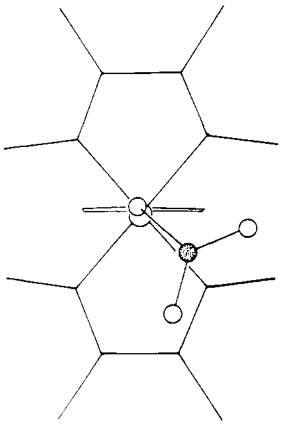

Figure 2. Perspective view along the Co–C bond.

$P(OCH_3)_3$, a small quantity (<10% yield) of $(CH_3O)_3PCo(DH)_2CH_2NO_2$ formed which was heavily contaminated with $(CH_3O)_3PCo(DH)_2NO_2$. ($LCo(DH)_2NO_2$ also formed in the case of L = substituted pyridine but to a negligible extent.) Later fractions yielded $H_2OCo(DH)_2P(O)(OCH_3)_2$.[6,22] It is known that this complex can be produced from nucleophilic attack at the phosphite ester carbon of cobaloximes containing trimethyl phosphite as a ligand.[6,22] For L = $P(C_6H_5)_3$, no useful product was obtained.

While this work was in progress, three preparations of $pyCo(DH)_2CH_2NO_2$ were reported. Widdowson and Roussi obtained this complex in a yield of 19% by alkylation of the cobalt(I) anion with $BrCH_2NO_2$.[23] These workers found alternatively that a yield of 24% could be obtained by alkylating $(py)_2Co^{II}(DH)_2$ with $BrCH_2NO_2$ in the presence of zinc dust. Beck and co-workers realized a yield of 58% of $pyCo(DH)_2CH_2NO_2$ by treating $pyCo(DH)_2Cl$ with $NaCH_2NO_2$ in THF.[21] This latter synthesis gives comparable results to that reported here but is not as convenient.[24]

Structure. An ORTEP drawing of a crystallographically independent molecule of $pyCo(DH)_2CH_2NO_2$ with the atom numbering scheme is shown in Figure 1. Bond lengths and selected bond angles are listed in Table III. The CH_2NO_2 group is bonded via C to the cobalt.

The cobalt atom has a distorted octahedral stereochemistry and is displaced (toward py) 0.02 Å above the plane of the four oxime N donors, which are coplanar within ±0.008 Å. The two oxime ligands make an angle of 0.2°. In addition, both make angles of 3.0° with the four-nitrogen-donor equatorial plane. These values suggest a slightly stepped conformation of the essentially planar equatorial ligands. The coordinated pyridine (planar within ±0.002 Å) makes an angle of 87.5° with the equatorial plane. The orientation of the py ligand is that always found in $pyCo(DH)_2R$ compounds, i.e., nearly bisecting the oxime bridges.[1,3,4,25] The C(9)–NO_2 group is planar within ±0.007 Å and makes an angle of 28.0° with the equatorial plane. Its orientation is shown in Figure 2.

The bond lengths and angles in the oxime ligands are quite normal.[1,3,4] The Co–C bond length of 2.002 (3) Å is not significantly different from the value of 1.998 (5) Å reported for the methyl complex,[3] whereas the Co–N(py) distance is only 2.028 (3) Å. The C(9)–Co–N(6) angle is 176.01 (8)°, the bending being away from the NO_2 group. The Co–C(9)–N(5) angle is 113.7 (2)° and does not differ significantly from those for Co–C–C of 114.3 (2) and 114.0 (2)° found in $pyCo(DH)_2$-*i*-C_3H_7.[1]

Table IV. Structural Data for $pyCo(DH)_2R$ Complexes

R	Co–N(py), Å	Co–C, Å	d,[a] Å	α,[b] deg
i-C_3H_7[c]	2.099 (2)	2.085 (3)	0.02	4.0
CH_3[d]	2.068 (3)	1.998 (5)	0.04	3.2
CH_2COOCH_3[e]	2.040 (6)	2.040 (6)		
CH_2NO_2[f]	2.028 (3)	2.002 (3)	0.02	0.2

[a] Displacement of Co out of the four-nitrogen-donor atom equatorial plane. [b] Angle between the planes passing through the oxime ligands. [c] Reference 1. [d] Reference 3. [e] Reference 25. [f] This work.

The most important structural result is that the Co–N(py) bond length is significantly shorter than those so far reported for any other alkylcobaloximes, which vary from 2.040 (6) to 2.099 (2) Å (see Table IV). This is the first structural evaluation of a complex containing the CH_2NO_2 ligand. The result indicates that the CH_2NO_2 group exerts a trans influence weaker than that of CH_3 and slightly weaker than that of CH_2COOCH_3. For a typical acido ligand, N_3, the Co–N(py) bond length is 1.973 (5) Å.[26] On the other hand, *i*-C_3H_7 lengthens the trans Co–N(py) bond more than CH_3.[1] Thus, as expected, acceptor groups such as NO_2 and $COOCH_3$ attract electron density from the carbon atom bound to cobalt, decreasing its trans-influencing ability. On the contrary, methyl groups which increase electron density on the σ-bonded carbon atom increase its trans-influencing ability. Work in progress in these laboratories suggests that the effects of the CH_2NO_2 group on structure, reactivity, and spectra is intermediate between those of the more trans-directing alkyl groups and the less trans-directing acido groups. The results of these comparative studies will be reported once a larger number of compounds has been studied.[27]

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Registry No. $pyCo(DH)_2CH_2NO_2$, 73202-88-7; $pyCo(DH)_2Cl$, 23295-32-1.

Supplementary Material Available: Tables of hydrogen atom parameters, anisotropic temperature factors, and structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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Triborane(7) Adducts of Phosphine and Methylphosphines

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The base strength of phosphine (PH_3) toward borane(3) is considerably weaker than the base strength of methyl-substituted phosphines. Thus, phosphine–borane(3) $PH_3{\cdot}BH_3$[1]

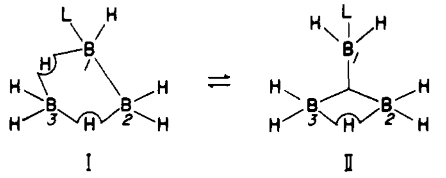

Figure 1. Structures of the phosphine adducts of triborane(7) (L = PH_3, CH_3PH_2, $(CH_3)_2PH$). II is the low-temperature, stable form.

dissociates to diborane(6) and phosphine above −30 °C,[2] whereas the BH_3 adducts of methylphosphines are undissociated at room temperature.[3] The phosphine adducts of triborane(7) are expected to be more stable than those of borane(3) with respect to the dissociative decomposition, since the acid strength of triborane(7) generally is considered to be stronger than that of borane(3).[4] It was of interest to us to examine the stabilities of the triborane adducts of the series of methylphosphines. Of these series, only trimethylphosphine–triborane(7) had been prepared. This stable solid had been synthesized by the direct reaction of tetraborane(10) with trimethylphosphine.[5] The BH_3 adducts of the series of methylphosphines had also been prepared by the direct reaction of diborane with the appropriate phosphine.[1-3] Although it had been found that the reaction pattern of tetraborane(10) with the series of methylamines was markedly different from that of diborane(6) with the same series of amines,[6] it seemed reasonable to attempt the syntheses of the remaining triborane(7) adducts of the methylphosphines by the direct method.

Results and Discussion

A. Syntheses and Properties. Treatments of tetraborane(10) with phosphine, methylphosphine, and dimethylphosphine above 0 °C resulted in the formation of the borane(3) and triborane(7) adducts of the respective phosphines (eq 1–3).

$$\begin{aligned} &B_4H_{10} + 2PH_3 \rightarrow PH_3{\cdot}BH_3 + PH_3{\cdot}B_3H_7 \\ &\qquad\qquad\qquad\qquad \downarrow \\ &\qquad\qquad\qquad\quad PH_3 + {}^1\!/_2B_2H_6 && (1) \\ &B_4H_{10} + 2CH_3PH_2 \rightarrow CH_3PH_2{\cdot}BH_3 + CH_3PH_2{\cdot}B_3H_7 && (2) \\ &B_4H_{10} + 2(CH_3)_2PH \rightarrow (CH_3)_2PH{\cdot}BH_3 + (CH_3)_2PH{\cdot}B_3H_7 && (3) \end{aligned}$$

Symmetrical cleavage of tetraborane(10) occurred as in the reactions of diborane(6) with the phosphines.[1-3] These triborane(7) adducts, which could be separated from the more volatile borane(3) adducts were stable, colorless liquids of low volatility. Phosphine–triborane(7) also formed when tetrahydrofuran–triborane(7) was treated with PH_3. The displacement reaction in a dichloromethane solution was nearly complete at 0 °C (eq 4).

$$PH_3 + THF{\cdot}B_3H_7 \rightarrow PH_3{\cdot}B_3H_7 + THF \qquad (4)$$

Phosphine–triborane(7), which appeared to be the least stable of the three triborane(7) adducts, showed only slight decomposition after standing at room temperature for 24 h. The two methylphosphine–triborane(7) adducts showed no decomposition up to 1 month at room temperature. The observed stability of $PH_3{\cdot}B_3H_7$ is in sharp contrast to the instability of $PH_3{\cdot}BH_3$ and reflects the strong Lewis acidity of triborane(7) toward PH_3 relative to that of borane(3). Similar stability differences between the adducts of the two boranes have been seen for ether adducts; the BH_3 adduct of tetra-

Table I. NMR Data[a] for the Triborane(7) Adducts of Methylphosphines

	^1H									^{11}B							^{31}P				
		H_P			H_B		H_C				B(1)				B(23)						
compd	temp, °C	δ	J_{PH}, Hz	J_{HBPH}, Hz	δ	J_{PBH}, Hz	δ	J_{PCH}, Hz	J_{HPCH}, Hz	temp, °C	δ	J_{PB}, Hz	J_{HB}, Hz	J_{BB},	δ	J_{HB}, Hz	temp, °C	δ	J_{BP}, Hz	J_{HP}, Hz	J_{HBP}, Hz
$PH_3{\cdot}B_3H_7$	+25	4.49	398	2.2[b]	1.23	10.8				+30	−51.3	70		12	−10.2		+25	−96.3	70	400	10.7
	−90	4.55	403		1.96 ($H_{(2,3)}$)[c]					−55	−51.6	74	90		−11.2	102					
					1.76 ($H_{(2,3)}$)[c]																
					0.68 ($H_{(1)}$)																
					−1.65 (H_b)																
$CH_3PH_2{\cdot}B_3H_7$	+25	4.67	400		1.03	8.1	1.43	12.9	6.3	+25	−49.5	81		12	−12.9		+25	−56.3	84	400	
	−80	4.69	405		1.67 ($H_{(2,3)}$)		1.38	13.0	6.3	−80	−50.3	82	85		−14.6	100					
					1.45 ($H_{(2,3)}$)																
					0.38 ($H_{(1)}$)																
					−1.77 (H_b)																
$(CH_3)_2PH{\cdot}B_3H_7$	+25	4.77	393		0.92	8.0	1.42	12.8	6.0	+25	−46.9	92			−14.5		+25	−24.5	93	400	
	−90	4.83	400		1.51 ($H_{(2,3)}$)		1.33	12.4	6.2	−90	−47.5	95	78		−16.0						
					1.3 ($H_{(2,3)}$)																
					0.18 ($H_{(1)}$)																
					−1.85 (H_b)																
$(CH_3)_3P{\cdot}B_3H_7$	+25				0.72	6.5	1.27	11.5		+25	−45.0	102			−15.6		+25	−1.3	100		

[a] Shifts are indicated relative to tetramethylsilane, $BF_3{\cdot}O(C_2H_5)_2$, and 85% orthophosphoric acid for ^1H, ^{11}B, and ^{31}P, respectively, shifts to higher field being taken as negative. The ^1H shifts were measured relative to the CH_2Cl_2 shift which was taken as δ 5.28. [b] Based on the multiplet (octet) structure of the signal. [c] Each of the H(2,3) signals is a doublet (Figure 2).

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hydrofuran readily decomposes at room temperature to the ether and diborane(6),[7] whereas THF·B_3H_7 has been isolated as an unstable solid at room temperature.[8]

B. NMR Spectra and Nonrigidity of the Phosphine Adducts of Triborane(7). The ^{11}B, ^1H, and ^{31}P NMR data for the triborane(7) adducts of the series of methylphosphines are listed in Table I. The data are consistent with those expected for the structures shown in Figure 1, which were drawn on the basis of the reported structures of $NH_3{\cdot}B_3H_7$[9] and CO-B_3H_7.[10] Like the triborane(7) adducts of amines[11] and ethers,[12] the molecules of these phosphine adducts of fluxional at room temperature with respect to a tautomeric motion of the seven hydrogen atoms in the B_3H_7 unit.[13] Because of the rapid tautomeric motion at room temperature, the B(2,3) signals of B_3H_7 adducts usually appear as multiplets.[11-13] The octet structure, which is expected due to the equal coupling of the boron atoms to all seven hydrogen atoms, was not observed for the phosphine adducts of triborane(7) studied here. Instead, a complex multiplet consisting of apparent odd-number peaks was seen for the B(2,3) signal of each adduct. This may be due to the additional couplings of the B(2,3) atoms to the B(1) atom and to the phosphorus atom. Similar complications of the spectral appearance were observed for some of the amine adducts of triborane(7).[11] It was noted, however, that the equal coupling of the seven hydrogen atoms to the phosphorus atom was seen in the ^1H and ^{31}P NMR spectra of $PH_3{\cdot}B_3H_7$; the ^{11}B spin-decoupled H_B signal was a doublet (J_{PH_B} = 10.8 Hz), and each member of the quartet of the ^{31}P signal appeared to be a quartet of *octets* (J = 10.7 Hz). Furthermore, an octet structure due to the H_P–H_B coupling (J = 2.2 Hz) was discernible in the ^{11}B spin-decoupled H_P signal of the $PH_3{\cdot}B_3H_7$.

At sufficiently low temperatures the tautomeric motion became slow relative to the NMR time scale, and the spectra at the low temperatures reflected the static structure (II in Figure 1) of the molecules. Thus, the B(1) signal (the high-field signal) became an apparent quartet due to the coupling of the B(1) atom to the phosphorus atom and to the two hydrogen atoms, where $J_{PB} \simeq J_{HB}$, and the B(2,3) signal became a triplet due to the coupling to the two terminal hydrogen atoms. These spectral features at the low temperatures were indeed the same as those reported for the B_3H_7 adducts of HPF_2,[14] $PF_2N(CH_3)_2$,[14] and PF_2X (X = F, Cl, Br).[15] The temperature dependence of the ^1H NMR spectra was observed also. As the temperature was lowered, the doublet signal of the H_B atoms broadened and then split into the signals of H(1), H(2,3), and H(bridge) atoms. The assignment for each signal was confirmed by single frequency decoupling experiments. It was noted that the H(2,3) signal of $PH_3{\cdot}B_3H_7$ appeared as a doublet. The H(2,3) signals of $CH_3PH_2{\cdot}B_3H_7$ and $(CH_3)_2PH{\cdot}B_3H_7$ were doublets also, but their doublet feature was obscured by the presence of the multiplet signal of the methyl protons on the high-field side of the H(2,3) signals. Each member of the H(2,3) doublet of $PH_3{\cdot}B_3H_7$ was further split into a doublet (Figure 2). If the H(2,3) atoms were coupled to the phosphorus atom[16a,c] and to the bridge hydrogen atom (H_b)[16b] the signal would be a double doublet. If, however, the phosphine ligand was fixed on one side of the molecule at the low temperatures,[16c] two of the four H(2,3) atoms would become nonequivalent to the other two hydrogen atoms and the H(2,3) signal would appear as a complex (or simply broad) second-order spectrum. The exact cause of the observed double-doublet feature has not yet been established. Further studies are needed for the elucidation of the cause.

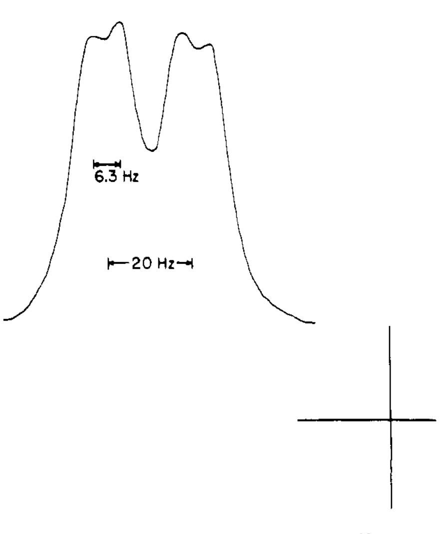

Figure 2. H(2,3) signal of $PH_3{\cdot}B_3H_7$ at −90 °C (^{11}B spin decoupled, solvent CD_2Cl_2).

Table II. Comparison of NMR Data for the BH_3 and B_3H_7 Adducts of Methylphosphines

	adducts	PH_3	CH_3PH_2	$(CH_3)_2PH$	$(CH_3)_3P$	ref
$\delta(^{11}B)$	BH_3	−60.8	−58.8	−57.2	−55.1	*b*
	B_3H_7	−51.3	−49.5	−46.9	−45.0	*a*
$\delta(^{31}P)$	BH_3	−113	−68.5	−30.8	−1.8	*b*
	B_3H_7	−96.3	−56.3	−24.5	−1.3	*a*
J_{BP}, Hz	BH_3	27	43	54	64	*b*
	B_3H_7	80	81	92	102	*a*

[a] This work. [b] References 18–20.

The temperature at which the ^{11}B spectrum of the static structure became recognizable was highest for the PH_3 adduct in the series and went down with increasing methyl substitution; these temperatures were approximately −50, −70, and −85 °C for $PH_3{\cdot}B_3H_7$, $CH_3PH_2{\cdot}B_3H_7$, and $(CH_3)_2PH{\cdot}B_3H_7$, respectively. Trimethylphosphine–triborane(7) did not show the spectrum of the static form even at −90 °C. Apparently the ease of the hydrogen tautomerism for the series of the triborane(7) adducts is related to the base strengths of the phosphine ligands. Within this series of the compounds, the trend observed is in accord with the theoretical prediction reported by Brown and Lipscomb.[17]

The change in chemical shifts and coupling constants for the series of the adducts ran parallel with those observed for the series of methylphosphine adducts of borane(3).[18-20] As

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the methyl substitution progressed, the resonance signals of the phosphorus atom and the boron atom (attached to the phosphorus) both shifted downfield, and the B–P coupling constant increased. However, the values of the chemical shifts and the coupling constants for each corresponding pair of compounds were different. The B–P coupling constant was larger, and the ^{31}P shift value was more positive for each triborane(7) adduct than for the corresponding borane(3) adduct. See Table II. These differences were considered to reflect the stronger acid strength of triborane(7), over that of borane(3), toward the phosphines. The qualitative relationship between the B–P coupling constant and the dative bond strength had been noted earlier by several investigators.[18-21]

Experimental Section

Chemicals. Laboratory stock tetraborane(10) which had been purified as described elsewhere[11] was used. Phosphine[22] and methylphosphines[23] were prepared by the literature methods. Reagent grade dichloromethane and tetrahydrofuran were stored over molecular sieves and $LiAlH_4$, respectively. Trimethylphosphine–triborane(7) was prepared by the direct, stoichiometric reaction of B_4H_{10} with $P(CH_3)_3$.[5] The borane(3) adduct of $P(CH_3)_3$ was sublimed out from the product mixture. Volatile compounds were handled in conventional vacuum lines.

Instruments. The NMR spectra were recorded on a Varian XL-100-15 spectrometer equipped with a spin-decoupler unit (Gyrocode) and a variable-temperature control unit. The operating frequencies were 100, 40.5, and 32.1 MHz for ^{1}H, ^{31}P, and ^{11}B nuclei, respectively. The mass spectral data were obtained on an AEI MS-30 mass spectrometer operating in the electron impact mode at 70 eV.

Reactions of B_4H_{10} with Phosphines. A 0.94-mmol sample of B_4H_{10} was dissolved in 2 mL of CH_2Cl_2 in a 100-mL round-bottom flask equipped with a Teflon needle valve, and a 2.86-mmol sample of PH_3 was condensed in the flask. The flask was then allowed to warm to room temperature and stand for 2 h while the solution was agitated. The volatile components were then pumped out at 0 °C. The solvent, PH_3, B_2H_6, $PH_3{\cdot}BH_3$ and B_4H_{10} were the volatile constituents. The triborane(7) adduct, $PH_3{\cdot}B_3H_7$, that remained in the flask could be distilled out slowly at room temperature. The yields were 40–60% on the basis of the amount of B_4H_{10} used.

The reactions of B_4H_{10} with CH_3PH_2 and $(CH_3)_2PH$ were performed similarly, except that the reactants were mixed in 1:2 (borane:phosphine) ratios. (The use of a large excess of these phosphines resulted in the formation of the diborane(4) adducts of the phosphines. The fast reaction of $(CH_3)_3P{\cdot}B_3H_7$ with $(CH_3)_3P$ at room temperature to give $(CH_3)_3P{\cdot}BH_3$ and $B_2H_4{\cdot}2P(CH_3)_3$ was noted earlier.[24]) The borane(3) adducts were separated from the triborane(7) adducts by pumping on the mixtures of 0 °C and then briefly at room temperature and were identified by their ^{11}B NMR spectra. The yields of the clear liquid methylphosphine adducts of triborane(7) were virtually quantitative. The mass spectra of these three adducts were typical of triborane(7) adducts, as the highest *m*/*e* appeared at two units less than the molecular ion masses of the adducts.[11]

Reaction of $THF{\cdot}B_3H_7$ with PH_3. A 0.96-mmol sample of tetrahydrofuran–triborane(7) was prepared[8] in a reaction tube (22-mm o.d. Pyrex tube), and the adduct was dissolved in diethyl ether (ca. 2 mL). A 1.25-mmol sample of PH_3 was condensed into the tube at −196 °C, and the tube was allowed to warm to −80 °C. The tube was then allowed to warm to higher temperatures in stepwise increments of 10 °C, while the solution was agitated continuously. At each step, the pressure of the system was monitored for the absorption of the PH_3 vapor by the solution. A decrease in the pressure was not observed until the mixture was warmed to 0 °C. Unchanged phosphine was fractioned out from the reaction mixture when the pressure change became undetectable. The phosphine that was recovered was 0.32 mmol, indicating that the displacement reaction was 97% complete. Upon removal of other volatile components from the reaction mixture at −23 °C, a clear liquid remained in the reaction tube. The ^{11}B NMR spectrum of this liquid in a CH_2Cl_2 solution was that of $PH_3{\cdot}B_3H_7$ containing a small amount of $THF{\cdot}B_3H_7$.[12]

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Registry No. $PH_3{\cdot}B_3H_7$, 77589-49-2; $CH_3PH_2{\cdot}B_3H_7$, 77589-50-5; $(CH_3)_2PH{\cdot}B_3H_7$, 77589-51-6; $(CH_3)_3P{\cdot}B_3H_7$, 12543-29-2; B_4H_{10}, 18283-93-7; PH_3, 7803-51-2; CH_3PH_2, 593-54-4; $(CH_3)_2PH$, 676-59-5; $THF{\cdot}B_3H_7$, 12544-89-7.

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New Route for the Synthesis of Tricyclopentadienyluranium Halides

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A facile synthetic route for UCp_4, UCp_3, $U(COT)_2$, and other related organoactinides has been achieved by the direct reaction of a fresh reactive uranium powder from electrolytic amalgamation with respective organic substrates.[1] In this work we further demonstrate the applicability of the uranium powder method to the simple synthesis of UCp_3X, where X = Cl, Br, and I, respectively. The uranium powder was reacted with cyclopentadiene and alkyl halides simultaneously under a mild condition to obtain the respective complexes. Previously these complexes were prepared by treating uranium tetrahalides with alkali or thalium cyclopentadienide.[2-5]

Experimental Section

Infrared spectra were obtained on a Perkin Elmer 397 IR spectrophotometer. Proton NMR spectra were recorded at 80.0 MHz on a Varian Associates FT-80A. Chemical shifts to high field of internal standard (Me_4Si) are given as positive. Mass spectra were obtained with use of a Varian-Mat 112 spectrometer. Gaseous products were analyzed with a Varian 3700 gas chromatograph. Elemental analyses were performed by Universal Consultant Corp. and are shown in Table I. All the operations were carried out under nitrogen in a glovebag or in an evacuated system. Organic solvents were distilled from drying agents prior to use. The starting material, uranium amalgam, was prepared as described elsewhere.[6] Thermal decomposition at 10^{-4} torr and 150 °C gave the reactive metal powder. The compound UCp_3 was freshly prepared prior to use as described elsewhere.[1]

Reactions of Ethyl Bromide or Iodide and Cyclopentadiene with Uranium Powder. Fifty milliliters of a benzene solution of ethyl bromide (3 mL) or ethyl iodide (3 mL) and 3 mL of freshly distilled cyclopentadiene were added to a round-bottom flask containing 5 g of freshly prepared uranium powder in an evacuated system. The reaction mixture was heated and refluxed until it turned from colorless to brown within a few minutes. After a 4-h reaction period, the gaseous products were collected and analyzed; the results are shown in Table II. The mixture was filtered; the filtrate was pumped to dryness, washed with hexane several times, and finally dried in vacuo. The solid was characterized as tricyclopentadienyluranium(IV) bromide and iodide. The yields were 85% and 90% for UCp_3Br and UCp_3I, respectively.

Reactions of Methylene Chloride or Carbon Tetrachloride and Cyclopentadiene with Fresh Uranium Powder. Fifty milliliters of a benzene solution of methylene chloride (3 mL) or carbon tetrachloride (3 mL) and 3 mL of freshly distilled cyclopentadiene were added to a flask containing 5 g of freshly prepared uranium powder in an

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