cm^3/mol (from the bulk density of water) and 12 cm^3/mol (from the ionic radius of Cs^+ of 0.169 nm given by Pauling[19]), so at first glance it seems that expulsion of 1 mol of Cs^+ should allow for accommodation of only 0.67 mol of H_2O. Thus, either the effective volume of Cs^+ within the lattice is considerably larger than its ionic radius would indicate, or the effective volume of a water molecule within the lattice is considerably smaller than it is in bulk water or some combination of the two. Since it is unreasonable to postulate a water density within the lattice which is greater (by a factor of nearly 5!) than the bulk value to account for the discrepancy, we attribute the majority of the effect to a much larger effective volume for Cs^+. Geometric arguments based on the sizes of Cs^+ and H_2O in relation to the size of the octahedral cavity[10,20-22] can be made which are in agreement with this conclusion. Briefly, even though the Cs^+ cation does not completely fill the cubic cavity (which is 0.5 nm on a side[10,20-22]), it is just large enough to preclude the presence of water molecules. Thus, void space is left within the cavity which does not have the proper geometry to accommodate the incorporation of interstitial water. A more detailed description of this "discreteness of size" effect will be reported in a future contribution, along with a discussion of the insight provided by such measurements of solvent transport ito the remarkable sensitivity of the formal potential of these nickel ferrocyanide films to the identity of the presence of various alkali metal cations.

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Facile Cleavage of C–H Bonds. Reaction of Trimethylaluminum with Bis(diphenylphosphinoyl)methane: Synthesis and Molecular Structure of $[Al(CH_3)][(C_6H_5)_2P(O)CP(O)(C_6H_5)_2]_2[Al(CH_3)_2]_2$

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The ability of multidentate ligands to promote metal–metal interactions in bimetallic complexes is often considered an attractive feature in many organometallic systems. To this end, many workers have employed the bidentate phosphine ligand bis(diphenylphosphino)methane. The recent popularity of this ligand may be traced to the fact that the close proximity of the two phosphorus atoms can often facilitate interesting behavior in bimetallic complexes.[1-5] Relative to organo-main group chemistry, this ligand has also been shown to play a role in various organoaluminum catalytic systems.[6-8] Surprisingly, the corresponding transition metal and main group metal chemistry of the dioxygen analogue of bis(diphenylphosphino)methane, bis(diphenylphosphinoyl)methane ($[(C_6H_5)_2P(O)CH_2P(O)(C_6H_5)_2]$) remains largely unexplored. Herein, we report the synthesis[9] and molecular structure of $[Al(CH_3)][(C_6H_5)_2P(O)CP(O)(C_6H_5)_2]_2[Al(CH_3)_2]_2$ isolated from reaction of the bidentate ligand with trimethylaluminum in chlorobenzene. A particularly significant point about bis(diphenylphosphinoyl)methane is the fact that the hydrogen atoms of the central methylene carbon are sufficiently acidic so as to undergo Al–R/C–H bond cleavage thus resulting in the unusual organoaluminum title compound. The X-ray crystal structure of the compound is shown in Figure 1.

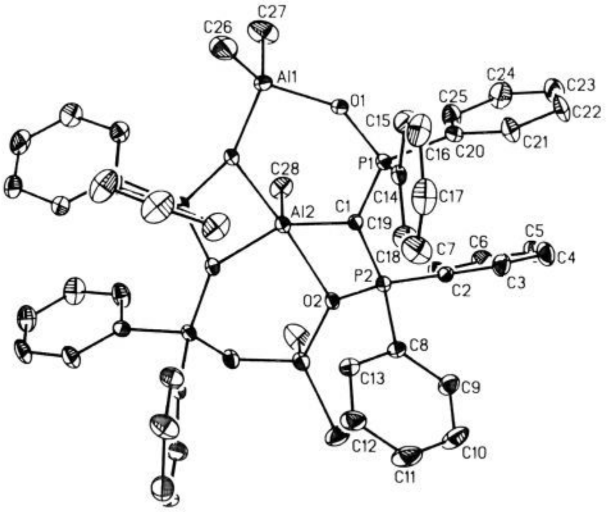

Figure 1. A view of the $[Al(CH_3)][(C_6H_5)_2P(O)CP(O)(C_6H_5)_2]_2[Al(CH_3)_2]_2$ molecule showing the atom labeling scheme. Thermal ellipsoids show 20% probability levels; hydrogen atoms have been omitted. Selected bond distances (Å) and angles (deg): Al1–O1, 1.772 (4); Al1–C26, 1.986 (9); Al1–C27, 1.977 (9); Al2–C1, 1.982 (6); Al2–C28, 1.994 (10); Al2–O2, 2.174 (4); P1–C1, 1.680 (6); P2–C1, 1.672 (6); P1–C20, 1.811 (6); P1–C14, 1.808 (7); P2–C2, 1.800 (6); P2–C8, 1.799 (7); C1–Al2–C28, 121.0 (2); C1–Al2–C1′, 118.0 (2); C28–Al2–C1′, 121.0 (2); O2–Al2–O2′, 163.2 (2).

X-ray intensity data were collected on a Nicolet R3m/V diffractometer by using an $\omega/2\Theta$ scan technique with Mo Kα radiation ($\lambda = 0.71073$ Å) at 26 °C. The title compound crystallizes in the monoclinic space group $C2/c$ with unit cell parameters $a = 25.756$ (4) Å, $b = 10.126$ (2) Å, $c = 23.038$ (4) Å, $\beta = 119.54$ (1)°, $V = 5227.17$ Å^3, and $D_{calcd} = 1.25$ g cm^{-3} for $Z = 4$. The structure was solved by direct methods and refined, based on 2104 observed reflections with intensities $I \geq 3\sigma(I)$, by using SHELXTL.[10] Least-squares refinement converged at $R = 0.056$ ($R_w = 0.070$). Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms, located from difference Fourier maps, were placed in idealized positions with fixed isotropic temperature factors.

This laboratory has long had an interest in the interactions of organoaluminum species with macrocyclic ligands. While initially we were concerned with reaction of organoaluminum species with

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(9) Inside the drybox a reaction vessel was charged with bis(diphenylphosphinoyl)methane (5.0 mmol) and chlorobenzene (25 mL). An excess of trimethylaluminum (7.5 mmol) was slowly added via syringe. The reaction vessel was removed from the drybox and heated (100 °C) in an oil bath for several hours. The system was vented periodically to release gas which was eliminated during the course of the reaction. Upon cooling to room temperature a multitude of colorless extremely air-sensitive crystals were obtained in quantitative yield: ^1H NMR (C_6D_6) δ −1.22 (s, 3 H, Al(CH_3)), −0.93 (s, 6 H, 2 Al(CH_3)), −0.80 (s, 3 H, Al(CH_3)), −0.27 (s, 3 H, Al(CH_3)), 7.31 (m, 40 H, C_6H_5).

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oxygen-based macrocyclic ligands, crown ethers,[11-13] our attention recently shifted to nitrogen-[14-17] and sulfur-based[18,19] macrocyclic ligands. Additionally, we have also recently begun an investigation into the organoaluminum chemistry of open-chain multidentate amines.[20-22] An examination of the organoaluminum chemistry of multidentate phosphorus ligands represents a logical extension of this work.

As can be seen from Figure 1, $[Al(CH_3)][(C_6H_5)_2P(O)CP(O)(C_6H_5)_2]_2[Al(CH_3)_2]_2$ contains two bis(diphenylphosphinoyl)methanide units bridged by three organoaluminum moieties: two dimethylaluminum fragments and one methylaluminum fragment. Particularly significant is the fact that the central aluminum atom, in addition to being bonded to one methyl carbon atom and one oxygen atom of each ligand, is also bonded to the methylene carbon atom of each ligand. Thus, the title compound results from a condensation reaction in which four $Al-CH_3$ bonds were cleaved in addition to all four C–H bonds of the methylene carbon atoms of the two ligands. Methane was eliminated during the course of the reaction. Such condensation reactions are well documented for Al–R/N–H systems.[23-31] Characteristically, such systems eliminate alkane while reaction products are Al–N cages possessing Al_2N_2 fragments. To the best of our knowledge, the title compound represents the first report of a condensation product resulting from cleavage of Al–R and C–H fragments. Furthermore, it is quite unusual for the methylene hydrogen atoms of a bis(diphenylphosphino)methane-based bidentate ligand to exhibit such reactivity. Indeed, in the recently reported product $[Al(CH_3)]_2[(C_6H_5)_2PCH_2P(C_6H_5)_2]$, isolated from reaction of trimethylaluminum with bis(diphenylphosphino)methane, the methylene hydrogen atoms proved to be completely inert to reaction with $Al(CH_3)_3$ as only the 2:1 (AlR_3 to ligand) complex was observed.[32] The observed lability of the methylene hydrogen atoms of bis(diphenylphosphinoyl)methane is undoubtedly due to increased acidity resulting from the presence of the oxygen atoms.

Several points are worthy of note regarding structure and bonding in $[Al(CH_3)][(C_6H_5)_2P(O)CP(O)(C_6H_5)_2]_2[Al(CH_3)_2]_2$. The molecule contains a 2-fold axis of rotation containing atoms Al2 and C28. The central aluminum atom, Al2, is five-coordinate being bonded to one methyl carbon atom in addition to the two central methanide carbon atoms of the two ligands. These four atoms constitute a plane. The coordination sphere of the pentacoordinate aluminum atom is completed by an oxygen atom from each ligand situated on either side of the AlC_3 plane. The O–Al–O bond angle is 163.3 (2)°, while the mean C–Al–C bond angle of the central AlC_3 plane is 120°. The coordination geometry of Al2, thus, may be described as trigonal bipyramidal. The variation in Al–O distances in the title compound is worthy of note. At a distance of 1.772 (4) Å the Al1–O1 bond is quite strong. This distance is placed in perspective when one considers the value of 2.02 (2) Å for the Al–O interaction found in the bis(trimethylaluminum)dioxane adduct $[Al(CH_3)_3]_2[C_4H_8O_2]$.[33] Conversely, the Al2–O2 distance of 2.174 (4) Å must be considered quite long. The mean Al–C distance in the title compound of 1.986 (9) Å is within the expected range. With P–C bond distances of 1.680 (6) Å and 1.672 (6) Å for P1–C1 and P2–C1, respectively, it is reasonable to assume resonance stabilized double bond character over these two bonds.

Although Lewis base species possessing C–H fragments are generally quite inert to reaction with AlR_3, the isolation of the title compound indicates, that under appropriate conditions, facile Al–R and C–H bond cleavage can occur resulting in interesting organoaluminum products. Additional studies on related ligands and organoaluminum species are forthcoming.

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Supplementary Material Available: Tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters (4 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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The X-ray Structure of Flavohemoglobin: A Semisynthetic Hydroxylase[†]

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Hemoglobin (Hb) catalyzes monoxygenase reactions in a cytochrome P-450-like manner.[1] This activity requires cytochrome P-450 reductase, which transfers electrons between the two-electron donor, NAD(P)H, and the single-electron acceptor, the

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[†] E. T. Kaiser passed away on July 18, 1988. We would like to dedicate this paper to his memory.

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