Figure 1. computer-generated view of the non-hydrogen atoms of complex 3.
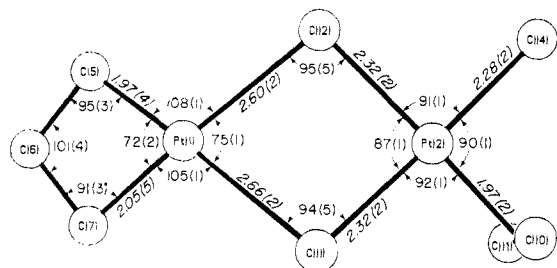

Figure 2. Computer-generated view of the platinacyclobutane ring and dichlorodiplatinum ring system with corresponding bond lengths and angles.

to 95 °C for 5–15 min, reaction occurred as shown in eq 2.

The following are most significant features of the NMR spectra for complex 3: (a) there is a proton resonance at 7.4 ppm integrating for 2 H and coupled to ^{195}Pt by 60 Hz, these are assigned to the olefinic protons; (b) there is a carbon resonance at 120 ppm which is coupled to these protons and to ^{195}Pt by 94 Hz; (c) in addition, there are two carbons with doublet multiplicity coupled to ^{195}Pt by 338 Hz which indicates a σ bond; (d) finally, there are only five carbon resonances for the nine-carbon structure indicating symmetrical magnetic environments for the hydrocarbon portion.[3] **X-ray Analysis.**[5] Even though the NMR spectral data were consistant with the organic portion of 3, the platinum NMR spectrum consisted of two resonances at 2184.4 and 2795.8 ppm downfield relative to Na$_2$Pt(CN)$_4$ as an external standard. Thus, an X-ray crystal structure was sought to elaborate the inorganic portion. The results of the analysis are shown in Figures 1 and

(3) For previous results on the NMR spectral assignments for platinacyclobutanes, see: Waddington, M. D.; Jennings, P. W. *Organometallics* **1982,** *1,* 1370; **1983,** *2,* 1269.

(4) Ling, S. S. M.; Puddephatt, R. J. *J. Organomet. Chem.* **1983,** 255.

(5) X-ray Determination of Complex 3: Yellow-orange crystals of 3 were grown by allowing heptane to diffuse into a chloroform solution. A specimen suitable for X-ray analysis (0.16 × 0.22 × 0.33 mm) was mounted on a glass fiber and data collection was carried out on a Nicolet R3ME automated diffractometer using $\theta/2\theta$ scans and graphite monochromated Mo Kα radiation (λ = 0.71069 Å). Unit cell constants of a = 10.963 (3) Å, b = 13.606 (3) Å, and c = 21.170 (7) Å were determined by a least-squares fit of 25 2θ values from diffractometer measurements in the range 19 < 2θ < 33.[6] The space group was found to be *pbca*, on the basis of systematic extinctions, and the calculated density is 2.88 g/cm^3 for C$_{22}$H$_{18}$Cl$_4$Pt$_2$ in the assymetric unit. Intensity data were collected for all unique reflections in the range 3 < 2θ < 50, and 1174 were observed with $I \geq 3\sigma(I)$. Absorption corrections were made by the Gaussian integration method using crystal dimensions between indexed crystal faces. The structure was refined to an R value of 0.080. Carbon positions were refined with isotropic thermal parameters. All structure determinations and refinement calculations were carried out with the SHELXTL package of programs on the Nicolet R3mE crystallographic system.[6]

(6) Programs used for centering of reflections, autoindexing, refinement of cell parameters, axial photographs, and data collections were those described in: "Nicolet P3/R3 Data Collection Manual"; Calabrese, J. C., Ed.; Nicolet XRD Corp.: Madison, WI, 1983.

2, which also contain data on selected bond angles and distances. In this complex, it appears that one platinum atom exists as a typical 4-coordinate, square-planar Pt(II) and the other as a 6-coordinate, octahedral Pt(IV). Since the resonance lines are sharp in the ^{1}H, ^{13}C, and ^{195}Pt spectra, it is apparent that 3 is a mixed-valent complex.[4] The dichlorodiplatinum ring is puckered by 28 (1)° and the platinacyclobutane ring is puckered by 11 (3)° from linearity. Moreover, the C(5)–C(7) bond distance is 2.37 (6) Å, which preclues any thoughts that the cyclopropane exists and that an edge complex is present. Due to the excessive electron density of the platinum and chlorine atoms it was necessary to constrain the C–C bond lengths to idealized values. No constraints were imposed on nonbonded carbon atoms or on the platinum and chlorine atoms.

Since the olefin appears by NMR and X-ray data to be bonded to the Pt(IV), it would be expected to be subject to nucleophilic attack. Thus, on treatment with LAH, a nearly quantitative yield of the hydrogenated analogue of 1 was obtained. This structure was determined by comparison with an authentic sample with NMR and mass spectroscopy.

While the Pt(IV)–olefin bond is new, it is important to note that this platinacyclobutane ring is also the first example of a *cis*-2,4-dialkyl-substituted system. This is significant since this type product has been proposed but never observed.

Supplementary Material Available: Tables of atomic coordinates, isotropic thermal parameters, bond lengths and angles, and anisotropic thermal parameters (2 pages). Ordering information is given on any current masthead page.

Flash Photolysis Investigations of RhCl(CO)(PPh$_3$)$_2$: Reaction Dynamics of the Wilkinson's Catalysis Intermediate "RhCl(PPh$_3$)$_2$"

David Wink and Peter C. Ford*

*Department of Chemistry, University of California
Santa Barbara, California 93106*

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The catalysis chemistry of rhodium(I) phosphine complexes continues to hold much interest 2 decades since the description of such reactions by Wilkinson.[1] However, despite considerable quantitative scrutiny,[1-3] the mechanistic details of key catalytic steps for even the original Wilkinson's catalyst RhCl(PPh$_3$)$_3$ are not fully resolved.[3] The reason lies within the very nature of catalytic processes, namely, that the activation of substrates often involves reactions of unstable transient species, the properties of which can only be inferred from kinetic rate laws or from spectral studies under conditions considerably different from those of an operating catalyst. In some cases it may be possible to use flash photolysis to generate significant concentrations of such a transient and to investigate the reactions of that species more directly. In the present case we report the flash photolysis of the metal car-

(1) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966,** 1711–1732.

(2) (a) Halpern, J.; Wong, C. S. *J. Chem. Soc., Chem. Commun.* **1973,** 629–630. (b) Tolman, C. A.; Meakin, P. Z.; Lindner, D. L.; Jesson, J. P.; *J. Am. Chem. Soc.* **1974,** *96,* 2762–2774. (c) Halpern, J.; Okamoto, T.; Zakhariev, A. *J. Mol. Catal.* **1976,** *2,* 65–69.

(3) (a) Tolman, C. A.; Faller, J. W. In "Homogeneous Catalysis with Metal Phosphine Complexes"; Pignolet, L. H., Ed.; Plenum press: New York, 1983; Chapter 2. (b) Halpern, J. *Trans. Am. Crystallogr. Assoc.* **1978,** *14,* 59–70.
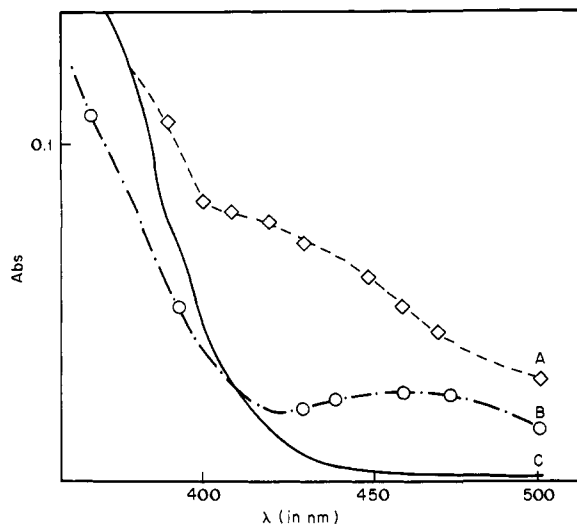
Figure 1. Transient spectra resulting from the flash photolysis of $RhCl(CO)(PPh_3)_2$ in benzene solution. (A) Spectrum observed to 100 μs after flash ($\lambda_{irr} > 315$ nm). Points indicated represent actual experimental observations; curve is drawn for illustrative purposes. (B) Spectrum observed 20 ms after flash. (C) Spectrum of $RhCl(CO)(PPh_3)_2$.

bonyl $RhCl(CO)(PPh_3)_2$, which gives a transient believed to be $RhCl(PPh_3)_2$ (I)[4] (eq 1), an intermediate crucial to proposed

$$RhCl(CO)(PPh_3)_2 \underset{k_{-1}}{\overset{h\nu}{\rightleftharpoons}} \underset{I}{RhCl(PPh_3)_2} + CO \qquad (1)$$
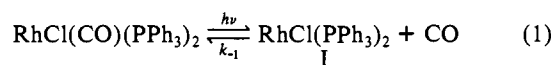
mechanisms of Wilkinson's catalyst reactions including olefin hydrogenation.[5] Reported here are kinetics studies of the reactions of I with various substrates. To our knowledge this represents the first report of a direct investigation of this key but elusive intermediate.

When $RhCl(CO)(PPh_3)_2$ in degassed benzene was subjected to flash photolysis[6] ($\lambda_{irr} > 315$ nm, pulse duration about 20 μs), transient absorption was observed with the spectral characteristics illustrated in Figure 1. This transient (when monitored at λ_{mon} 420 nm) decayed via second-order kinetics over a period of several milliseconds. When the solution was flashed under CO (1.0 atm, 0.006 M in benzene[7]), no transient having a lifetime longer than the flash was detected; however, a long-lived transient with the same spectrum as $RhCl(PPh_3)_3$ was seen when the flash photolysis was carried out in the presence of excess PPh_3 (0.05 M).[8] Thus CO, not phosphine, photolabilization appears to be the major primary photoreaction.

When the flash photolysis of $RhCl(CO)(PPh_3)_2$ was carried out in the absence of other reactants but with λ_{mon} 450 nm, it was

noted that the transient absorption decayed in two stages. The relatively rapid second-order decay noted at 420 nm was followed by a slower first-order decay back to $RhCl(CO)(PPh_3)_2$ with a k_{obsd} of 1.8 s^{-1}. The spectrum of the longer lived transient (Figure 1) is very close to that of the dimer $[RhCl(PPh_3)_2]_2$, described previously[9] and discussed in the mechanistic schemes for Wilkinson's catalyst.[3] Presumably, $[RhCl(PPh_3)_2]_2$ is formed via the dimerization of I:

$$2RhCl(PPh_3)_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [RhCl(PPh_3)_2]_2 \qquad (2)$$
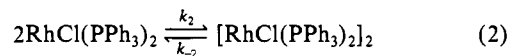
The stopped-flow kinetics of the reaction between $[RhCl(PPh_3)_2]_2$ (prepared thermally)[9] and CO (P_{co} 1.0 atm) in benzene to give $RhCl(CO)(PPh_3)_2$ were also studied.[10] First-order kinetics were again observed with the nearly identical k_{obsd}, 1.7 s^{-1} (298 K). This observation implies that the reaction of the dimer with CO occurs via rate-limiting dissociation to I, i.e., $k_{obsd} = k_{-2}$, followed by rapid reaction of the latter with CO.

Calculation of k_{-1} and k_2 from the flash photolysis data requires an estimate of the extinction coefficient of I at λ_{mon} in order to determine the concentrations of this species. This estimate was made by assuming that the reaction with excess PPh_3 (see above) trapped all I as $RhCl(PPh_3)_3$. From the known spectrum of the latter species,[9] the initial concentration, thus the extinction coefficient (8×10^2 M^{-1} cm^{-1} at 420 nm), of I was calculated. From this the second-order rate constant for the disappearance of I was determined to be 1×10^8 M^{-1} s^{-1}. The amount of dimer produced by the flash photolysis in the absence of added reactants (calculated from the spectrum of the long-lived intermediate) indicated that under these conditions about 40% of I dimerized in competition with the back reaction with the photoliberated CO to give $RhCl(CO)(PPh_3)_2$. Thus k_{-1} and k_2 were estimated as 6×10^7 M^{-1} s^{-1} and 4×10^7 M^{-1} s^{-1}, respectively. Notably, the ratio k_{-2}/k_2, the equilibrium constant for dissociation of the dimer calculated from the kinetic flash photolysis data is 5×10^{-8} M, in agreement with the estimate by Tolman and co-workers ($<(6 \times 10^{-6})$ M, from spectral data)[2b] for the dissociation constant of $[RhCl(PPh_3)_2]_2$.

When the flash photolysis of $RhCl(CO)(PPh_3)_2$ was carried out as above but under dihydrogen (1.0 atm, 0.0028 M),[2b] I underwent first-order reaction ($k_{obsd} = 2.8 \times 10^2$ s^{-1}) to give a new transient spectrum having an even smaller absorbance than that of the carbonyl complex over the spectral range 360–450 nm. This new transient decayed to give $RhCl(CO)(PPh_3)_2$ again over a period of seconds. We interpret these observations in terms of the reaction of I with H_2 to give the dihydride (eq 3), followed

$$RhCl(PPh_3)_2 + H_2 \xrightarrow{k_3} H_2RhCl(PPh_3)_2 \qquad (3)$$
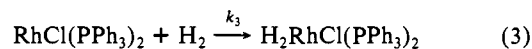
by reaction of the latter with CO to regenerate $RhCl(CO)(PPh_3)_2$. If a second-order rate law is assumed, then k_3 is 1.0×10^5 M^{-1} s^{-1}, very much in agreement with Halpern's estimate of k_3 ($>(7 \times 10^4)$ M^{-1} s^{-1}) drawn from kinetic analysis of the Wilkinson's catalysis.[2a] Flash photolysis under D_2 (1.0 atm) gave identical spectral changes and a calculated k_3 of 0.7×10^5 M^{-1} s^{-1}, i.e., a kinetic isotope effect k_3^h/k_3^d of about 1.4.

Flash photolysis of $RhCl(CO)(PPh_3)_2$ under ethylene (1.0 atm, 0.11 M) gives spectral changes consistent with the formation of the ethylene complex[1] $RhCl(H_2C=CH_2)(PPh_3)_2$ within duration of the flash. This observation provides a lower limit of 1×10^6 M^{-1} s^{-1} for the second-order rate constant for the reaction of I with ethylene. The back reaction of the ethylene adduct with CO to reform $RhCl(CO)(PPh_3)_2$ was also rather rapid and occurred within a period of a few milliseconds.

In summary, the flash photolysis of $RhCl(CO)(PPh_3)_2$ in benzene leads principally to formation of the coordinatively unsaturated Wilkinson's catalyst intermediate $RhCl(PPh_3)_2$ (or its

(4) In this paper we follow the common practice of representing this intermediate as $RhCl(PPh_3)_2$, although we believe it probable that the "vacant" coordination site is occupied by a weakly coordinated solvent molecule. See: de Croon, M. H. J. M.; van Nisselrooij, P. F. M. T.; Kuipers, H. J. A. M.; Coenen, J. W. E. *J. Mol. Catal.* **1978**, *4*, 325–335.

(5) (a) Jardine, F. H. *Prog. Inorg. Chem.* **1982**, *28*, 63–201. (b) James, B. R. "Homogeneous Hydrogenation"; Wiley-Interscience: New York, 1973; pp 204–250.

(6) (a) The flash photolysis apparatus was that described previously[6b] modified by the use of a Hewlett-Packard 86 computer for data analysis. Wavelength selection was accomplished by use of an aqueous $NaNO_3$ solution as a UV and IR filter. The benzene used in these studies was scrupulously deaerated by freeze/pump/thaw cycles and dried by distillation from a Na/K amalgam. All solutions were prepared by vacuum manifold techniques. (b) Durante, V. A.; Ford, P. C. *Inorg. Chem.* **1979**, *18*, 588–593.

(7) Braker, W.; Mossman, A. L. "The Matheson Unabridged Gas Databook: A Compilation of Physical and Thermodynamic Properties of Gases"; Matheson Gas Products: East Rutherford, NJ, 1974; Vol. 1, p 11.

(8) The flash photolysis of $RhCl(PPh_3)_3$ and of $RhCl(CO)(PPh_3)_2$ in the presence of PPh_3 will be described in a separate article. However, $[PPh_3]$ dependence studies of the rates of $RhCl(PPh_3)_3$ formation from I give a second-order rate constant of 2×10^6 M^{-1} s^{-1} for this reaction. Given the rate constant of 0.71 s^{-1} determined[2a] for the dissociation of PPh_3 from $RhCl(PPh_3)_3$ in benzene, the equilibrium constant for dissociation is calculated to be 0.4×10^{-6} M, consistent with the previous estimate of $<10^{-5}$ M.[2a]

(9) Geoffroy, G. L.; Keeney, M. E. *Inorg. Chem.* **1977**, *16*, 205–207.

(10) Stopped-flow kinetics were carried out using a Gibson-Durram D110 spectrophotometer equipped for the handling of solutions under deaerated conditions (Trautman, R. J.; Gross, D. C.; Ford, P. C. *J. Am. Chem. Soc.*, in press.

solvated analogue), which, in the absence of other reactants, recombines with CO or dimerizes via very rapid reactions. In the presence of added PPh$_3$, ethylene, or dihydrogen, adducts of I are formed. Rates of addition of the former two are quite rapid while dihydrogen addition occurs with a rate significantly slower. In all cases, however, the initial adducts formed react eventually with the photolabilized CO to reform the more stable starting complex RhCl(CO)(PPh$_3$)$_2$. These observations are consistent with a previous continuous photolysis investigation which reported no net photochemistry of this species in the absence of oxygen.[11] Preliminary flash photolysis studies[12] of the iridium analogue Vaska's complex IrCl(CO)(PPh$_3$)$_2$ demonstrate the formation of a transient analogous to I although the subsequent reactions display significant differences.

(11) Geoffroy, G. L.; Denton, D. A.; Keeney, M. E.; Bucks, R. R. *Inorg. Chem.* **1976**, *15*, 2382–2385.

(12) Wink, D.; Ford, P. C., studies in progress.

Seven-Coordinate Aluminum in [AlCl$_2$·benzo-15-crown-5][AlCl$_3$Et]

Simon G. Bott, Hosny Elgamal, and Jerry L. Atwood*

*Department of Chemistry, University of Alabama
University, Alabama 35486*

Crown ethers have been utilized as multidentate ligands to form unusual or unique coordination states for numerous metals.[1] One particularly fruitful area has been the reaction between crown ethers and ML$_2$ species, resulting in a number of modes of complexation involving both direct M–O interaction and L···O hydrogen bonding.[2-11] A general condition for the former to occur, as reported by Christensen et al.,[12] is that the ratio (R) of the metal ion diameter to the crown cavity diameter be between 0.75 and 0.90.[13] Within this range, however, two types of complex can exist—those in which the metal and oxygens are coplanar, resulting in a bipyramidal structure having L axial, and those in which cis sites are occupied by L, leaving the metal lying out of the plane of the oxygens. Which mode occurs is again largely dependent on R, lower values leading to the "included" metal (e.g., Ca(NCS)$_2$·benzo-15-crown-5·S (S = H$_2$O, CH$_3$OH)[6] has the calcium

(1) See, For example: "Synthetic Multidentate Macrocyclic Compounds"; Izatt, R. M., Christensen, J. J., Eds.; Academic Press: New York, 1978. Goldberg, I. In "Inclusion Compounds"; Eds. Atwood, J. L.; Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984.

(2) Hogen Esch, T. E.; Smid J. *J. Am. Chem. Soc.* **1969**, *91*, 4580.

(3) Dunitz, J. D.; Seiler P. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2750.

(4) Van Remoortere, F. P.; Boer, R. P.; Steiner, E. C. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1420.

(5) Cradwick, P. D.; Poonia, N. S. *Acta Crystallogr., Sect. B* **1977**, *B33*, 197.

(6) Owen, J. D. *J. Chem. Soc., Dalton Trans.* **1978**, 1418.

(7) Malmsten, L. A. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1702.

(8) Bhagwat, V. W.; Manohar, H.; Poonia, N. S. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 289.

(9) Holt, E. M.; Alcock, N. W.; Hendrixson, R. R.; Malpass, G. D.; Ghiradelli, R. G.; Palmer, R. A. *Acta Crystallogr., Sect. B* **1981**, *B37*, 1080.

(10) Sakkura, T.; Kobayashi, K.; Tsuboyama, S.; Kohno, Y.; Azuma, N.; Ishizu, K. *Acta Crystallogr., Sect. C* **1983**, *C39*, 206.

(11) Paige, C. B.; Richardson, M. F. *Can. J. Chem.* **1984**, *62*, 322.

(12) Christensen, J. J.; Hill, J. D.; Izatt, R. M. *Science (Washington, D.C.)* **1971**, *174*, 459.

(13) The two numbers associated with R arise from the fact that the crown cavity is given a minimum and a maximum value in the literature.

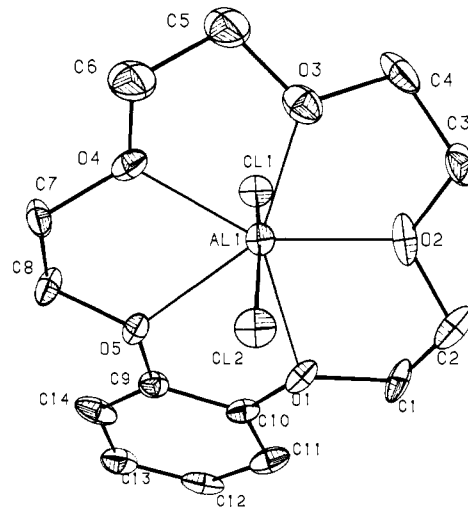Figure 1. [AlCl$_2$·benzo-15-crown-5]$^+$ cation. The Cl–Al–Cl angle is 169° and the lengths involving Al(1) are Al(1)–O(1) = 2.28 (1), Al(1)–O(2) = 2.03 (1), Al(1)–O(3) = 2.06 (1), Al(1)–O(4) = 2.08 (1), Al(1)–O(5) = 2.30 (1), Al(1)–Cl(1) = 2.202 (5), and Al(1)–Cl(2) = 2.197 (7) Å.

lying 1.22 Å out of plane, R = 1.01–1.31, whereas Ca(NCS)$_2$·18-crown-6[3] contains the calcium coplanar with the oxygens, R = 0.70–0.86).

Reaction of EtAlCl$_2$ with 12-crown-4 and 18-crown-6 produces cationic complexes of aluminum coordinated to four oxygens and two cis chlorines. The diameter of Al^{3+} is 1.34 Å, and this gives a value for R of 0.90–1.10 for these complexes.[14] Thus by analogy with the calcium series, reaction of EtAlCl$_2$ with benzo-15-crown-5 (R = 0.61–0.79) produces the title compound, corresponding to the 2:1 complex of AlCl$_3$ with the same crown.[15] The X-ray investigation revealed that the cation consists of the first structurally characterized seven-coordinate aluminum,[16,17] the coordination polyhedron being a pentagonal bipyramid with five equatorial oxygens and two axial chlorines (Figure 1).

The aluminum is coplanar with the oxygens and is displaced away from the aromatic group. Thus the Al–O distances for O(2), O(3), and O(4) are much shorter than those for the two oxygens adjacent to the benzo group. The latter two distances are among the longest Al–O lengths so far reported,[18] but justification for referring to them as bonds arises from both the near ideality of the pentagonal-bipyramidal geometry[19] combined with the definite bonding distances to the other three oxygens and the elongated Al–Cl distances (2.200 (3) Å compared to 2.143 (6) Å in the anion).

(14) R for 12-crown-4 is 0.91–1.10, while R for 18-crown-6 is 0.42–0.51. However, with a ratio as low as the latter, the aluminum atom opts for an octahedral configuration like that of the 12-crown-4 derivative (Elgamal, H.; Robinson, G. H.; Bott, S. G.; Weeks, J. A.; Hunter, W. E.; Atwood, J. L., unpublished results).

(15) Wada, F.; Matsudo, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 421.

(16) Single crystals of the title compound were obtained by the slow cooling of a toluene solution. Space group *Pbca*; cell constants a = 21.306 (9) Å, b = 17.747 (4) Å, c = 13.267 (3) Å, with eight formula units per unit cell and D_c = 1.40 g cm^{-3}. Least-squares refinement based on 1667 observed reflections led to a final R = $\sum(|F_o| - |F_c|)/\sum|F_o|$ = 0.100. The rather high R value is due to disorder in the anion. This has the effect of smearing the contribution of the ethyl group over at least four positions. The details of data collection and refinement are as given in Holton et al.: Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45. Anisotropic thermal parameters were used for all atoms except those of the ethyl group of the anion. Hydrogen atoms were not located.

(17) Reaction of 0.010 mol of benzo-15-crown-5 with 0.020 mol of EtAlCl$_2$ in toluene produces an immediate two-phase system characteristic of the liquid clathrate effect (Atwood, J. L. In "Inclusion Compounds"; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.: Academic Press: London, 1984). Upon standing, large, colorless, air-sensitive crystals of the title compound are deposited from the lower layer.

(18) Rogers, R. D. Ph.D. Thesis, University of Alabama, University, AL, 1982.

(19) Drew, M. G. B. *Prog. Inorg. Chem.* **1977**, *23*, 67.