9-Fluorenone and 9,10-phenanthrenequinone products were analyzed by ^{1}H NMR, ^{13}C NMR, IR, and melting points except where noted. IR spectra were obtained on a Perkin-Elmer Model 283 spectrophotometer. ^{1}H NMR spectra were obtained either at 60 MHz on a Varian EM-360 spectrometer or at 90 MHz on a JEOL FX-90Q (FT) spectrometer using tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were obtained at 22.6 MHz on a JEOL FX-90Q (FT) spectrometer. All ^{13}C spectra were obtained with complete broad-band proton decoupling. Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected.

2,2′-Dilithiobiphenyl.[11] In a typical reaction, 8.7 mL of *tert*-butyllithium in pentane (14.8 mmol, 1.7 M solution) was added dropwise (15 min) to a cold (−78 °C) stirred ethyl ether solution (40 mL) of 2,2′-diiodobiphenyl (1.5 g, 3.7 mmol). The resulting yellow mixture was stirred at −78 °C for 0.5 h and then slowly (1.5 h) warmed to room temperature. After being stirred for 1 h, the solution was used immediately.

Reaction of 2,2′-Dilithiobiphenyl with $Re(CO)_4PPh_3Br$. To a stirred, cold (0 °C) solution of $Re(CO)_4PPh_3Br$ (1.48 g, 2.21 mmol) in 100 mL of ethyl ether was added dropwise via cannula an ether solution (30 mL) of 2,2′-dilithiobiphenyl (2.20 mmol). The temperature was increased gradually (2 h) to room temperature. The solvent was removed in vacuo while the products were coated on 5 g of silica gel. Chromatography on silica gel (eluted first with pentane then gradually increasing ether content to 3%), collection of the yellow band, and removal of solvent on the rotary evaporator gave 0.356 g (89%) of 9-fluorenone as a yellow solid.

Reaction of 2,2′-Dilithiobiphenyl with $Re(CO)_5Br$. To a stirred, cold (−78 °C) solution of $Re(CO)_5Br$ (1.5 g, 3.7 mmol) in 40 mL of THF was added dropwise an ether solution (30 mL) of 2,2′-dilithiobiphenyl (3.7 mmol) over 0.5 h. The yellow suspension slowly (3 h) warmed to a brown-green color at room temperature. Silica gel (5 g) was added and the solvent removed in vacuo. The coated silica gel was transferred to the top of a silica gel column (160 g of silica gel; 125 × 25 cm; pentane/ether, 8:2). Collection of the yellow band and removal of solvent on the rotary evaporator gave 9-fluorenone. Recrystallization from ethanol gave 0.273 g of yellow needles (71%, mp 81–82 °C).

Reaction of 2,2′-Dilithiobiphenyl with $Re(CO)_5Br$ Followed by Oxidative Quenching. To a stirred, cold (−78 °C) solution of $Re(CO)_5Br$ (1.5 g, 3.7 mmol) in 40 mL of THF was added dropwise an ether solution (30 mL) of 2,2′-dilithiobiphenyl (3.7 mmol) over 0.5 h. The reaction mixture was slowly warmed to the desired temperature (Table I) and then stirred for 0.5 h. After the solution was cooled again to −78 °C, 0.4 mL of bromine in 25 mL of methanol was added via syringe. The mixture was then slowly (1.5 h) warmed to room temperature and the solvent removed in vacuo with reaction products coated on silica gel (5 g). Chromatography on silica gel, collection of the yellow band (pentane/ethyl ether, 8:2) and then, if observed, a second yellow band (pentane/ethyl ether, 75:25), gave 9-fluorenone and 9,10-phenanthrenenquinone, respectively. Purification by recrystallization from ethanol gave yellow needles of mp 81–82 °C and orange crystals of mp 207–209 °C, respectively. See Table I for yields.

Acknowledgment. We wish to thank the National Science Foundation (CHE-8312644) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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Interaction of Organoaluminum Compounds and Crown Ethers. Formation in Solution of $R_2Al(crown)^+$ and $RAl(halide)(crown)^+$ Ions[1]

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^{1}H NMR studies indicate that solutions prepared from R_2AlX (X = Br and I) and 15-crown-5 contain significant amounts of $R_2Al(crown)^+$ and $RAlX(crown)^+$ ions. These cations are thought to have pentagonal-bipyramidal structures in which all oxygens of the crown ether occupy equatorial positions about the Al, and R and X occupy apical positions. ^{1}H NMR spectra of solutions prepared from R_3Al and 15-crown-5 give no evidence for formation of ions.

We recently reported that addition of an appropriate cryptand to a dialkylmagnesium compound leads to disproportionation to ions, for example, as indicated in eq 1.[2]

$$2R_2Mg + \text{cryptand} \rightleftharpoons RMg(\text{cryptand})^+ + R_3Mg^- \text{ (or } R_6Mg_2^{2-}) \quad (1)$$

In favorable cases disproportionation is quantitative in solutions, and solids containing $RMg(cryptand)^+$ and either R_3Mg^- or $R_6Mg_2^{2-}$ ions have been isolated and characterized by single-crystal X-ray diffraction techniques.[2,3] Crown ethers can induce a similar disproportionation. In solutions, however, the average size of the species accompanying the $RMg(crown)^+$ ion has never been smaller than $R_5Mg_2^{2-}$; the one solid that has been characterized contains $RMg(crown\ ether)^+$ and polymeric $(R_5Mg_2^-)_n$ ions.[4]

We decided to investigate if a similar disproportionation could be induced in organoaluminum compounds by such additives. Enhanced conductivities observed when some mono- or bidentate coordinating agents are added to solutions of trialkylaluminum compounds have been attributed to partial formation of ions, for example, as in eq 2.[5]

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Table I. ^1H NMR Spectra of Solutions of Trialkylaluminum Compounds (R_3Al) and 15-Crown-5 at 25 °C[a]

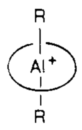
			absorption,[c] δ		
R	$[crown]:[R_3Al]$[b]	[crown], M	CH_3	CH_2	crown
Me	0	0	−0.38		
Me	0.15	0.13	−0.44		3.37
Me	0.29	0.14	−0.47		3.34
Me	0.33	0.35	−0.54		3.39
Me	0.6	0.39	−0.47		3.34
Me	1.2	0.39	−0.45		3.41
Et	0	0	1.07	0.30	
Et	0.29	0.27	1.13	−0.07	3.51
Et	0.7	0.42	1.24	0.05	3.42

[a] The solvent is benzene-d_6–toluene for the Me_3Al solutions and benzene-d_6–hexane (approximately 50:50 v/v) for the Et_3Al solutions. [b] The ratios are those determined by actual integration of the areas of the R and crown ether absorptions. [c] Chemical shifts are reported in parts per million (δ) relative to C_6D_5H at δ 7.15 for the Et_3Al solutions and to $PhCH_3$ at δ 2.09 for the Me_3Al solutions.

With Me_3Al and the coordinating agent $R_3P{=}NSiR_2N{=}PR_3$, NMR evidence indicates that the equilibrium lies predominantly to the right.[6]

$$2R_3Al + 2C \rightleftharpoons R_2AlC_2^+ + R_4Al^- \qquad (2)$$

Although cryptands are more effective than crown ethers in promoting disproportionation of organomagnesium compounds, crown ethers should be more effective with organoaluminum compounds. When a cryptand of an appropriate size envelops a metal atom such as Mg, room is left for only one external attachment.[2] $RMg(cryptand)^+$ can be formed, but $R_2Al(cryptand)^+$ could not. $RAl(cryptand)^{2+}$ is feasible sterically, but formation of a divalent ion certainly would be more difficult. By contrast, a crown ether could encircle an Al of $R_2Al(crown)^+$ in the manner indicated in 1, the oxygens occupying equatorial positions and the two organic groups occupying apical positions. Similar coordination of RMg^+ (2) leaves one face of the Mg exposed. Although there is yet no evidence about details of the structures of $RMg(crown)^+$ ions in solution, the crown ether oxygens may be arranged in a manner to more fully envelop the Mg so that one face is not completely unoccupied. Because the lengths of Mg–O and Al–O bonds are similar, we expected 15-crown-5 to be more likely than 12-crown-4 or 18-crown-6 to promote disproportionation.



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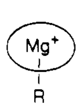

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R_3Al and 15-Crown-5. ^1H NMR spectra of representative benzene solutions containing 15-crown-5 and Me_3Al or Et_3Al are summarized in Table I. Only single unbroadened absorptions are observed for the alkyl groups and the crown ether, though the positions of these absorptions are shifted slightly from those of either component alone. The small magnitudes of the shifts make it unlikely that disproportionation of the sort indicated in eq 2 is significant. Because only one rather than two sets of alkyl absorptions are noted and, even when the crown ether is in excess, only one rather than two crown ether absorptions, it also is improbable that disproportionation is significant. As described below, when $R_2Al(crown)^+$ ions are observed, they do not equilibrate on the NMR time scale with other organoaluminum species or with free crown ether. Even the $RMg(crown)^+$ ions that have been observed do not equilibrate on the NMR time scale with other organomagnesium species, yet approach and bonding necessary for exchange could be easier to the Mg than to the Al, with its additional organic group (compare 1 and 2). It is likely that the small alterations in chemical shifts are due to the ordinary coordination, shown in eq 3, between organoaluminum compounds and ether oxygens.

$$R_3Al + O< \rightleftharpoons R_3Al{-}O< \qquad (3)$$

This accords with the structures that Atwood and co-workers have determined for several solids formed from Me_3Al and crown ethers.[7,8] In all of the structures, including one[7] ($[Me_3Al]_4[15\text{-crown-}5]$) incorporating 15-crown-5, each Me_3Al is bonded to only one crown ether oxygen. In solution, of course, formation and cleavage of such Al–O bonds are expected to be sufficiently rapid on the NMR time scale that only single absorptions will ordinarily be seen for the alkyl groups or the crown ether.

R_2AlX and 15-Crown-5. We then investigated solutions prepared from crown ethers and R_2AlX compounds to see if $R_2Al(crown)^+$ ions would be formed when the group to be transferred could be halide rather than alkyl. At the time this work was begun, the only closely related reports that we knew of concerned isolation and crystal structures of solids consisting of $AlCl_2(crown)^+$ and $EtAlCl_3^-$ ions.[9,10] It was known, however, that addition of mono- or bidentate coordinating agents enhances the conductivity of Et_2AlCl much more than of Et_3Al.[11] Moreover, NMR spectra of solutions of Et_2AlCl and amines had been interpreted as indicating some formation of $Et_2Al(amine)^+$ and $Et_2AlCl_2^-$ ions.[12] Since this work was submitted for publication, Raston and co-workers have reported a ^1H NMR spectrum of a solution of a R_2Al^+-$AlCl_4^-$ salt (R includes a pyridine group that coordinates to the Al) and also a crystal structure for this salt.[13] Particularly closely related to the present work are structure determinations by Atwood and co-workers of solid $Me_2Al(15\text{-crown-}5)^+Me_2AlCl_2^-$ and $Me_2Al(18\text{-crown-}6)^+Me_2AlCl_2^-$.[14]

When solutions of 15-crown-5 (in benzene) and Et_2AlBr (in benzene–hexane) or Et_2AlI (in benzene–toluene) were combined, a second liquid phase formed.[15] ^1H NMR spectra of either the Et_2AlI or Et_2AlBr preparations were

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(15) Such behavior has been noted in a related system[10] and considered more generally for somewhat different systems [Atwood, J. L. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic: London, 1984; Vol. 1, Chapter 9].

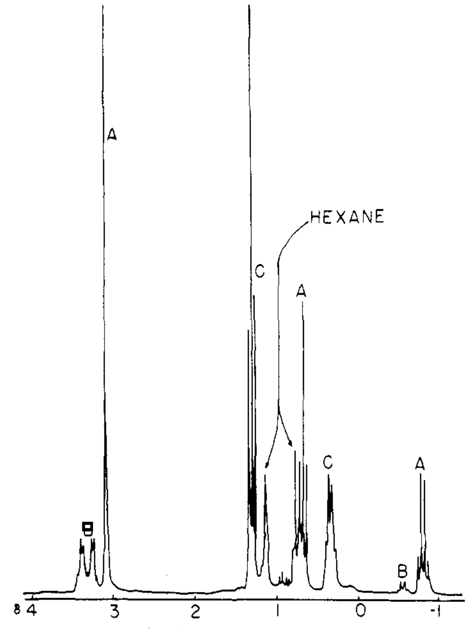


Figure 1. The 200-MHz ^1H NMR spectrum of the lower phase of a mixture prepared from Et_2AlBr and 15-crown-5 in benzene–hexane. The ratio of crown ether residues to ethyl groups in this phase is about 0.20. Absorptions labeled A are assigned to $Et_2Al(crown)^+$, those labeled B to $EtAlBr(crown)^+$, and those labeled C to aluminate anions.

similar and showed the lower, more viscous phase to contain the majority of the ethyl groups and crown ether residues. Experiments with 15-crown-5 and Pr_2AlI gave similar results, but attempts to prepare even relatively dilute solutions from 15-crown-5 and Me_2AlBr or Me_2AlI led to immediate formation of precipitates. The NMR spectrum of the lower phase of a sample prepared from a 0.4 ratio of crown ether to Et_2AlBr in benzene–hexane is shown in Figure 1. The actual ratio of crown ether residues to ethyl groups in this phase is determined from relative areas of NMR absorptions to be about 0.20. We will discuss in turn the groups of absorptions labeled A, B, and C.

$R_2Al(crown)^+$. On the basis of several pieces of evidence, we attribute the absorptions labeled A to a cation of composition $R_2Al(crown)^+$.

(1) The areas of the absorptions labeled A in this spectrum and in all others indicate a ratio of ethyl groups to crown ether residues of 2.

(2) The position (δ −0.79) of the quartet due to the ethyl CH_2 is about 1.1 ppm upfield from the corresponding absorption of Et_2AlBr. Extreme upfield positions are also noted for absorptions of α-hydrogens of $RMg(crown)^+$ and $RMg(cryptand)^+$ ions.[2-4]

(3) After several hours, the lower phase obtained from a preparation using either Et_2AlBr or Et_2AlI (but not Pr_2AlI) develops substantial amounts of precipitate. After such a solid is washed with toluene, its ^1H NMR spectrum in CD_2Cl_2 shows mainly absorptions corresponding to those labeled A in Figure 1. This is illustrated by Figure 2, which shows the spectrum of a CD_2Cl_2 solution of a solid obtained in a similar fashion from benzo-15-crown-5 and Et_2AlI. This spectrum has only one set of ethyl absorptions and one major set of crown ether absorptions; areas of these absorptions indicate that the ratio of ethyl groups to crown ether residues is 2. The only other significant absorptions are due to a small amount of uncoordinated crown ether. Such CD_2Cl_2 solutions and the solids from which they are prepared must contain mainly $Et_2Al(crown)^+$ and X^-. In fact, the solid-state ^{13}C NMR spectrum of a precipitate obtained from Et_2AlI and 15-crown-5 shows only one set of ethyl absorptions (and one crown ether absorption).

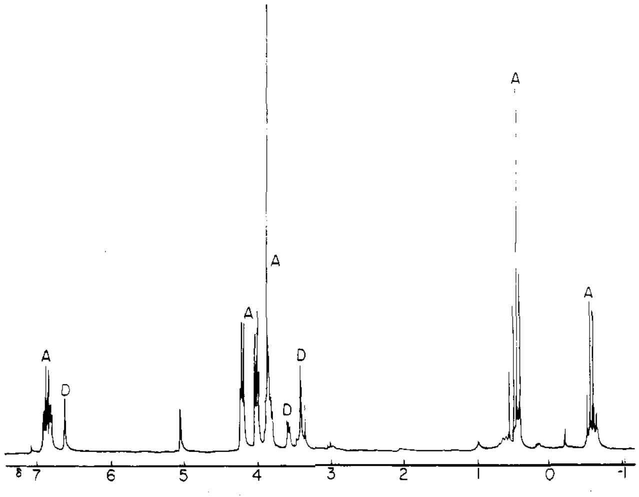
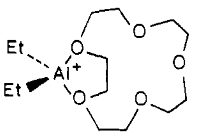


Figure 2. The 200-MHz ^1H NMR spectrum of a CD_2Cl_2 solution of a solid prepared from Et_2AlI and benzo-15-crown-5. The absorptions labeled A are assigned to $Et_2Al(crown)^+$ and those labeled D to uncoordinated crown ether.

(4) In a nuclear Overhauser difference experiment with a CD_2Cl_2 solution of a crude solid prepared from Et_2AlI and 15-crown-5, irradiation of the crown ether absorption (A) enhanced the ethyl CH_2 absorption (A) by 7.8% and the CH_3 absorption (A) by 3.7%. Irradiation of the ethyl CH_2 absorption enhanced the crown ether absorption by 5.2% and the CH_3 absorption by 2.2%, and irradiation of the CH_3 absorption enhanced the crown ether absorption by 6.0%. These significant enhancements indicate that the crown ether and ethyl groups responsible for the absorptions labeled A are in close proximity.

The evidence is more in accord with the $Et_2Al(crown)^+$ ion having a "threaded" structure 1 rather than a structure, such as 3, in which only a few crown ether oxygens are coordinated to Al. The proposal of a threaded structure is supported by the observation that, on the NMR time scale at least, the ion is symmetrical; only one set of ethyl absorptions and one 15-crown-5 absorption are noted. If the ion had a structure such as 3, then the crown ether would exhibit more than one absorption unless all of its oxygens interchange rapidly. Another observation, however, makes rapid oxygen interchange unlikely. Figure 3 shows the ^1H NMR spectrum of the lower phase of a mixture prepared from a 0.7 ratio of 15-crown-5 to Et_2AlI in benzene–toluene. The actual ratio of crown ether residues to ethyl groups in this phase is determined from areas in the NMR spectrum to be about 0.32. In addition to absorptions similar to those in the spectrum in Figure 1, this spectrum also shows an absorption (labeled E) that we attribute to free (uncoordinated) crown ether. This assignment is made because the absorption has a position similar to that of the crown ether alone in this solvent mixture and is larger in solutions that have greater crown ether to Et_2AlI ratios. The observation of absorptions both for the crown ether in $R_2Al(crown)^+$ and for free crown ether indicate that equilibration between crown ethers of these two types is slow on the NMR time scale. Therefore, if the $R_2Al(crown)^+$ species has an unsymmetrical crown



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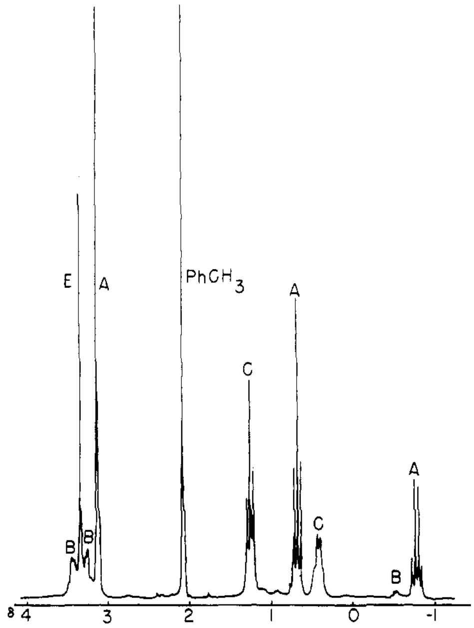


Figure 3. The 200-MHz ^{1}H NMR spectrum of the lower phase of a mixture prepared from Et_2AlI and 15-crown-5 in benzene–toluene. The ratio of crown ether residues to ethyl groups in this phase is about 0.32. A notable difference between this spectrum and that in Figure 1 is the presence of an absorption (labeled E) which is assigned to uncoordinated crown ether.

ether (e.g., as in 3) but this is not noted in the ^{1}H NMR spectrum because of rapid equilibration of the oxygens, then that equilibration must take place *without the crown ether exchanging with the free crown ether in the solution.* This seems unlikely, though it would be interesting if rapid internal equilibration were occurring.

Another piece of evidence particularly consistent with a threaded structure for species A is the observation that its ethyl groups do not exchange on the NMR time scale with other ethylaluminum species in the solutions. Exchange between organoaluminum species ordinarily is rapid.[5] Since access by external groups to the Al in a threaded structure is blocked unless the Al escapes from the enveloping crown ether or loses an R group (to form $RAl(crown)^{2+}$), however, the ways in which organic groups ordinarily exchange between aluminums are precluded.

Many efforts were made to obtain crystalline solids suitable for X-ray analysis. Although Me_2Al(benzo-15-crown-5)$^+Br^-$, isolated from benzo-15-crown-5 and Me_2AlBr, was the most promising, its structure could be solved only by applying constraints on some bond lengths and angles and is of poor quality. The determination is sufficient, however, to demonstrate that the structure is of the type illustrated in 1; all oxygens of the crown ether surrounded the Al in an approximately equatorial fashion, and the C–Al–C angle is approximately 173°. The more accurately determined structure of Me_2Al(15-crown-5)$^+$ that was reported recently showed it to have structure 1, with all oxygens strongly bonded to the Al (Al–O = 2.13 (1), 2.18 (2), and 2.26 (1) Å) and C–Al–C = 178 (1)°.[14] $R_2Al(crown)^+$ is isoelectronic with $R_2Mg(crown)$. Threaded structures recently have been proposed for some $Ar_2Mg(crown)$[16] and $R_2Mg(crown)$[4] species observed in solution and found by X-ray diffraction studies for solid $Ar_2Mg(crown)$,[17] $R_2Mg(crown)$,[18] and $R_2Zn(crown)$[18] species.

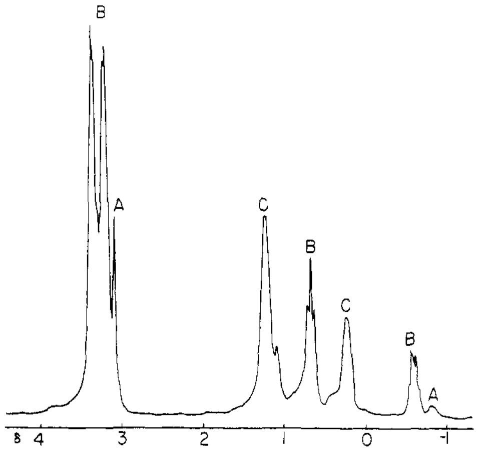
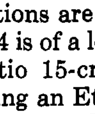


Figure 4. The 200-MHz ^{1}H NMR spectrum of the lower phase of a mixture prepared from "$Et_{1.5}AlBr_{1.5}$" and 15-crown-5 in benzene–hexane. Note that, in contrast to the spectrum in Figure 1, the absorptions (labeled B) assigned to $EtAlBr(crown)^+$ are very much larger than those (labeled A) assigned to $Et_2Al(crown)^+$.

$RAlX(crown)^+$. In addition to the crown ether absorption labeled A, the NMR spectra in Figures 1 and 3 each have a weaker crown ether absorption (labeled B) that is a multiplet. In the various samples prepared from Et_2AlBr and Et_2AlI, the ratio of crown ether absorption B to crown ether absorption A is generally in the range 0.15–0.25. In these and other spectra a corresponding absorption (also labeled B) for an ethyl CH_2 always is apparent. The corresponding CH_3 absorption overlaps the CH_3 absorption of species A and only sometimes is evident.

For several reasons, we attribute the B absorptions to species of composition $EtAlX(crown)^+$. (1) The areas of the absorptions indicate the presence of one ethyl group for each crown ether residue. (2) The absorption of the ethyl CH_2 is remarkably upfield (δ −0.55 in Figure 1 and −0.53 in Figure 3), as was the ethyl CH_2 absorption (A) assigned to $Et_2Al(crown)^+$. That the absorption of the ethyl CH_2 of $EtAlX(crown)^+$ is somewhat downfield from that of $Et_2Al(crown)^+$ is consistent with substitution of a halogen for an alkyl group. (3) Addition of 15-crown-5 to ethylbromoaluminum solutions in which the ethyl to halogen ratios are lower than the ratio of 2 in the samples used for the spectra in Figures 1 and 3 furnishes lower phases whose B absorptions are much more prominent. The spectrum in Figure 4 is of a lower phase that resulted from mixing in 0.5 ratio 15-crown-5 and an organoaluminum solution having an Et to Br ratio of approximately 1. This spectrum shows $EtAlBr(crown)^+$ (species B) to be the dominant cation. Conversely, NMR spectra of samples prepared from 15-crown-5 and organoaluminum solutions having Et to Br ratios greater than 2 exhibit weaker absorptions for species B than do the spectra in Figures 1 and 3 (see the Experimental Section for an example).

$EtAlX(crown)^+$ ions probably also have threaded structures (4). Since in such a structure the two faces of



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the crown ether are different, the ^{1}H NMR absorption of

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the crown ether is expected to be an AA′BB′ multiplet,[19] as is observed. AA′BB′ patterns have been observed for RMg(crown)$^+$ ions.[3,4]

Since $Et_2Al(crown)^+$ and $EtAlX(crown)^+$ ions are present in significant amounts, could $AlX_2(crown)^+$ ions also be present? Equations 4–6 are some equilibria involving anions. There are no significant unidentified crown ether absorptions, although a small absorption might have been missed if it fell under the absorption of the crown ether of $EtAlX(crown)^+$. Efforts to prepare $AlI_2(crown)^+$ from AlI_3 and 15-crown-5 in benzene gave only solids.

$$2Et_2AlX + crown \rightleftharpoons Et_2Al(crown)^+ + Et_2AlX_2^- \quad (4)$$

$$2Et_2AlX + crown \rightleftharpoons EtAlX(crown)^+ + Et_3AlX^- \quad (5)$$

$$2Et_2AlX + crown \rightleftharpoons AlX_2(crown)^+ + Et_4Al^- \quad (6)$$

Aluminate Anions. The ethyl absorptions labeled C are prominent in the spectra in Figures 1, 3, and 4. There are no corresponding crown ether absorptions, so these absorptions must be due to anions such as $Et_2AlX_2^-$ and Et_3AlX^-, neutral compounds such as Et_2AlX, and other species formed by their disproportionation and association. Since spectra of all samples in which the halogen was Br or I exhibited only a single set of such ethyl absorptions, equilibration of ethyl groups between the species responsible for the absorptions labeled C must be rapid on the NMR time scale. Ethyl groups of the $Et_2Al(crown)^+$ and $EtAlX(crown)^+$ ions, of course, do not participate in this equilibration. Exchange of the ethyl groups in tetravalent anions such as $Et_2AlX_2^-$ or Et_3AlX^- presumably is facilitated by the presence of at least traces of trivalent species (e.g., Et_2AlX) to which an additional group can be coordinated or transferred. In fact, the ethyl absorptions labeled C sometimes are slightly broader in samples in which crown ether is in excess (free crown ether is present), and it is in such samples that concentrations of trivalent species might be lowest and hence exchange slowest.

Relation of Relative Amounts of Species to Reactant Ratio. The relative sizes of the absorptions vary with the crown ether to Et_2AlX ratio. When the ratio of crown ether to ethyl groups *in the phase being observed* is approximately 0.25, spectra are similar to that in Figure 1. The absorption for free crown ether first becomes evident at ratios of about 0.25–0.30. As the crown ether to ethyl ratio further increases, the absorption due to free crown ether increases, but the ratios of the $Et_2Al(crown)^+$ and $EtAlX(crown)^+$ ethyl absorptions to the C ethyl absorptions do not increase.

Most features of the spectra of samples prepared by using varying ratios of crown ether to Et_2AlBr or Et_2AlI can be rationalized by the proposals above for the nature of the species responsible for the A, B, and C absorptions. At low crown ether to ethyl group ratios, crown ether is limited and the C ethyl absorptions are large, due either to the presence of excess Et_2AlX, which equilibrates with the anions, or to the formation of more complicated anions, such as $Et_4Al_2X_3^-$ and $Et_5Al_2X_2^-$. The C ethyl absorptions vary significantly in position since these absorptions are weighted averages of absorptions of several species whose relative amounts vary considerably with variations in the crown ether to ethyl group ratio. Positions of the ethyl and crown ether absorptions (A and B) attributed to the cations are more nearly constant; the shifts that are seen probably result particularly from the influence of alterations in anion composition. Whether halide or ethyl will be lost from an ethylaluminum halide to form a cation depends not only on stabilities of $Et_2Al(crown)^+$ and $EtAlX(crown)^+$ but also on the stabilities of the anions that are formed. The large changes in relative amounts of the cations as the Et to X ratio is altered (e.g., compare Figures 1 and 4) indicate the importance of anion stability.

Increases in the crown ether to ethyl ratio above that at which free crown ether first appears do not further increase the ratio of $Et_2Al(crown)^+$ plus $EtAlX(crown)^+$ absorptions to ethyl C absorptions. Apparently once a certain amount of crown ether is present, more does not lead to significant additional formation of the $Et_2Al(crown)^+$ and $EtAlX(crown)^+$ cations. In all spectra of samples containing free crown ether, the relative areas of the C ethyl absorptions equal or even slightly exceed those expected if eq 4 and 5 completely describe the contents of the lower phases (the only species being $Et_2Al(crown)^+$ accompanied by an equal amount of $Et_2AlX_2^-$ and $EtAlX(crown)^+$ accompanied by an equal amount of Et_3AlX^-). These observations indicate that the concentration of halide ion must be small. As evident from eq 7, to the extent that halide ion is present, there will be no ^1H NMR absorption for an anion and the C ethyl absorptions will be reduced. Halide ion must be present significantly, of course, in solutions formed when $Et_2Al(crown)^+X^-$ solids are dissolved in CD_2Cl_2, a more polar solvent.[20]

$$Et_2AlX + crown \rightleftharpoons Et_2Al(crown)^+ + X^- \quad (7)$$

Even in the presence of free crown ether, the ratio of the C ethyl absorptions to the cation ethyl absorptions (A and B) often is slightly larger than would be expected if eq 4 and 5 completely describe the systems. Since the relative size of the C ethyl absorptions is not decreased by further increases in crown ether, it is unlikely that such discrepancies are due to the presence of significant amounts of unreacted Et_2AlX or of larger ions such as $Et_4Al_2X_3^-$ or $Et_5Al_2X_2^-$. These minor discrepancies may be due to somewhat higher Et to X ratios in the lower phases that we are studying than in the Et_2AlX used to prepare the samples.[21]

The ^1H NMR spectra that are obtained when the ratio of 15-crown-5 to Et_2AlX in the preparations is small are not fully rationalized by the explanations above. At low ratios, coordination of the crown ether to intact Et_2AlX may be significant.[22] If under these circumstances, the limited amount of crown ether were to be incorporated (as in eq 4 and 5) completely in $Et_2Al(crown)^+$ and $EtAlX(crown)^+$, then the residual Et_2AlX would lack any coordination (except that provided by halogen bridge bonds, which generally are less favorable[5] than bonds to ether oxygens).

This work indicates that solutions containing substantial amounts of $Et_2Al(crown)^+$ and $EtAlX(crown)^+$ cations can

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[19] This assumes that the crown ether ring remains conformationally labile on the NMR time scale. If it did not, then an ABCD multiplet is expected.

[20] The CD_2Cl_2 solutions of $Et_2Al(crown)^+X^-$ have the same relative amounts of Et, Al, X, and crown ether as do solutions prepared in hydrocarbons from equimolar amounts of Et_2AlX and crown ether. Therefore, the ions in the CD_2Cl_2 solutions could be converted to the same mixtures of species (including aluminate ions and free crown ether) found in the lower phases formed from Et_2AlX and crown ether in hydrocarbons if such mixtures also would be more stable in CD_2Cl_2. When the solids were dissolved in CD_2Cl_2, no evidence was noted for such changes in composition, even after several days.

[21] Other possible contributions to the discrepancies include (1) formation of some $AlX_2(crown)^+$ and hence also of some Et_4Al^- (eq 6) which would increase the relative size of the C ethyl absorptions, (2) Et to X ratios in the initial "Et_2AlX" slightly exceeding 2, and (3) errors in integration.

[22] Formation of $AlX_2(crown)^+$ ions or further ionization to form divalent ions such as $EtAl(crown)^{2+}$ also might possibly be involved.

be prepared from Et_2AlX compounds and 15-crown-5. It is likely that a variety of related cations with different organic groups can be prepared in a similar fashion.

Experimental Section

^1H NMR spectra were recorded at 200 MHz. Absorption positions are reported in parts per million (δ); except where otherwise noted, the reference was internal benzene (C_6D_5H), assumed to absorb at δ 7.15. Absorptions are reported by using the following notations: s, singlet; t, triplet; q, quartet; m, a more complex multiplet; c, complex overlapping absorptions; br, broad. The ^1H nuclear Overhauser enhancement measurements were obtained at 360 MHz by using a Fourier transform difference method. Eight free induction decays with the decoupler set exactly on a given resonance were taken; eight free induction decays with the decoupler off resonance then were subtracted. This procedure was repeated until adequate signal to noise was achieved. A 90° observation pulse and a recovery time of $10T_1$ were used. The minimum signal enhancement detectable was about 0.5%. The CP-MAS ^{13}C NMR spectrum was taken at 25 MHz and was proton-decoupled. Absorption positions are reported in parts per million (δ); the reference was external hexamethylbenzene, assumed to absorb at δ 132.0.

Air-sensitive operations were performed under an atmosphere of purified nitrogen by using standard Schlenk techniques or in a glovebox. All glassware was dried for 4 h at 135 °C prior to use.

The solutions of Me_3Al (2.3 M in toluene) and of Et_2AlI (1.0 M in toluene) and Pr_3Al, $AlBr_3$, AlI_3, and 15-crown-5 were commercial samples (Aldrich Chemical Co.) and were used without purification as was also the solution of Et_3Al (1.5 M in hexane) (Morton Thiokol, Inc., Alfa Products). Benzo-15-crown-5 was prepared by using a literature procedure.[23] Solutions of Me_2AlBr (0.60 M in ~80:20 v/v benzene–toluene), Me_2AlI (0.60 M in ~80:20 v/v benzene–toluene), Et_2AlBr (0.90 M in ~50:50 v/v benzene–hexane), and Pr_2AlI (0.68 M in benzene) were prepared from the corresponding R_3Al and AlX_3 plus some benzene.[24] A solution of $EtAlBr_2$ (0.90 M in ~75:25 v/v benzene–hexane) was prepared in the same manner from the Et_2AlBr solution, $AlBr_3$, and benzene. Benzene, benzene-d_6, toluene, and methylene chloride were distilled from CaH_2 under an atmosphere of nitrogen.

Preparation of R_3Al–Crown Ether Solutions. The crown ether was weighed into a vial containing a magnetic stirring bar and dissolved in 0.4 mL of C_6D_6. A solution of the organoaluminum compound was added dropwise from a syringe. The compositions and spectra of representative solutions are summarized in Table I.

Preparation of R_2AlX–Crown Ether Solutions. The solution of R_2AlX was added dropwise to a solution of 15-crown-5 in benzene. The solution was stirred for about 10 min and then allowed to stand undisturbed for about 10 min. If a phase separation was evident, the upper phase was removed with a pipette, and then for NMR spectra a sample of the lower phase was removed carefully with a pipette. A small amount of benzene-d_6 was added to achieve a deuterium lock. Specific amounts of reagents used for some representative preparations, and the spectra obtained from them are described below.

Et_2AlBr–15-Crown-5. Benzene–hexane solution of Et_2AlBr (1.50 mL, 0.90 M, 1.35 mmol) and 15-crown-5 (123 mg, 0.56 mmol) in benzene (2.0 mL): ^1H NMR (lower phase) [Figure 1] δ 3.39 and 3.26 (H_A's and H_B's of AA′BB′ multiplet, 5.6, crown B), 3.08 (s, 20, crown A), 1.30 (t, J = 8.1 Hz, 12.5, CH_3 C), 0.67 (t, J = 8.1 Hz, ~6, CH_3 A (overlaps CH_3 B and CH_3 of hexane)), 0.34 (q, J = 7.9 Hz, 8.1, CH_2Al C), −0.55 (q, J = 8.1 Hz, 0.5, CH_2Al B), −0.79 (q, J = 8.1 Hz, 4.0, CH_2Al A). Note that very little hexane was in the lower phase.

$Et_{1.5}AlBr_{1.5}$–15-Crown-5. Benzene–hexane solutions of Et_2AlBr (0.50 mL, 0.90 M, 0.45 mmol) and $EtAlBr_2$ (0.50 mL, 0.90 M, 0.45 mmol) plus 15-crown-5 (96 mg, 0.44 mmol) in benzene (2.0 mL): ^1H NMR (lower phase) [Figure 4] δ 3.36 and 3.23 (H_A's and H_B's of AA′BB′ pattern, 24, crown B), 3.10 (s, ~2, crown A), 1.23 (br, 8.2, CH_3 C), 0.68 (t, J = 8.2 Hz, 4.4, CH_3 B and probably also contains CH_3 C), 0.24 (br, 3.5, CH_2Al C), −0.60 (q, J = 7.7 Hz, 2.0, CH_2Al B), −0.82 (q, J = 8.3 Hz, 0.4, CH_2Al A). Relatively little hexane was in the lower phase but probably did contribute somewhat to the areas of the δ 1.23 and 0.68 absorptions.

$Et_{2.5}AlBr_{0.5}$–15-Crown-5. Benzene–hexane solution of Et_2AlBr (0.33 mL, 0.90 M, 0.30 mmol), hexane solution of Et_3Al (0.40 mL, 1.5 M, 0.60 mmol), and 15-crown-5 (110 mg, 0.50 mmol) in benzene (2.0 mL): ^1H NMR (lower phase) δ 3.66 (br, 2.3, crown ?), 3.03, (br s, 20, crown A), 1.31 (br, 12.6, CH_3 C + ?), 0.69 (br t, J = 7.7 Hz, 5.7, CH_3 A), 0.18 (br, 6.1, CH_2Al C), −0.78 (br q, J = 8.1 Hz, 4.0, CH_2Al A). Several smaller absorptions, including ones probably due to modest amounts of hexane, are not described.

Et_2AlI–15-Crown-5. (1) Toluene solution of Et_2AlI (0.75 mL, 1.0 M, 0.75 mmol) and 15-crown-5 (114 mg, 0.52 mmol) in benzene (2.0 mL): ^1H NMR (lower phase) [Figure 3] δ 3.43 and 3.26 (H_A's and H_B's of AA′BB′ pattern, ~6.0, crown B), 3.34 (s, ~6.6, free crown), 3.14 (s, 19.4, crown A), 1.26 (t, J = 8.0 Hz, 8.8, CH_3 C), ~0.73 (CH_3 B overlapped by δ 0.68 absorption), 0.68 (t, J = 8.1 Hz, 6.9, CH_3 A, area includes CH_3 B absorption), 0.42 (q, J = 7.7 Hz, 5.5, CH_2Al C), −0.53 (q, J = 8.0 Hz, 0.4, CH_2Al B), −0.78 (q, J = 8.1 Hz, 4.0, CH_2Al A). (2) Toluene solution of Et_2AlI (2.29 mL, 1.0 M, 2.29 mmol) and 15-crown-5 (339 mg, 1.54 mmol) in benzene (2.0 mL). Precipitation took place about 4 h after mixing. The precipitate (~1 g) was subjected to reduced pressure for 10 h: ^{13}C NMR (CP-MAS) δ 67.5 (br s, crown), 13.2 (br s, CH_3), 11.6 (br s, CH_2CH_3).

Et_2AlI–Benzo-15-crown-5. (1) Toluene solution of Et_2AlI (0.54 mL, 1.0 M, 0.54 mmol) and benzo-15-crown-5 (145 mg, 0.54 mmol) in benzene (2.0 mL): ^1H NMR (lower phase, the absorptions were broad) δ 7.13–6.58 (c, 26, aryl H's of crown ether and toluene), 3.70–3.32 (c, 32, crown CH_2's), ~1.50–1.10 (br s, ~9, CH_3), ~0.75–0.40 (c, ~10, CH_3CH_2), −0.69 (br q, ~4, CH_2). (2) Toluene (2 mL) was layered over a mixture resulting from a toluene solution of Et_2AlBr (1.6 mL, 1.0 M, 1.6 mmol) and a solution of monobenzo-15-crown-5 (347 mg, 1.29 mmol) in toluene (2 mL). Crystals formed over a period of ~2 days. The solution was decanted from the crystals which then were washed with toluene and dried in vacuo: ^1H NMR (CD_2Cl_2, internal standard was $CDHCl_2$ assumed to absorb at δ 5.32) [Figure 2] δ 6.91 and 6.83 (H_A's and H_B's of AA′BB′ multiplet, 4.1, aryl H's of $Et_2Al(crown)^+$), 6.64 (s, 0.9, aryl H's of free crown), 4.23 (m, 4.2, CH_2OAr of $Et_2Al(crown)^+$), 4.04 (m, 4.2, CH_2CH_2OAr of $Et_2Al(crown)^+$), 3.89 (s, 9.4, other crown CH_2's of $Et_2Al(crown)^+$, area includes the overlapped absorption of CH_2OAr of free crown), 3.60 (0.8, m, CH_2CH_2OAr of free crown), 3.44 (s, 1.9, other CH_2's of free crown), 0.50 (t, J = 8.1 Hz, 6.1, CH_3), −0.53 (q, J = 8.1 Hz, 4.0, CH_2Al).

Pr_2AlI–15-Crown-5. Benzene solution of Pr_2AlI (1.56 mL, 0.68 M, 1.06 mmol) and 15-crown-5 (103 mg, 0.47 mmol) in benzene (2.0 mL): ^1H NMR (lower phase) δ 3.37 (H_A's of AA′BB′ multiplet, 4.2, crown B), 3.16 (s 11.0, free crown, area includes the overlapped absorption of H_B's of AA′BB′ multiplet of crown B), 3.06 (s, 19.6, crown A), 1.85 (m, 6.7, CH_2CH_3 C), 1.20 (t, J = 7.2 Hz, 11.7, CH_3 C), 1.06 (t, J = 7.2 Hz, 10.0, CH_3 A, area includes overlapped absorption of CH_3 B), 0.89 (m, ~5.3, CH_2CH_3 of A, area includes overlapped absorption of CH_2CH_3 of B), 0.66 (t, J = 7.7 Hz, 6.5, CH_2Al C), −0.56 (m, 1.4, CH_2Al B), −0.79 (H_A's of AA′BB′ multiplet, 4.0, CH_2Al A).

Me_2AlX–15-Crown-5. Benzene–toluene solution of Me_2AlBr or Me_2AlI (0.11 mL, 0.60 M, 0.066 mmol) and 15-crown-5 (11 mg, 0.050 mmol) in benzene (10 mL). A precipitate formed immediately. ^1H NMR spectra of the filtered solution showed principally absorptions due to free crown ether and only weak absorptions that could be attributed to CH_3Al species.

Me_2AlBr–Benzo-15-crown-5. A precipitate was obtained by using a procedure similar to that described immediately above. The precipitate was stirred in benzene–CH_2Cl_2 and then allowed to stand. After several days, some of the small needles that were present were removed and used for the X-ray crystal structure determination.

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iments, Professor Lloyd Jackman for helpful discussions, and Thomas Neenan and Richard Fitzpatrick for supplying the benzo-15-crown-5.

Registry No. 15-crown-5, 33100-27-5; [15-crown-5][Me_3Al], 114491-48-4; [15-crown-5][Et_3Al], 114491-49-5; Et_2AlBr, 760-19-0; Et_2AlI, 2040-00-8; Pr_2AlI, 53211-90-8; Me_2AlBr, 3017-85-4; Me_2AlI, 2938-72-9; $Et_2AlBr_2^-$, 88873-39-6; $Et_2AlI_2^-$, 114491-50-8; [Pr_2Al(15-crown-5)]$^+$[Pr_2AlI_2]$^-$, 114491-53-1; Me_2Al(benzo-15-crown-5)$^+Br^-$, 114504-78-8; Me_2Al(benzo-15-crown-5)$^+I^-$, 114504-79-9; EtAlBr(15-crown-5)$^+$, 114504-77-7; EtAlI(15-crown-5)$^+$, 114491-54-2.

Crystal and Molecular Structure of an Oxo-Centered Bis[(pentamethylcyclopentadienyl)uranium]magnesium Phosphoylide Complex

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The crystal and molecular structure of a novel oxo-centered trimetal cluster of two uraniums and one magnesium has been determined by X-ray diffraction in the hexagonal space group $P6_522$ (No. 179); cell parameters: $a = b = 17.578$ (5) Å, $c = 46.813$ (7) Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 12527$ (5) Å^3, with $R = 0.0634$, $R_w = 0.0575$, and $R_G = 0.0641$. A Cp* is coordinated to each of the two uraniums, and the two are connected by two bridging [$CH_2P(Ph)_2CH_2$]$^-$ ligands. Chlorides bridge between each uranium and the magnesium, and the coordination sphere about magnesium is completed by two $CH_2{=}PMePh_2$ molecules. In addition to the μ_3-oxo ligand, the two uraniums are also bridged by a μ_2-oxide.

Organo-f-element oxo complexes are rare. Among the actinides, several complexes in which Cp_3An^+ (An = U or Th)[1] or Cp_2U^{2+} groups[2] are coordinated to polyoxoanions have been structurally characterized. In addition, mixed oxyhydroxides containing CpU fragments may have been prepared, and $[Cp_3U]_2O$ has been mentioned, but no complete characterization of any of these species has yet appeared.[3] A few organolanthanide complexes containing an oxo ligand are known,[7] including one which contains a μ_5-O.[8] In addition, catalysts that are postulated to contain organo-f-element fragments bound to a support through oxide bridges have been reported.[9] To add to this body of data, we report the structure of a novel compound, $\{Cp^*U[\mu\text{-}(CH_2)P(Ph)_2(CH_2)]\}_2Mg[CH_2PMePh_2]_2(\mu_3\text{-}O)(\mu_2\text{-}O)(\mu_2\text{-}Cl)_2$ (1; Cp* = $(CH_3)_5C_5^-$, Me = CH_3, Ph = C_6H_5), in which two organouranium moieties and an organomagnesium group are linked by μ_2- and μ_3-oxides.

Table I. Crystal, Data Collection, and Reduction Parameters for 1

formula	$C_{76}H_{88}Cl_2MgO_2P_4U_2$[a]
fw	1728.71[a]
space group	$P6_522$ (No. 179)
$a = b$, Å	17.578 (5)
c, Å	46.813 (7)
$\alpha = \beta$, deg	90
γ, deg	120
V, Å^3	12527 (5)
Z	6
D(calcd), g/cm^3	1.32
μ, cm^{-1}	39.03
transmissn coeff	0.81–1.08
radiatn	Mo Kα, λ = 0.71073 Å
scan type	Ω
scan rate, deg/min	2–24
2θ range, deg	3–35
total observns	8859
unique observns	4661
unique data with $I > 3\sigma(I)$	1590
no. of parameters	161
R[b]	0.0634
R_w[b]	0.0575
R_G[b]	0.0641

[a] Excludes solvent molecule. [b] $R = \sum(|F_o - F_c|)/\sum(F_o)$, $R_w = \sum(|F_o - F_c|(w)^{1/2}/\sum(F_o(w)^{1/2})$, and $R_G = [\sum(|F_o - F_c|^2)/\sum(F_o)^2]^{1/2}$, where $w = 1/\sigma^2(F)$.

In contrast to a well-documented transition-metal chemistry,[10] oxo-centered trimetallic clusters of the f-elements are very rare. In addition to μ_3-oxides in several minerals and oxyhalides,[11] only $(UO_2)_2U_2O_2(OC_6H_5)_{10}(THF)_4$[12] and $U_4O_2(O_2CNEt_2)_4$,[13] which contain two U_3O units

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(3) While $[Cp_3U]_2O$ has been mentioned in the secondary literature,[4] its characterization and properties are not reported in the primary literature or in the habilitation thesis[5] where its synthesis is described. An incompletely characterized bright green precipitate, which is postulated to be an oxyhydroxide, forms in basic aqueous solutions of Cp_3UCl.[6]

(4) See, for example: Kanellakopulos, B. In *Organometallics of the f-Elements*; Marks, T. J., Fischer, R. D., Eds.; D. Reidel: Boston, 1978; pp 1–35.

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