DA}$  was obtained in which the high-power decoupler was turned off during data acquisition.<sup>9b</sup> In the second ex-

(13) (a) Fyfe, C. A.; Gobbi, G. C.; Kennedy, G. J.; de Schutter, C. T.; Murphy, W. J.; Ozubko, R. S.; Slack, D. A. *Chem. Lett.* **1984**, 163–166 and references therein. (b) Müller, D.; Gessner, W.; Behrens, H.-J.; Scheler, G. *Chem. Phys. Lett.* **1981**, 79, 59–62 and references therein.

(14) (a) Schramm, S.; Oldfield, E. *J. Am. Chem. Soc.* **1984**, 106, 2502–2506. (b) Schramm, S.; Kirkpatrick, R. J.; Oldfield, E. *J. Am. Chem. Soc.* **1983**, 105, 2483–2485. (c) Meadows, M. D.; Smith, K. A.; Kinsey, R. A.; Rothgeb, T. M.; Skarjune, R. P.; Oldfield, E. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, 79, 1351–1355.

(15) (a) Freude, D.; Hunger, M.; Pfeifer, H.; Scheler, G.; Hoffman, J.; Schmitz, W. *Chem. Phys. Lett.* **1984**, 105, 427–430. (b) Hunger, M.; Freude, D.; Pfeifer, H.; Bremer, H.; Jank, M.; Wendlandt, K.-P. *Chem. Phys. Lett.* **1983**, 100, 29–33. (c) Mastikhin, V. M.; Mudrakovskii, I. L. *React. Kinet. Catal. Lett.* **1982**, 20, 351–355.

(16) Hanson, B. E.; Wagner, G. W.; Davis, R. J.; Motell, E. *Inorg. Chem.* **1984**, 23, 1635–1636 and references therein.

(17) (a) Wakefield, B. J. "The Chemistry of Organolithium Compounds"; Pergamon Press: New York, 1974. (b) Adkins, H.; Scanley, C. *J. Am. Chem. Soc.* **1951**, 73, 2854–2856.

(18) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, 103, 6650–6667.

(19) (a) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, 106, 2214–2216. (b) Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.*, in press.

(20) (a) Kaminsky, W.; Luker, H. *Makromol. Chem., Rapid Commun.* **1984**, 5, 225–228. (b) Kaminsky, W.; Miri, M.; Sinn, H.; Woldt, R. *Makromol. Chem., Rapid Commun.* **1983**, 4, 417–421. (c) Sinn, H.; Kaminsky, W.; Vollmer, H.-J.; Woldt, R. *Angew. Chem., Int. Ed. Engl.* **1980**, 19, 390–392.

(21) Bowman, R. G.; Burwell, R. L., Jr. *J. Catal.* **1980**, 63, 463–475.

(22) Frye, J. S.; Maciel, G. E. *J. Magn. Reson.* **1982**, 48, 125–131.

(23) (a) Alemany, L. B.; Grant, D. M.; Alger, T. D.; Pugmire, R. J. *J. Am. Chem. Soc.* **1983**, 105, 6697–6704. (b) Opella, S. J.; Frey, M. H.; Cross, T. A. *J. Am. Chem. Soc.* **1979**, 101, 5854–5856.

**Table I.** Solid-State <sup>13</sup>C NMR Chemical Shift Data for Neat and Supported Organothorium Complexes<sup>a</sup>

complex <sup>b</sup>	Cp' ring	Th-CH <sub>3</sub>	Cp' CH <sub>3</sub>	others
Cp <sub>2</sub> 'Th(CH <sub>3</sub> ) <sub>2</sub>	123.1	68.4	12.0	
Cp <sub>2</sub> 'Th(CH <sub>3</sub> ) <sub>2</sub> /DA	125.0		11.0	
Cp <sub>2</sub> 'Th( <sup>13</sup> CH <sub>3</sub> ) <sub>2</sub> /DA <sup>c</sup>	124.2	71.0	10.2	-20 (Al-CH <sub>3</sub> )
Cp <sub>2</sub> 'Th( <sup>13</sup> CH <sub>3</sub> ) <sub>2</sub> /DA <sup>d</sup>	127.0	71.8	10.9	-12 (Al-CH <sub>3</sub> )
Cp <sub>2</sub> 'Th(CH <sub>3</sub> ) <sub>2</sub> /PDA	124.6		10.6	
Cp <sub>2</sub> 'Th( <sup>13</sup> CH <sub>3</sub> ) <sub>2</sub> /PDA	125.0	66.3	10.7	
[Cp <sub>2</sub> 'Th(μ-H)H] <sub>2</sub>	123.5		12.7	
[Cp <sub>2</sub> 'Th(μ-H)H] <sub>2</sub> /DA	125.6		10.7	
Cp <sub>2</sub> 'Th(CH <sub>3</sub> )(CH <sub>2</sub> CMe <sub>3</sub> )	123.2	72.6	12.4	102.0 (Th-CH <sub>3</sub> ), 37.4(β-C,γ-C)
Cp <sub>2</sub> 'Th(CH <sub>3</sub> )Cl	126.3	67.6	12.5	
Cp <sub>2</sub> 'Th(CH <sub>3</sub> )[OCH( <i>t</i> -Bu) <sub>2</sub> ]	123.2 <sup>e</sup>	58.4	13.5	94.4 (O-CH), 38.5( <i>t</i> -BuC), <sup>e</sup> 30.6( <i>t</i> -Bu Me) <sup>e</sup>
Cp <sub>2</sub> 'Th(CH <sub>3</sub> )(OCMe <sub>3</sub> )	122.2	53.2	11.9	79.2 (O-C), 34.4 ( <i>t</i> -Bu Me)

<sup>a</sup> In ppm downfield from Me<sub>4</sub>Si (see Experimental Section for details). <sup>b</sup> For abbreviations, see text. <sup>c</sup> At 15.0 MHz (<sup>13</sup>C). <sup>d</sup> At 37.735 MHz (<sup>13</sup>C). <sup>e</sup> Average chemical shift (resonance is split or broadened, probably due to hindered rotation in the OCH(*t*-Bu)<sub>2</sub> ligand).

periment, a Bloch decay spectrum (<sup>13</sup>C pulse, data acquisition, followed by a delay to allow <sup>13</sup>C magnetization to return) was obtained in a sealed glass sample tube at 22.49 MHz with a JEOL FX-90Q spectrometer without magic angle spinning or high-power decoupling.

High-field <sup>13</sup>C CPMAS NMR spectra of Cp<sub>2</sub>'Th(<sup>13</sup>CH<sub>3</sub>)<sub>2</sub>/DA (12 000 accumulations, 3.0-ms contact time, 5.0-s repetition time) and [(CH<sub>3</sub>)<sub>2</sub>AlCl]<sub>2</sub> (5000 accumulations, 5.0-ms contact time, 1.0-s repetition) were performed by the Colorado State University Regional NMR Center on a Nicolet NT-150 (37.735 MHz, <sup>13</sup>C) spectrometer. The Cp<sub>2</sub>'Th(<sup>13</sup>CH<sub>3</sub>)<sub>2</sub>/DA sample was checked for deterioration upon return via the <sup>13</sup>C CPMAS NMR spectrum. The spectrum obtained was identical with that obtained prior to mailing. The returned [(CH<sub>3</sub>)<sub>2</sub>AlCl]<sub>2</sub> sample was checked via <sup>1</sup>H (solution) NMR and showed no decomposition.

The organothorium complexes were checked for purity via routine <sup>1</sup>H NMR (Varian EM-390, 90 MHz, CW, or JEOL FX-90Q, 90 MHz, FT). The structural assignments for the <sup>13</sup>C CPMAS NMR were facilitated via solution <sup>13</sup>C NMR obtained with total and gated decoupling (JEOL FX-90Q, 22.49 MHz, FT).

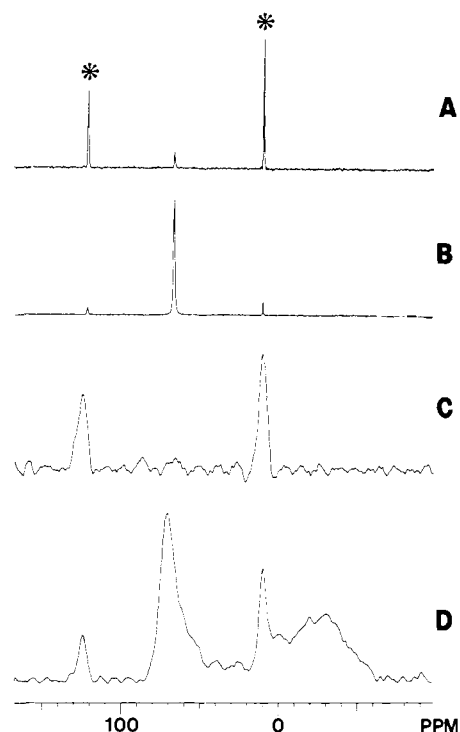
**Results**

<sup>13</sup>C CPMAS NMR spectra reported in this section were obtained at 15.0 MHz (for <sup>13</sup>C) unless otherwise noted. Chemical shift data for the <sup>13</sup>C CPMAS NMR spectra are collected in Table I.

**Reactions of DA with Organoactinides.** The <sup>13</sup>C CPMAS NMR spectrum of neat Cp<sub>2</sub>'Th(CH<sub>3</sub>)<sub>2</sub> powder is presented in Figure 1A. The peaks may be assigned by comparison to solution <sup>13</sup>C and <sup>13</sup>C{<sup>1</sup>H} spectra as (chemical shift, δ in ppm from (CH<sub>3</sub>)<sub>4</sub>Si) Cp' ring carbon (δ 123.1), Th-CH<sub>3</sub> (δ 68.4), and Cp' CH<sub>3</sub> (δ 12.0). The <sup>13</sup>C NMR spectrum of neat Cp<sub>2</sub>'Th(<sup>13</sup>CH<sub>3</sub>)<sub>2</sub> (99% <sup>13</sup>C enriched) is shown in Figure 1B. The chemical shifts are identical with those of the natural abundance compound. In addition, the line widths at half-height (ν<sub>1/2</sub>) for the Cp' ring carbon and Cp' CH<sub>3</sub> resonances of neat Cp<sub>2</sub>'Th(<sup>13</sup>CH<sub>3</sub>)<sub>2</sub> are indistinguishable from those in the unenriched complex; ν<sub>1/2</sub> = 14 and 8 Hz, respectively. The line width for the Th-CH<sub>3</sub> resonance increases only slightly, from 14 to 20 Hz. Thus, there is little or no broadening due to <sup>13</sup>C-<sup>13</sup>C dipolar coupling in the spectrum of Cp<sub>2</sub>'Th(<sup>13</sup>CH<sub>3</sub>)<sub>2</sub>; i.e., the effects of <sup>13</sup>C-<sup>13</sup>C dipolar coupling are small enough to be eliminated by the MAS.<sup>4</sup>

The <sup>13</sup>C CPMAS NMR spectrum of Cp<sub>2</sub>'Th(CH<sub>3</sub>)<sub>2</sub> supported on DA (Figure 1C) shows resonances attributable only to the pentamethylcyclopentadienyl ligands at δ 125.0 and 11.0. Line widths are approximately 7-10 times greater than for the neat complex. Some of this broadening may be due to weighting of the FID to enhance the signal-to-noise ratio. In order to probe the fate of the methyl ligands originally attached to Th, Cp<sub>2</sub>'Th(<sup>13</sup>CH<sub>3</sub>)<sub>2</sub> was also reacted with DA. The <sup>13</sup>C CPMAS NMR spectrum of this system (Figure 1D) also exhibits resonances at δ 124.2 and 10.2 for the ring ligands as in the unenriched case (Figure 1C). In addition, two new resonances appear at δ 71.0 and ca. -20. The former peak may be straightforwardly assigned to a Th-CH<sub>3</sub> group by comparison to the spectrum of Cp<sub>2</sub>'Th(CH<sub>3</sub>)<sub>2</sub> (Figure 1A) and similar complexes containing a Th-CH<sub>3</sub> bond (vide infra). The very broad upfield resonance has been assigned to an Al-CH<sub>3</sub> surface species (vide infra).

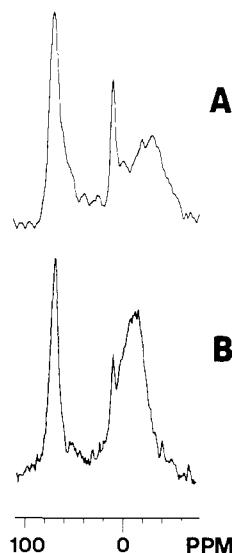
A <sup>13</sup>C CPMAS NMR spectrum of Cp<sub>2</sub>'Th(<sup>13</sup>CH<sub>3</sub>)<sub>2</sub>/DA was also obtained at higher magnetic field strength (37.735-MHz <sup>13</sup>C).



**Figure 1.** <sup>13</sup>C CPMAS NMR spectra (15.0 MHz) of (A) neat Cp<sub>2</sub>'Th(CH<sub>3</sub>)<sub>2</sub> (2000 scans), (B) neat Cp<sub>2</sub>'Th(<sup>13</sup>CH<sub>3</sub>)<sub>2</sub> (900 scans), (C) 50 μmol of Cp<sub>2</sub>'Th(CH<sub>3</sub>)<sub>2</sub>/0.5 g of DA (24 000 scans), and (D) 50 μmol of Cp<sub>2</sub>'Th(<sup>13</sup>CH<sub>3</sub>)<sub>2</sub>/0.5 g of DA (55 000 scans). In each spectrum, repetition time was 4 s and contact time was 3 ms. \* indicates resonances due to (CH<sub>3</sub>)<sub>5</sub>C<sub>5</sub>.

Most importantly, the broad upfield peak at ca. -12 ppm is noticeably narrowed at 37.735 MHz (Figure 2B) as compared to the 15.0-MHz spectrum (Figure 2A). It can be seen that the relative height of this peak is increased relative to the Th-CH<sub>3</sub> and Cp' CH<sub>3</sub> resonances, and also that the chemical shift of the peak maximum is displaced ca. 8 ppm downfield. This result is consistent with broadening arising principally from <sup>27</sup>Al (I = 5/2) quadrupolar effects which are not averaged out by MAS at lower field strengths,<sup>4,24-30</sup> rather than by chemical shift dispersion, since in the former case line narrowing would be expected at higher

(24) Kundla, E.; Alla, M. *Magn. Reson. Related Phenom.* **1979**, *20*, 92.  
 (25) Naito, A.; Ganapathy, S.; McDowell, C. A. *J. Magn. Reson.* **1982**, *48*, 367-381.  
 (26) Zumbulyadis, N.; Henrichs, P. M.; Young, R. H. *J. Chem. Phys.* **1981**, *75*, 1603-1611.  
 (27) Hexam, J. G.; Frey, M. H.; Opella, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 224-226.  
 (28) Balimann, G. E.; Groombridge, C. J.; Harris, R. K.; Packer, K. J.; Say, B. J.; Tanner, S. F. *Philos. Trans. R. Soc. London Ser. A* **1981**, *No. 299*, 643-663.  
 (29) Opella, S. J.; Hexem, J. G.; Frey, M. H.; Cross, T. A. *Philos. Trans. R. Soc. London, Ser. A* **1981**, *No. 299*, 665-683.  
 (30) Böhm, J.; Fenzke, D.; Pfeifer, H. *J. Magn. Reson.* **1983**, *55*, 197-204.



**Figure 2.** High-field region of the  $^{13}\text{C}$  CPMAS NMR spectrum of 50  $\mu\text{mol}$  of  $\text{Cp}'_2\text{Th}(^{13}\text{CH}_3)_2/0.5$  g of DA: (A) at 15.0 MHz (55 000 4-s repetitions, 3-ms contact time), (B) at 37.735 MHz (12 000 5-s repetitions, 3-ms contact time).

field, while increased line broadening would be expected for the latter effect. A number of other line broadening mechanisms are arguably unimportant. Thus, magnetic field inhomogeneity may be excluded as a major broadening source for the upfield line since spectra of neat complexes are very sharp (e.g., Figure 1A,B) and, indeed, the  $\text{Cp}'$  and  $\text{Th-CH}_3$  resonances in the supported complexes are relatively narrow (Figure 1C,D). Likewise, missetting of the magic angle may be ruled out since with proper experimental technique the magic angle may be set within  $\pm 0.1^\circ$  using an internal  $\text{KBr}$  sample.<sup>22</sup> The resonance due to the ring carbons of the  $\text{Cp}'$  ligands is quite sensitive to the setting of the magic angle and is an excellent internal check in these systems. The line width and line shape for the ring carbons in Figure 1C,D are comparable to those for the ring methyl resonance, indicating that proper spinning angle has been achieved. The complex is highly enriched (99%) in  $^{13}\text{C}$ , but  $^{13}\text{C}$ - $^{13}\text{C}$  dipolar coupling effects should be rather small by comparison to Figure 1A,B, where little or no broadening was observed in going from neat  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2$  to  $\text{Cp}'_2\text{Th}(^{13}\text{CH}_3)_2$ .

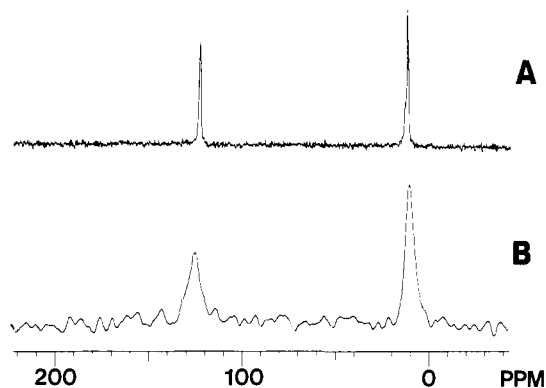
Broadening and/or splitting of  $^{13}\text{C}$  and  $^{29}\text{Si}$  resonances have been observed previously in cases of directly attached  $^{14}\text{N}$  ( $I = 1$ ),<sup>24-30</sup>  $^2\text{H}$  ( $I = 1$ ),<sup>31</sup> and  $^{35}\text{Cl}$  ( $I = 3/2$ )<sup>30,32</sup> nuclei. Splitting or broadening of  $^{13}\text{C}$  bound to  $^{27}\text{Al}$  is expected if the  $^{27}\text{Al}$  ( $I = 5/2$ ,  $Q = 0.149e \times 10^{-24} \text{ cm}^2$ ) quadrupole interaction is comparable in magnitude to the Zeeman interaction.<sup>24,27,29,30</sup> In that case, the  $^{27}\text{Al}$  quadrupolar interaction tilts the axis of  $^{27}\text{Al}$  quantization away from the applied field direction so that residual  $^{27}\text{Al}$ - $^{13}\text{C}$  dipolar coupling is not removed by MAS. The magnitude of the residual coupling depends on  $e^2qQ$  (the nuclear quadrupole coupling constant),  $\eta$  (the asymmetry parameter,  $(q_{xx} - q_{yy})/q_{zz}$ ), and the magnitude and orientation of the  $^{27}\text{Al}$ - $^{13}\text{C}$  internuclear vector. Although insufficient local surface metrical data are available in the present system to accurately compute the details of the dipolar splitting (further studies are in progress), reported  $^{27}\text{Al}$   $e^2qQ/h$  values in the range 7-38 MHz for alkyls and halides<sup>33,34</sup> are comparable to the  $^{27}\text{Al}$  Zeeman interaction energy of 15.63 MHz at the present field strength. Thus, a major perturbation of the  $^{13}\text{C}$  line shape is not unexpected. It will be seen that similar  $^{27}\text{Al}$  quadrupolar effects are evident in the spectra of model compounds (vide infra).

(31) Hall, L. D.; Lim, T. K. *Carbohydr. Res.* **1983**, *124*, C1-C4.

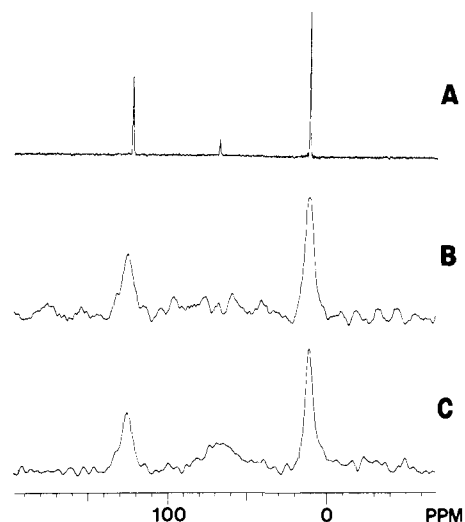
(32) Lyerla, J. R. *Contemp. Top. Polym. Sci.* **1979**, *3*, 143-213.

(33) Dewar, M. J. S.; Patterson, D. B.; Simpson, W. I. *J. Am. Chem. Soc.* **1971**, *93*, 1030-1032.

(34) Dewar, M. J. S.; Patterson, D. B.; Simpson, W. I. *J. Chem. Soc., Dalton Trans.* **1973**, 2381-2390.



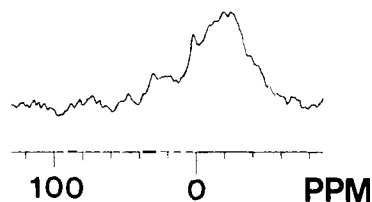
**Figure 3.**  $^{13}\text{C}$  CPMAS NMR spectra (15.0 MHz) of (A) neat  $[\text{Cp}'_2\text{Th}(\mu\text{-H})\text{H}]_2$  (2200 scans) and (B) 25  $\mu\text{mol}$  of  $[\text{Cp}'_2\text{Th}(\mu\text{-H})\text{H}]_2/0.5$  g of DA (30 000 scans). In each spectrum, repetition time was 4 s and contact time was 3 ms.



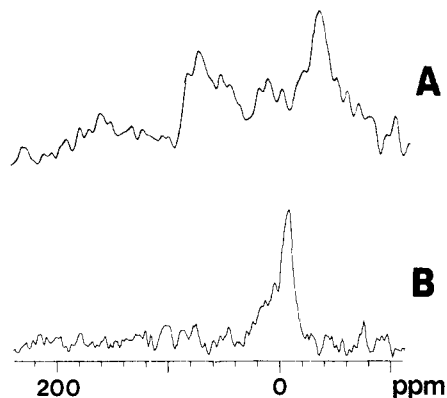
**Figure 4.**  $^{13}\text{C}$  CPMAS NMR spectra (15.0 MHz) of (A) neat  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2$  (2000 scans), (b) 50  $\mu\text{mol}$  of  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2/0.5$  g of PDA (24 000 scans), and (C) 50  $\mu\text{mol}$  of  $\text{Cp}'_2\text{Th}(^{13}\text{CH}_3)_2/0.5$  g of PDA (60 000 scans). In each spectrum, repetition time was 4 s and contact time was 3 ms.

A number of NMR experiments were performed to investigate the motional characteristics of the  $\text{Cp}'_2\text{Th}(^{13}\text{CH}_3)_2$  complexes adsorbed on DA. A  $^{13}\text{C}$  CPMAS NMR spectrum obtained with the high-power  $^1\text{H}$  decoupler turned off during data acquisition and a  $^{13}\text{C}$  Bloch decay NMR spectrum were featureless. These results imply that molecular motion is not sufficiently rapid and isotropic to significantly average C-H dipolar interactions.<sup>9b</sup> Since cross-polarization dynamics are sensitive to molecular motion,<sup>9b,23</sup>  $^{13}\text{C}$  CPMAS NMR spectra were also obtained with cross-polarization times of 0.8, 3.0, and 10.0 ms. Although signal-to-noise ratios varied between the spectra, the relative signal intensities within each spectrum were virtually identical. Hence, any motional processes significantly averaging the C-H dipolar interactions cannot differ greatly in anisotropy.<sup>9b</sup>

Interrupted decoupling spectra were obtained with delays of 40 and 125  $\mu\text{s}$  inserted before data acquisition. At 40  $\mu\text{s}$ , dipolar dephasing for fairly rigid protonated carbon groups such as methines and methylenes is sufficient that these resonances are selectively broadened and essentially disappear.<sup>23</sup> The usually greater rotational freedom of methyl groups lessens this effect and longer delay times (ca. 125  $\mu\text{s}$ ) are required to attenuate methyl resonances.<sup>23</sup> Even then, these resonances usually do not disappear entirely. Nonprotonated carbons are not significantly affected by this technique. The  $^{13}\text{C}$  CPMAS spectrum of  $\text{Cp}'_2\text{Th}(^{13}\text{CH}_3)_2/\text{DA}$  with a 40- $\mu\text{s}$  delay was essentially identical with the normal spectrum (1- $\mu\text{s}$  delay). With a 125- $\mu\text{s}$  delay, the resonances assigned to  $\text{Th-CH}_3$ ,  $\text{Cp}'\text{-CH}_3$ , and  $\text{Al-CH}_3$  were greatly attenuated relative to the  $\text{Cp}'\text{-C}$  resonance, although they



**Figure 5.**  $^{13}\text{C}$  CPMAS NMR spectrum (15.0 MHz) of a poly(methylaluminumoxane) sample (10000 4-s repetitions, 3-ms contact time).



**Figure 6.**  $^{13}\text{C}$  CPMAS NMR spectra of  $[(\text{CH}_3)_2\text{AlCl}_2]_2$ : (A) at 15.0 MHz (32000 4-s repetitions, 3-ms contact time), (B) at 37.735 MHz (5000 1-s repetitions, 5-ms contact time).

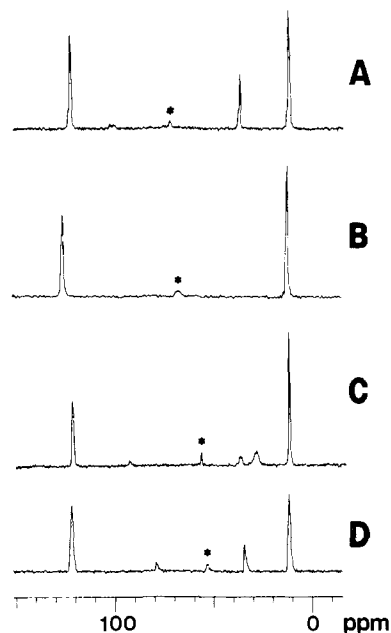
did not disappear entirely. Thus, the assignment of these three resonances to methyl groups appears secure.

Figure 3A presents the solid-state  $^{13}\text{C}$  NMR spectrum of  $[\text{Cp}'_2\text{Th}(\mu\text{-H})_2]$ . Two resonances are observed at  $\delta$  123.5 and 12.7. The  $^{13}\text{C}$  NMR spectrum of this complex supported on DA is reported in Figure 3B. The only resonances observed occur at  $\delta$  125.6 and 10.7. No broad upfield peak (ca. -20 ppm) is observed in this spectrum.

**Reactions of PDA with Organoactinides.** Figure 4A reiterates the  $^{13}\text{C}$  CPMAS NMR spectrum of neat  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2$  for convenience. The solid-state  $^{13}\text{C}$  NMR spectrum of this complex supported on PDA is presented in Figure 4B. Only resonances due to the  $\text{Cp}'$  ligands are observed at  $\delta$  4.6 and 10.6. When  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2$  is supported on PDA (Figure 4C), another resonance appears in the NMR spectrum at ca. 66.3 ppm in addition to the ring resonances. This new peak is in the region characteristic of Th- $\text{CH}_3$  functionalities in  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2\text{OR}$  complexes (vide infra).

**Model Compounds.** To obtain additional information on  $^{13}\text{C}$  CPMAS line shapes in typical  $^{27}\text{Al}$ - $\text{CH}_3$ -containing solids, several model compounds were examined. The 15.0-MHz  $^{13}\text{C}$  CPMAS NMR spectra of typical poly(methylaluminumoxane) samples  $-(\text{OAl}(\text{CH}_3))_n-$ ,<sup>20</sup> exhibit a broad resonance at ca. -17 to -20 ppm with a line width and line shape (e.g., Figure 5) almost identical with the broad upfield resonance in the 15.0-MHz  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2/\text{DA}$  spectrum (Figure 1D).  $^{13}\text{C}$  CPMAS NMR spectra of  $[(\text{CH}_3)_2\text{AlCl}_2]_2$  were obtained at two field strengths (Figure 6). At 15.0 MHz, the resonance is split into a multitude of broadened peaks. At higher field, the spectrum coalesces considerably and the most intense resonance appears to shift to the lower field. The changes in line shape and chemical shift for the Al- $\text{CH}_3$  resonance are similar to those observed for the broad upfield resonance in  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2/\text{DA}$ . It is interesting to note that the Al- $\text{CH}_3$   $^{13}\text{C}$  resonance is split more severely in the  $[(\text{C}-\text{H}_3)_2\text{AlCl}_2]_2$  spectrum than in the aluminoxane. This may result from differences in  $e^2qQ/h$  and  $\eta$  for the two systems. While the quadrupolar coupling constant and asymmetry parameters have not been measured for either of the present systems, we note that  $e^2qQ/h = 25.5$  MHz and  $\eta = 0.51$  for  $[(\text{CH}_3\text{CH}_2)_2\text{AlCl}_2]_2$ ,<sup>33</sup> and  $e^2qQ/h = 20.8$  MHz and  $\eta = 0.73$  for  $[(\text{CH}_3)_2\text{AlOCH}_3]_3$ .<sup>34</sup>

In order to determine how the Th- $\text{CH}_3$  chemical shift varies as a function of Th coligands,  $^{13}\text{C}$  CPMAS NMR spectra were obtained for a series of  $\text{Cp}'_2\text{Th}(\text{CH}_3)\text{X}$  complexes (Figure 7). The



**Figure 7.**  $^{13}\text{C}$  CPMAS NMR spectra (15.0 MHz) of neat  $\text{Cp}'_2\text{Th}(\text{CH}_3)\text{X}$ : (A) X =  $\text{CH}_2\text{CMe}_3$  (4400 scans), (B) X = Cl (1600 scans), (C) X =  $\text{OCH}(t\text{-Bu})_2$  (13000 scans), (D) X =  $\text{OCMe}_3$  (2400 scans). In each spectrum, repetition time was 4 s and contact time was 3 ms. \* indicates the Th- $\text{CH}_3$  resonance. See Table I for complete spectral assignments.

resonance for the Th- $\text{CH}_3$  group occurs at 72.6, 67.6, 58.4, and 53.2 ppm for X =  $\text{CH}_2\text{CMe}_3$ , Cl,  $\text{OCH}(t\text{-Bu})_2$ , and  $\text{OCMe}_3$ , respectively (see Table I for full assignment of spectra). As the  $\pi$ -donor capacity of the X ligand increases, the Th- $\text{CH}_3$  resonance shifts to higher field.

## Discussion

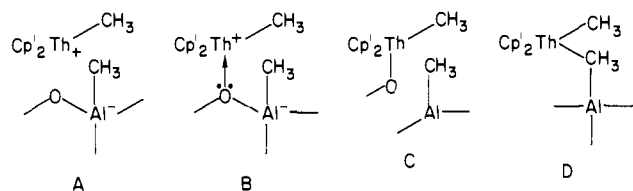
Viewed in concert with our complementary surface chemical data,<sup>1</sup> the present study illustrates the type of adsorbate-support structural information that can be acquired with  $^{13}\text{C}$  CPMAS NMR. Interestingly, the  $^{27}\text{Al}$  quadrupolar perturbations prove to be an asset rather than a liability in probing the metal alkyl- $\text{Al}_2\text{O}_3$  interactions.

Perhaps the most striking and broadly implicative observation comes from studies of  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2/\text{DA}$ . A new, broad resonance is observed at -20 ppm (Figure 1D) in addition to the expected  $\text{Cp}'$  and Th- $^{13}\text{CH}_3$  signals. This upfield peak is completely reproducible, appearing in the spectra of five independent, but similarly prepared, samples of this system. On the basis of the  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2$  (natural abundance),  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2$  (99%  $^{13}\text{C}$ ), and  $[\text{Cp}'_2\text{Th}(\mu\text{-H})_2]$  experiments, this feature is clearly assignable to a methyl group. The chemical shift, line shape, the field dependence of the line shape and the dipolar dephasing experiments lead us to propose that it arises from the transfer of a methyl functionality from Th to an  $\text{Al}^{3+}$  site (presumably coordinatively unsaturated) on the DA surface. This contention is strongly supported by the results with model compounds having  $^{27}\text{Al}$ - $\text{CH}_3$  functionalities. The solid-state  $^{13}\text{C}$  NMR spectra of poly(methylaluminumoxanes) (at 15.0 MHz) exhibit a broad resonance at -17 to -20 ppm which essentially reproduces the line width and line shape of the broad, upfield peak in the  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2/\text{DA}$  system. The resonance for  $[(\text{CH}_3)_2\text{AlCl}_2]_2$  occurs at -9 ppm in the solid-state  $^{13}\text{C}$  spectrum (Figure 6B) while the spectrum of  $[(\text{CH}_3)_3\text{Al}]_2$  in solution displays a peak at -8 ppm assigned to the terminal  $\text{CH}_3$  group.<sup>35</sup> As noted previously (under Results) the line width of the proposed Al- $\text{CH}_3$  resonance is attributable to  $^{27}\text{Al}$ - $^{13}\text{C}$  quadrupolar coupling effects which are not averaged by MAS at low magnetic field strengths. Thus, in the present study, the low magnetic field was a distinct advantage,

(35) Olah, G. A.; Surya Prakash, G. K.; Liang, G.; Henold, K. L.; Haigh, G. B. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 5217-5221.

since it allowed the detection of the Al-CH<sub>3</sub> interaction. This result is the first persuasive evidence that alkyl groups from a precatalyst molecule (in this case, Cp'<sub>2</sub>Th(CH<sub>3</sub>)<sub>2</sub>) can be transferred to the constituent metal ions (Al<sup>3+</sup>) of a metal oxide support.

Several structures (e.g., A-D) may be proposed to account for



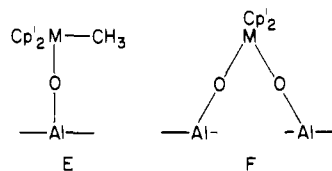
the <sup>13</sup>C NMR spectrum of the Cp'<sub>2</sub>Th(<sup>13</sup>CH<sub>3</sub>)<sub>2</sub>/DA system, which appears to be the predominant surface organometallic species on DA. As regards bridging Th(μ-CH<sub>3</sub>)Al interactions (e.g., D), the present -20 ppm chemical shift is at considerably higher field than bridging methyl groups in Cp<sub>2</sub>M(μ-CH<sub>3</sub>)<sub>2</sub>Al(CH<sub>3</sub>)<sub>2</sub> compounds<sup>36</sup> where δ<sub>bridge</sub> 20.7, δ<sub>terminal</sub> -6.3 (M = Sc) and δ<sub>bridge</sub> 7.9, δ<sub>terminal</sub> -7.9 (M = Y). On the other hand, the bridging methyl resonance in [Al(CH<sub>3</sub>)<sub>3</sub>]<sub>2</sub> is reported at -5.6 ppm.<sup>35</sup> Thus, while the great balance of the model compound data (aluminoxane, aluminum alkyl, Cp<sub>2</sub>M(μ-CH<sub>3</sub>)<sub>2</sub>Al(CH<sub>3</sub>)<sub>2</sub>) argues for a terminal Al-CH<sub>3</sub> assignment in Cp'<sub>2</sub>(Th(<sup>13</sup>CH<sub>3</sub>)<sub>2</sub>)/DA, a bridging or partially bridging (but freely rotating) Th(μ-CH<sub>3</sub>)Al interaction cannot be rigorously excluded.

As drawn, structures A-C can be viewed as canonical valence bond resonance structures. It can be argued, however, that the interaction of a surface Lewis base (oxygen) site on the DA with the organothorium fragment is probably weak (as in B) or non-existent (as in A) rather than strong (as in C) on the basis of the Th-CH<sub>3</sub> chemical shift in the Cp'<sub>2</sub>Th(<sup>13</sup>CH<sub>3</sub>)<sub>2</sub>/DA <sup>13</sup>C NMR spectrum (71.0 ppm). The corresponding shifts in a series of Cp'<sub>2</sub>Th(CH<sub>3</sub>)X complexes (vide supra) clearly show that oxygen π-donors displace this resonance to higher fields relative to the Th-CH<sub>3</sub> shift in neat solid Cp'<sub>2</sub>Th(CH<sub>3</sub>)<sub>2</sub>. In the Cp'<sub>2</sub>Th(<sup>13</sup>CH<sub>3</sub>)<sub>2</sub>/PDA system, where a strong Th-O-Al interaction appears likely (vide infra), the Th-CH<sub>3</sub> shift occurs at 66.3 ppm. In summary, the major surface reaction in the Cp'<sub>2</sub>Th(<sup>13</sup>CH<sub>3</sub>)<sub>2</sub>/DA system appears to involve a transfer of a methyl group from Th to Al. The experimental NMR evidence implicates significant or complete transfer and the formation of an Al-CH<sub>3</sub> functionality. The remaining organothorium fragment may be anchored to the surface via a Th-O interaction, but evidence for this is only circumstantial.

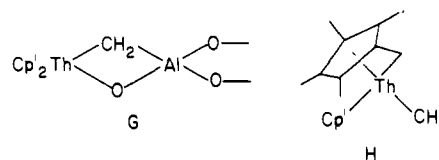
Several experiments were also performed to study the molecular and conformational dynamics of the Cp'<sub>2</sub>Th(<sup>13</sup>CH<sub>3</sub>)<sub>2</sub>/DA system, including turning off the decoupler during data acquisition, varying cross-polarization time, and carrying out a Bloch decay experiment. All data (see Results) are consistent with organometallic species which are relatively immobile on the alumina surface. That the bound organometallics cannot be extracted from the surface with noncoordinating hydrocarbon solvents is in accord with this spectroscopic result. In addition, an interrupted decoupling experiment strongly suggests that the three upfield resonances (at ca. 71, 10, and -20 ppm) in the Cp'<sub>2</sub>Th(<sup>13</sup>CH<sub>3</sub>)<sub>2</sub>/DA <sup>13</sup>C CPMAS NMR spectrum are assignable to freely rotating CH<sub>3</sub> groups while the peak at 124 ppm is due to the nonprotonated ring carbon atoms.

In the case of the Cp'<sub>2</sub>Th(<sup>13</sup>CH<sub>3</sub>)<sub>2</sub>/PDA system, where the support has a far higher surface OH coverage, considerably different solid-state <sup>13</sup>C NMR results are obtained than with DA supports. The Th-<sup>13</sup>CH<sub>3</sub> resonance is weaker and broader for Cp'<sub>2</sub>Th(<sup>13</sup>CH<sub>3</sub>)<sub>2</sub>/PDA than for the DA case and is shifted upfield by almost 5 ppm (in the same direction as for Cp'<sub>2</sub>Th(CH<sub>3</sub>)X, where X = oxygen π-donor ligand). Little or no evidence for an Al-CH<sub>3</sub> interaction is present. The above observations suggest that aluminoxy structures such as E and/or F represent the major surface species for Cp'<sub>2</sub>Th(<sup>13</sup>CH<sub>3</sub>)<sub>2</sub>/PDA.

(36) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* 1979, 45-53.



The present spectroscopic observations are in good accord with and significantly complement the surface chemical results.<sup>1</sup> Thus, the latter indicate that on DA up to He,25°/1, Cp'<sub>2</sub>Th(CH<sub>3</sub>)<sub>2</sub> methane evolution represents only ca. 9% of the available methyl groups. From deuterium labeling experiments, products such as E and F, G, and H comprise only ca. 6%, 2%, and 6%, respectively,



of the surface species produced up to He,25°/1 on DA.<sup>1</sup> It is no surprise then that such surface complexes are not observed in the CPMAS NMR experiments (the alkylidene carbon resonance of G should occur at a characteristic low-field position<sup>38,39</sup>). The surface chemical studies do not, however, provide an obvious insight into the forces that bind Cp'<sub>2</sub>Th(CH<sub>3</sub>)<sub>2</sub> to DA nor into the inertness of many (ca. 65-70%) of the adsorbate Th-CH<sub>3</sub> linkages to hydrogenolysis at 100 °C (Cp'<sub>2</sub>Th(CH<sub>3</sub>)<sub>2</sub> is very reactive in homogeneous solution<sup>18</sup>). The latter characteristic is additionally confirmed by NMR—samples of Cp'<sub>2</sub>Th(<sup>13</sup>CH<sub>3</sub>)<sub>2</sub>/DA heated for several hours at 100 °C under H<sub>2</sub> give CPMAS spectra identical with the starting material, with no major diminution of the Th-<sup>13</sup>CH<sub>3</sub> signal. The identification of species such as A-D by NMR rationalizes both the molecule-DA binding forces as well as the low reactivity of the major adsorbate toward hydrogenolysis. In regard to the latter issue, saturated methyl aluminates are expected to be relatively unreactive<sup>40</sup> while saturated, μ-donor ligated thorium fragments such as B or C are also likely to resist hydrogenolysis (alkoxy substitution greatly retards organoactinide hydrogenolysis in homogeneous solution<sup>18</sup>). It is furthermore conceivable that some surface coordination sites will sterically shield the adsorbed Cp'<sub>2</sub>Th(CH<sub>3</sub>)<sub>2</sub> molecules from hydrogenolysis.

On PDA up to He,25°/1, ca. 65% of the available methane is evolved.<sup>1,41</sup> The labeling experiments indicate that ca. >51%,<sup>42</sup> 2%, and 8% of the surface species are present as structure types E and F, G, and H, respectively. These data correlate well with the NMR results, which evidence a pronounced diminution of the Th-<sup>13</sup>CH<sub>3</sub> resonance intensity relative to the Cp' signals and a displacement of this resonance in the direction characteristic of Cp'<sub>2</sub>Th(CH<sub>3</sub>)OR complexes. Again, species G and H are in too low an abundance to be observed. In accord with the surface chemical data and the previous discussion, species such as E should resist hydrogenolysis. The CPMAS results suggest that on PDA, structures A-D do not play a major role.

(37) He, M.-Y.; Burwell, R. L., Jr.; Marks, T. J. *Organometallics* 1983, 2, 566-569.

(38) (a) Tebbe, F. N.; Harlow, R. L. *J. Am. Chem. Soc.* 1980, 102, 6149-6151. (b) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* 1978, 100, 3611-3613.

(39) (a) Ott, K. C.; deBoer, E. J. M.; Grubbs, R. H. *Organometallics* 1984, 3, 223-230. (b) Ott, K. C.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* 1982, 104, 2942-2944. (c) Lee, J. B.; Gajda, G. L.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* 1981, 103, 7358-7361. (d) Howard, T. F.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* 1980, 102, 6876-6878.

(40) Eisch, J. J. In "Comprehensive Organometallic Chemistry"; Wilkinson, G.; Stone, F. G. A., Eds.; Pergamon Press: Oxford, 1982; Chapter 6, p 630.

(41) These data are for Cp'<sub>2</sub>U(CH<sub>3</sub>)<sub>2</sub>/PDA. The thorium complex is expected to behave similarly.<sup>1</sup>

(42) 51% of the evolved methane arises via the protonolysis (S) pathway. The exact distribution between aluminoxy structures such as E and F is not known.

## Conclusions

The present  $^{13}\text{C}$  CPMAS investigation provides an important complement to the surface chemical results<sup>1</sup> in delineating adsorbate-alumina interactions for a highly active heterogeneous organoactinide catalyst. While the chemical results provide evidence for structures such as E-H, the surface NMR studies strengthen this formulation and, moreover, indicate that transfer of methyl groups from the actinide to surface aluminum sites has also occurred. To our knowledge, the latter result represents the first direct observation of this type of process for a supported catalyst. It is likely that such chemistry is not restricted to organoactinides and that similar processes not only occur but are important in numerous other catalytic systems comprised of relatively polar metal alkyls and high surface area metal oxides.<sup>43,44</sup>

(43) (a) Yermakov, Yu. I. *J. Mol. Catal.* **1983**, *21*, 35-55 and references therein. (b) Basset, J. M.; Chaplin, A. *J. Mol. Catal.* **1983**, *21*, 95-108 and references therein. (c) Iwamoto, M.; Kusano, H.; Kagawa, S. *Inorg. Chem.* **1983**, *22*, 3365-3366 and references therein. (d) Yermakov, Yu. I.; Kuznetsov, B. N.; Zakharov, V. A. "Catalysis by Supported Complexes"; Elsevier: Amsterdam, 1981. (e) Bailey, D. C.; Langer, S. H. *Chem. Rev.* **1981**, *81*, 109-148. (f) Zakharov, V. A.; Yermakov, Yu. I. *Catal. Rev.—Sci. Eng.* **1979**, *19*, 67-103. (g) Harley, F. R.; Vezry, P. N. *Adv. Organomet. Chem.* **1978**, *15*, 189-234. (h) Ballard, D. G. H. *J. Polym. Sci.* **1975**, *13*, 2191-2212. (i) Ballard, D. G. H. *Adv. Catal.* **1973**, *23*, 263-325.

**Acknowledgment.** We are grateful to the Department of Energy for support of this research under Contract DEAC 02-81ER10980. High-field solid-state  $^{13}\text{C}$  NMR spectra were performed by the Colorado State University Regional NMR Center, funded by National Science Foundation Grant CHE-8208821. We thank H. A. Stecher for several preliminary NMR spectra, C. M. Fendrick for a sample of  $\text{Cp}'_2\text{Th}(\text{CH}_3)(\text{CH}_2\text{CMe}_3)$ , and K. G. Moley for a sample of  $\text{Cp}'_2\text{Th}(\text{CH}_3)[\text{OCH}(t\text{-Bu})_2]$ . We thank Dr. Mark Delaney of Dow Chemical Co. for poly(methylaluminumoxane) samples and Professor R. L. Burwell, Jr., for stimulating discussions.

**Registry No.**  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2$ , 67506-90-5;  $\text{Cp}'_2\text{Th}(\text{CH}_3)_2$ , 94138-24-6;  $[\text{Cp}'_2\text{Th}(\mu\text{-H})_2]$ , 67506-92-7;  $\text{Cp}'_2\text{Th}(\text{CH}_3)(\text{CH}_2\text{CMe}_3)$ , 94138-25-7;  $\text{Cp}'_2\text{Th}(\text{CH}_3)\text{Cl}$ , 79301-20-5;  $\text{Cp}'_2\text{Th}(\text{CH}_3)[\text{OCH}(t\text{-Bu})_2]$ , 94138-26-8;  $\text{Cp}'_2\text{Th}(\text{CH}_3)(\text{OCMe}_3)$ , 79301-34-1;  $\text{Al}_2\text{O}_3$ , 1344-28-1;  $[(\text{CH}_3)_2\text{AlCl}]_2$ , 15171-31-0.

(44) (a) Gavens, P. D.; Bottrill, M.; Kelland, J. W.; McMeeking, J. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Chapter 22.5. (b) Galli, P.; Luciani, L.; Cecchini, G. *Angew. Makromol. Chem.* **1981**, *94*, 63-89. (c) Karol, F. J.; Wu, C.; Reichle, W. T.; Maraschin, N. *J. Catal.* **1979**, *60*, 68-76. (d) Firment, L. E. *J. Catal.* **1983**, *82*, 196-212. (e) Boor, J., Jr. "Ziegler-Natta Catalysts and Polymerizations"; Academic Press: New York, 1979; Chapters 6, 22.

## Copper(II) Complexes of Tyrosine-Containing Dipeptides. Effects of Side-Chain Groups on Spectral and Solution Chemical Properties and Their Structural Implication

Osamu Yamauchi,\* Kiyokazu Tsujide, and Akira Odani

Contribution from the Faculty of Pharmaceutical Sciences, Kanazawa University, 13-1 Takara-machi, Kanazawa 920, Japan. Received July 23, 1984

**Abstract:** With a view to obtaining information of the structures and stabilities of the Cu(II) complexes of tyrosine (Tyr)-containing dipeptides, spectroscopic and potentiometric studies have been carried out with the peptides to L-Tyr-X, where X refers to L-/D-alanine, -arginine, -Tyr, -tryptophan (Trp), -histidine (His), L-phenylalanine (Phe), L-/D-glutamic acid. The complex species and their stability constants have been determined by potentiometric titrations at 25 °C and  $I = 0.1$  (KNO<sub>3</sub>). All the peptides react with Cu(II) in the manner analogous to L-tyrosylglycine (L-Tyr-Gly), but the deprotonation of the peptide NH group is affected by the C-terminal side-chain groups. The dipeptides except L-Tyr-L-/D-His form at pH 8-11 a dimeric species, the maximum distribution of which occurs at pH ~9.5 in the 1:1 Cu(II)-peptide systems with the dimer accounting for as much as 80% of the total Cu(II) in 5 mM Cu(II)-L-Tyr-L-Trp. The constants for  $2(\text{monomer}) \rightleftharpoons \text{dimer}$  equilibria are in the range 2.04-3.70 log units. The absorption spectra of the 1:1 systems (~2 mM) exhibit a d-d peak at 610-630 nm ( $\epsilon$  90-150) at pH >6 and in the presence of the dimeric complex an additional peak at ~380 nm ( $\epsilon$  260-720), whose assignment to the charge transfer between Cu(II) and the phenolate group has been confirmed by the resonance Raman spectra of the isolated complexes,  $[\text{Cu}(\text{L-Tyr-Gly})]\cdot 0.5\text{H}_2\text{O}$  and  $\text{Na}_2[\text{Cu}_2(\text{L-Tyr-Gly})_2]\cdot 7.5\text{H}_2\text{O}$ . While the circular dichroism (CD) spectral magnitudes in the d-d region for the Cu(II)-dipeptide complexes with a C-terminal aliphatic amino acid are an additive function of those exhibited by the component amino acid complexes irrespective of the diastereoisomerism of the peptides, remarkable CD magnitude anomaly was observed for the active (L-L) peptides with a C-terminal aromatic amino acid, L-Tyr-L-X (X = Tyr, Trp, and Phe). The anomaly is diastereospecific and strictly coincident with the dimer formation, which is taken to imply distortion by the dimeric structure of the C-terminal side-chain orientation favoring the Cu(II)-aromatic ring interaction.

Tyrosine constitutes the N-terminus of endogenous analgesic peptides such as enkephalin<sup>1</sup> and endorphin<sup>2</sup> isolated from brain and is considered to be essential for their activity.<sup>3</sup> An analgesic dipeptide, L-tyrosyl-L-arginine (kyotorphin), was later isolated from

bovine brain by Takagi et al.,<sup>4</sup> which again indicates the importance of the N-terminal tyrosyl residue. Of the main biological transition metals, copper(II) is probably the most effective in binding small peptides at physiological pH,<sup>5</sup> and since the copper content is high especially in the synaptosomal fraction of brain which abounds in enkephalin and kyotorphin,<sup>6</sup> interactions of copper(II) with these opioid peptides may have physiological

(1) (a) Hughes, J. *Brain Res.* **1975**, *88*, 295-308. (b) Hughes, J.; Smith, T. W.; Kosterlitz, H. W.; Fothergill, L. A.; Morgan, B. A.; Morris, H. R. *Nature (London)* **1975**, *258*, 577-579.

(2) (a) Guillemin, R.; Ling, N.; Burgus, R. C. R. *Hebd. Seances Acad. Sci., Ser. D* **1976**, *282*, 783-785. (b) Ling, N.; Burgus, R.; Guillemin, R. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 3942-3946. (c) Bradbury, A. F.; Feldberg, W. F.; Smyth, D. G.; Snell, C. R. In "Opiates and Endogenous Opioid Peptides"; Archer, S., Collier, H. O. J., Goldstein, A., Kosterlitz, H. W., Simon, E. J., Takagi, H., Terenius, L., Eds.; Elsevier/North Holland Biochemical Press: Amsterdam, 1976; p 9. (d) Li, C. H.; Chung, D. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 1145-1148.

(3) Morley, J. S. *Annu. Rev. Pharmacol. Toxicol.* **1980**, *20*, 81-110.

(4) (a) Takagi, H.; Shiomi, H.; Ueda, H.; Amano, H. *Nature (London)* **1979**, *282*, 410-412. (b) Takagi, H.; Shiomi, H.; Ueda, H.; Amano, H. *Eur. J. Pharmacol.* **1979**, *55*, 109-111.

(5) Sigel, H.; Martin, R. B. *Chem. Rev.* **1982**, *82*, 385-426.

(6) (a) Ueda, H.; Tatsumi, K.; Shiomi, H.; Takagi, H. *Brain Res.* **1982**, *231*, 222-224. (b) Simantov, R.; Snowman, A. M.; Snyder, S. H. *Brain Res.* **1976**, *107*, 650-657.