

- (15) Prepared by diazotization of DL-[3-¹⁴C]serine: E. Fischer and W. A. Jacobs, *Chem. Ber.*, **40**, 1068 (1907).
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 (18) The earlier experiment³ using growing cells showed that ¹⁴C from [U-¹⁴C]uridine was incorporated into the pyrimidine base of the polyoxins but apparently not into the sugar moiety. It may be that [¹⁴C]phosphoribosyl pyrophosphate (PRPP) formed by the equilibrium, UMP ↔ uracil + PRPP, was diluted predominantly with endogenous PRPP during the long period of incubation.
 (19) ¹³C NMR analysis of ¹³C-enriched octosyl acid was not possible because the yield under these fermentation conditions was too low. Experiments are currently underway to obtain a mutant which produces octosyl acid in larger yields.
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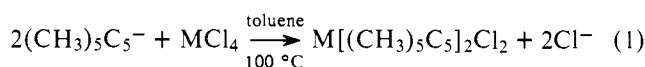
Received October 5, 1977

Bis(pentamethylcyclopentadienyl)actinide Chemistry: Properties of Stable Thorium and Uranium Dialkyls and Hydrides

Sir:

Currently two major goals in organoactinide chemistry¹ are to design ways of manipulating coordinative unsaturation for optimum chemical reactivity and to develop meaningful chemical comparisons between organoactinide reaction patterns and those of transition metal organometallics. In regard to the former point, one of our aims has been to explore the chemistry of species with fewer *pentahapto*cyclopentadienyl ligands (e.g., U[R(C₅H₄)₂]₂X₂,² U(C₅H₅)₂X₂³ (X = functional group) than in the more saturated M(C₅H₅)₃X (M = Th, U; X = functional group) derivatives.⁴ In this communication we report initial results on new bis(pentamethylcyclopentadienyl) derivatives of thorium and uranium. These compounds represent some of the most chemically reactive and versatile organoactinides prepared to date. Furthermore, in regard to the second point above, they provide a direct chemical comparison to an analogous series of transition metal (Ti, Zr) organometallics.⁵ Among the new compounds we discuss here are the most thermally stable actinide polyalkyls prepared to date and their facile reaction with hydrogen. We report the first organoactinide hydrides, which demonstrate the existence of isolable compounds with actinide-hydride bonds.⁶

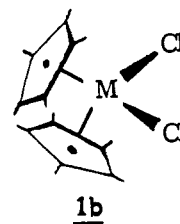
The reaction of pentamethylcyclopentadienide Grignard reagent (prepared by metalating pentamethylcyclopentadiene⁷ with isopropylmagnesium chloride in refluxing toluene) with thorium and uranium tetrachlorides produces, after filtration and removal of the solvent, crystalline bis(pentamethylcyclopentadienyl)actinide dichlorides in 70-90% yield.



1a, M = Th (colorless needles)

b, M = U (red-orange needles)

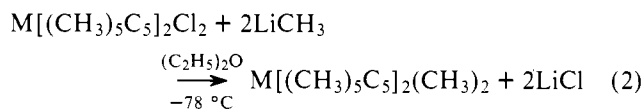
These air-sensitive new complexes were characterized by IR and ¹H NMR spectroscopy and by elemental analysis.^{8a} Cryoscopic molecular weight measurements in benzene show **1b** to be monomeric; **1a** is insufficiently soluble for such determinations.⁹ For **1b** we propose the monomeric solution structure shown; the solid-state structure of **1a** and **1b** must await diffraction studies. The lack of association in



1b

solution and the relatively low uranium coordination number in the present case stands in contrast to the associated U[R(C₅H₄)₂]₂X₂ species.²

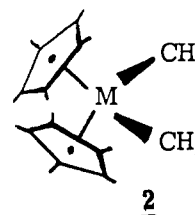
In diethyl ether solution, the bis(pentamethylcyclopentadienyl) dichlorides can be alkylated with methyl lithium according to eq 2.



2a, M = Th (colorless needles)

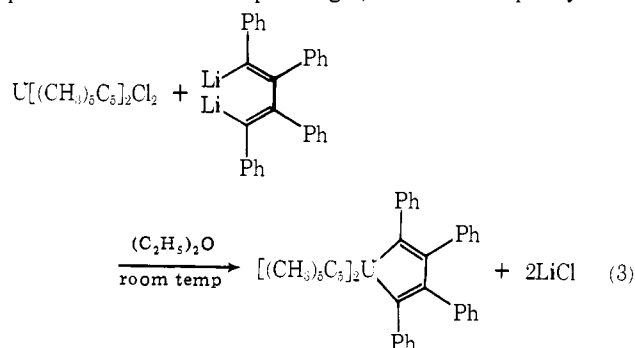
b, M = U (orange needles)

The products were isolated in 65-70% yield by evaporation of the ether and recrystallization from toluene. The air-sensitive new dialkyls were characterized by the same techniques as the dichlorides.^{8b} We find them to be monomeric in benzene^{8b} and propose the structure shown. Unlike previously reported actinide polyalkyls,^{1,2,10} **2a** and **2b** possess very high thermal



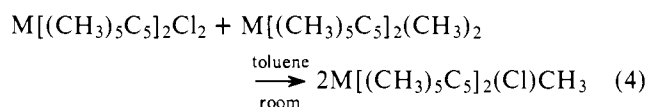
2

stability. In toluene solution at 100 °C, **2a** has a half-life of ~1 week, while **2b** has a half-life of ~16 h. Of thermal stability comparable with that of **2b** is the uranium metalocycle prepared via the route of eq 3 using 1,4-dithiotetraphenylbuta-



diene.¹¹ This product, after crystallization from toluene, was characterized by the chemical and physical methods described above.^{8c}

The reaction of **1** and **2** in toluene yields monoalkylated derivatives

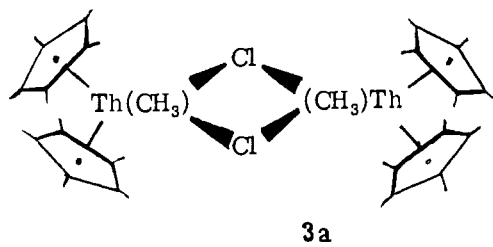


3a, M = Th (colorless needles)

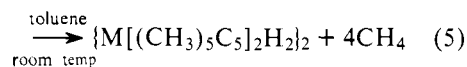
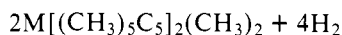
b, M = U (orange-red needles)

with eq 4 lying 90-95% to the right as determined by ¹H NMR spectroscopy. Interestingly, molecular weight measurements in benzene^{8d} show **3b** to be monomeric, while **3a** is dimeric. The

latter result is in accord with the larger ionic radius of thorium¹² and suggests the structure shown.



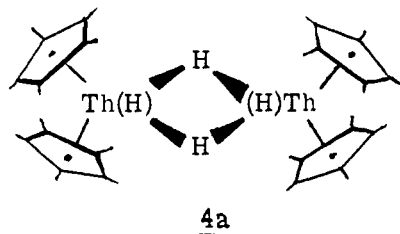
The thorium and uranium dimethyls react rapidly and stoichiometrically at room temperature with hydrogen to give organoactinide hydrides.



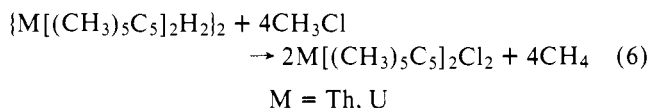
4a, M = Th (colorless crystals)

b, M = U (green-black solid)

Although **4a** is stable at 80 °C in toluene solution for long periods of time, **4b** reversibly loses 1.0 equiv of H₂ per dimer (by Toepler pump) at room temperature in what appears to be a binuclear reductive elimination. The facility of this latter dehydrogenation presumably reflects the accessibility of the uranium +3 oxidation state¹³ and has rendered complete characterization of **4b** more difficult. The structure of the organothorium dihydride is inferred from molecular weight measurements, which show it to be a dimer,^{8e} as well as infrared spectroscopic data. For {Th[(CH₃)₅C₅]₂H₂}₂ and {Th[(CH₃)₅C₅]₂D₂}₂ both terminal and bridge¹⁵ Th–H (Th–D) stretching frequencies are observed in the infrared at 1406 (1020),^{16a} 1361 (979),^{16b} 1215 (873),^{16c} and 1114 (802)^{16d} cm⁻¹. These data suggest the structure shown, which is analogous to that proposed for [Zr(tetrahydroindenide)₂H₂]₂,¹⁷ but differs from the titanium and zirconium bis(pentamethylcyclopentadienyl) dihydride structures, which are monomeric.⁵ The ¹H NMR spectrum of **4a** exhibits sharp



singlets at δ 2.31 (30 H) and 19.25 (2 H). The low-field position of the hydride resonance (which is absent in the deuteride) is characteristic of early transition metal hydrides.^{5,15,17,18} That a singlet is observed in toluene-*d*₈ down to -90 °C indicates rapid interchange of bridge and terminal hydrogen atoms.¹⁹ The unstable uranium dihydride exhibits a vibrational spectrum^{8f} similar to that of **4a**, suggesting an analogous structure. Both **4a** and **4b** react with excess methyl chloride to produce four equivalents of methane and the corresponding dichlorides in essentially quantitative yield.



In comparison with the bis(pentamethylcyclopentadienyl)-titanium and -zirconium systems,⁵ it should be noted that the hydrogenolysis of the actinide dimethyls is far more rapid. This observation as well as the dimeric structures of the organoac-

tinide dihydrides appears to reflect the greater preferred coordination numbers and larger ionic radii¹² of the actinide ions, hence less coordinatively saturated monomers. Such characteristics suggest that bis(pentamethylcyclopentadienyl)actinides will display high reactivity with respect to a variety of catalytically interesting processes, e.g., carbon monoxide insertion.^{20,21}

The ramifications of this work are fourfold. First, it demonstrates that thorium and uranium dialkyls can possess high thermal stability. Second, such organoactinides can exhibit very high chemical reactivity and can readily undergo heretofore unobserved transformations such as metal-carbon σ-bond hydrogenolysis. Third, organometallics with actinide-hydride bonds are isolable, and numerous stoichiometric and catalytic reaction patterns which require the existence of such species become conceptually viable. Fourth, and perhaps most surprising, is the observed congruence between the chemistry of M[(CH₃)₅C₅]₂(CH₃)₂ species where M = Th, U, Ti, and Zr. The degree of association and most likely the enhanced reactivity of the organoactinides reflects the larger ionic radii and higher coordinative unsaturation. Further studies in this area are in progress.

Acknowledgment. We thank the National Science Foundation (CHE76-84494) for generous support of this research.

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- (a) The thorium complex, **1a**, exhibits infrared absorptions at (Nujol mull) 1019 and 799 cm⁻¹, characteristic^{5,7a} of an η⁵-(CH₃)₅C₅ moiety; the ¹H NMR (C₆D₆) exhibits a sharp singlet at δ 1.98. Anal. Calcd for C₂₀H₃₀ThCl₂; C, 41.83; H, 5.27. Found: C, 42.60; H, 5.44. The uranium complex, **1b**, exhibits an identical IR spectrum. In the ¹H NMR spectrum (C₆D₆) an isotropically shifted^{8a} singlet is observed at δ 13.16, with a rather substantial line width (190 Hz). Anal. Calcd for C₂₀H₃₀UCl₂: 41.45; H, 5.23; mol wt, 579. Found: C, 40.56; H, 5.43; mol wt, 510 (cryoscopic in benzene). (b) The IR spectra of **2a** and **2b** as Nujol mulls are identical with those of the dichlorides. The ¹H NMR spectrum (C₆D₆) of **2a** exhibits sharp singlets at δ 1.92 (30 H) and -0.19 (6 H). Anal. Calcd for C₂₂H₃₆Th: C, 49.62; H, 6.81; mol wt, 533. Found: C, 48.50; H, 6.93; mol wt, 528 (cryoscopic in benzene). For **2b**, isotropically shifted ¹H NMR (C₆D₆) singlets are observed at δ 5.03 (30 H, line width = 5.3 Hz) and δ -124 (6 H, line width ≈ 7 Hz). Anal. Calcd for C₂₂H₃₆U: C, 49.06; H, 6.75; mol wt, 539. Found: C, 49.24; H, 6.40; mol wt, 540 (cryoscopic in benzene). (c) The metallocycle exhibits ¹H NMR resonances at δ 6.02 (singlet, 30 H), 5.72 (multiplet, 4 H), 4.52 (multiplet, 4 H), -0.27 (triplet, 2 H), -1.25 (triplet, 4 H), and -33.0 (multiplet, 4 H). Line widths are on the order of 3–7 Hz. Anal. Calcd for C₄₈H₆₀U: C, 66.70; H, 5.83; mol wt, 864. Found: C, 66.56; H, 6.10; mol wt, 859 (cryoscopic in benzene). (d) The IR spectra of **3a** and **3b** as Nujol mulls are identical with those of the dichlorides. For **3a** the ¹H NMR (C₆D₆) displays sharp singlets at δ 2.01 (30 H) and 0.41 (3 H). Anal. Calcd for C₄₂H₆₆Th₂Cl₂:

C, 45.61; H, 6.02; Cl, 6.41; mol wt, 1106. Found: C, 45.56; H, 6.13; Cl, 6.52; mol wt, 1121 (cryoscopic in benzene). For **3b**, the ^1H NMR (C_6D_6) exhibits singlets at δ 8.96 (30 H, line width = 6 Hz.), -154 (3 H, line width \approx 7 Hz). Anal. Calcd for $\text{C}_{21}\text{H}_{33}\text{Cl}$: C, 45.12; H, 5.95; Cl, 6.34; mol wt, 559. Found: C, 44.98; H, 5.89; Cl, 6.39; mol wt, 568 (cryoscopic in benzene). (e) Anal. Calcd for $\text{C}_{40}\text{H}_{64}\text{Th}_2$ (**4a**): C, 47.61; H, 6.41; mol wt, 1009. Found: C, 48.63; H, 6.63; mol wt, 1038 (cryoscopic in benzene). (f) For **4b**, broadened bands centered at 1345 and 1180 cm^{-1} are observed in the IR. The ^1H NMR spectrum (C_6D_6) shows a singlet at δ -2.15 (line width = 4 Hz); the hydride signal has not, as yet, been located.

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 (16) (a) $\nu_{\text{M-H}}/\nu_{\text{M-D}} = 1.38$. (b) $\nu_{\text{M-H}}$ was obscured by Nujol; the band position was calculated from $\nu_{\text{M-D}}$ assuming $\nu_{\text{M-H}}/\nu_{\text{M-D}} = 1.39$. (c) $\nu_{\text{M-H}}/\nu_{\text{M-D}} = 1.39$. (d) $\nu_{\text{M-H}}/\nu_{\text{M-D}} = 1.39$.
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Activation of Water Molecule. 1. Intermediates Bearing on the Water Gas Shift Reaction Catalyzed by Platinum(0) Complexes

Sir:

The heterogeneously catalyzed water gas shift reaction now employed in industry requires high temperature.¹ Homogeneous catalysts active at lower temperature are attracting considerable interest² because of the favorable thermodynamic equilibrium. Recently three groups have reported homogeneous catalytic systems consisting of metal carbonyls, i.e., $\text{Ru}_3(\text{CO})_{12}$ -base^{3,4} and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ -HCl-NaI-glacial acetic acid.⁵ The logical basis for employing metal carbonyls as catalysts might be the CO activation through coordination which facilitates nucleophilic attack by water.³⁻⁵

We wish to report here briefly a new approach based on a different strategy to activate the water molecule using low-valent transition metal complexes capable of forming hydrido hydroxo species, *trans*-H-M-OH. In view of HSAB principles and the strong trans influence of hydride,⁶ an enhanced nucleophilic reactivity⁷ toward CO is expected for the hydroxo ligand in the H-M-OH species. Possible candidates for such low-valent transition metal compounds are PtL_3 (L = tertiary phosphines).

The results of the water gas shift reactions catalyzed by some PtL_3 complexes are summarized in Table I. Typically the catalytic solution prepared from PtL_3 (0.1 mmol) and H_2O (2

Table I. The Water Gas Shift Reaction^a

Catalyst	Solvent	Temp. °C	Gaseous Products ^b		
			H ₂	CO ₂	Turn-over ^c
Pt[P(<i>i</i> -Pr) ₃] ₃	Acetone	100	9.4	8.2	8.8
	Acetone	125	16.0	15.8	159
	Acetone	153	37.5	31.6	345
	THF	100	7.0	6.6	68
	Pyridine	100	0.7	1.0	9
Pt(PEt ₃) ₃	Acetone	100	1.1	1.1	11
Pt(PPh ₃) ₃	THF	100	0	0	0

^a The reaction conditions shown in the text. ^b Millimoles.

^c Moles/mole of catalyst, 18 h.

mL) in an aprotic solvent (5 mL) was placed into a stainless steel bomb (100 mL) under a N_2 atmosphere and subsequently was charged with CO (20 atm). After heating at a fixed temperature for 18 h, the gaseous products in the vapor phase as well as dissolved in the liquid phase were analyzed by gas chromatography^{3,5} and quantitative titration.

A remarkable solvent effect is observed for the catalysis. Coordinating pyridine drastically reduces the catalytic activity of $\text{Pt}[P(*i*-Pr)_3]_3$ ⁸ (**1**). The colorless homogeneous reaction mixture in pyridine after the shift reaction (100 °C, 18 h) contains *trans*-{PtH(pyridine)[P(*i*-Pr)₃]₂}OH⁹ (**2**) which can be stabilized by anion metathesis with BF_4^- (68% yield). By contrast, from the catalytic reaction in acetone or THF carried out under the same conditions was obtained *trans*-{PtH(CO)-[P(*i*-Pr)₃]₂}OH (**3**) as the BPh_4^- salt¹⁰ in 90% yield.

The precursors **2** and **3** are readily traced from studies on the solution chemistry of PtL_3 . Extensive dissociation of **1** gives PtL_2 as by far the predominant species in solution.¹¹ Consequently the oxidative addition of water occurs with PtL_2 to give **2** via solvation of an incipient species $\text{PtH}(\text{OH})\text{L}_2$. The addition was found to be reversible as **1** was recovered from a mixture of **1** and H_2O in pyridine on concentration to dryness. The instability of **2** prevents its isolation and the rapid proton exchange between the hydrido ligand of **2** and water apparently obscures the hydrido ^1H NMR signal. In addition to the isolation of *trans*-{PtH(pyridine)[P(*i*-Pr)₃]₂} BF_4 , the existence of **2** is further evidenced by conductometric and pH measurements. Thus the system **1**/ H_2O in the system **1**/pyridine ($[\text{H}_2\text{O}] > 15$ M) shows a conductance (Λ 23.9 $\Omega^{-1} \text{cm}^2$ at 20 °C), and the dissociation of OH^- from **2** is manifested by the apparent pH (14.1) of the system **1**/ H_2O ($[\text{1}] = 9.8 \times 10^{-3}$ M, $[\text{H}_2\text{O}] = 22.2$ M in pyridine, 20 °C).¹²

A reaction mixture of the water gas shift reaction (100 °C, 18 h) catalyzed by $\text{Pt}(\text{PEt}_3)_3$ in acetone contains a water adduct $[\text{PtH}(\text{PEt}_3)_3]\text{OH}$,¹³ which was isolated as the BPh_4 salt¹⁴ in 72% yield. In this case, the formation of $[\text{PtH}(\text{CO})-(\text{PEt}_3)_2]\text{OH}$ was not observed. The formation of $[\text{PtH}-(\text{PEt}_3)_3]^+$ and $[\text{PtH}(\text{pyridine})[P(*i*-Pr)_3]_2]^+$ is ascribed to their inertness toward CO (1 atm, 25 °C), which accounts for the low catalytic activity of $\text{Pt}(\text{PEt}_3)_3$ in acetone or **1** in pyridine.

The catalytic activity of PtL_3 decreases in the order $P(*i*-Pr)_3 > \text{PEt}_3 \gg \text{PPh}_3$. The complete lack of catalytic activity in $\text{Pt}(\text{PPh}_3)_3$ is apparently due to the incapability of water adduct formation. The importance of water molecule activation is obvious.

Nucleophilic attack of OH^- at the coordinated CO will give $\text{PtH}(\text{CO}_2\text{H})\text{L}_2$. Evidence for the metal carboxylic acid is the formation of the potassium salt *trans*-PtH(CO₂K)[P(*i*-Pr)₃]₂, observed by ^1H NMR and IR spectra¹⁵ of the solution of *trans*-{PtH(CO)[P(*i*-Pr)₃]₂} BPh_4 treated with an excess of KOH in aqueous THF at room temperature. Further indirect support for the formation of the metal carboxylic acid is the successful isolation of *trans*-PtH(CO₂CH₃)[P(*i*-Pr)₃]₂¹⁶ (65%