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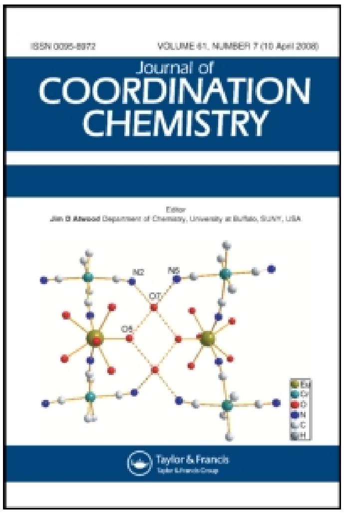

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Reaction of Triethylaluminum with Bis(Diphenylphosphinoyl)Methane. Synthesis and Molecular Structure of $[Al(C_2H_5)][(Ph_2P(O))_2C]_2[Al(C_2H_5)_2]_2$

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To cite this Article Lee, Baosheng , Sangokoya, Samuel A. , Pennington, William T. and Robinson, Gregory H.(1990) 'Reaction of Triethylaluminum with Bis(Diphenylphosphinoyl)Methane. Synthesis and Molecular Structure of $[Al(C_2H_5)][(Ph_2P(O))_2C]_2[Al(C_2H_5)_2]_2$', Journal of Coordination Chemistry, 21: 2, 99 — 105
To link to this Article: DOI: 10.1080/00958979009409177
URL: http://dx.doi.org/10.1080/00958979009409177

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J. Coord. Chem. 1990, Vol. 21. pp. 99–105
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REACTION OF TRIETHYLALUMINUM WITH BIS(DIPHENYLPHOSPHINOYL)METHANE. SYNTHESIS AND MOLECULAR STRUCTURE OF $[Al(C_2H_5)][(Ph_2P(O))_2C]_2[Al(C_2H_5)_2]_2$

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(Received January 20, 1989)

Reaction of triethylaluminum with bis(diphenylphosphinoyl)methane in toluene/heptane affords the crystalline condensation product $[Al(C_2H_5)][(Ph_2P(O))_2C]_2[Al(C_2H_5)_2]_2$. The title compound crystallizes in the monoclinic space group $C2/c$ with unit cell parameters $a = 26.157(9)$, $b = 10.261(3)$, $c = 24.607(9)$ Å, $\beta = 120.48(2)°$, $V = 5691.65$ Å^3 and $\rho = 1.23$ g cm^{-3} for $Z = 4$. Full-matrix least-squares refinement based on 2778 observed reflections converged at $R = 0.051$, $R_w = 0.068$. During the course of the reaction both of the central methylene C–H bonds of each ligand were cleaved, along with four Al–Et bonds, thereby eliminating four units of ethane, and resulting in a five-coordinate aluminum atom residing in a trigonal bipyramidal environment at the core of the molecule.

Keywords: Aluminum alkyl, phosphine, X-ray structure, pentacoordinate

INTRODUCTION

The bidentate phosphine ligand bis(diphenylphosphino)methane has been utilized extensively by workers in organo-transition metal chemistry particularly in cases where metal–metal interactions are desired in bimetallic complexes.[1–5] Although the organo-main group chemistry of this ligand has not developed in parallel with that of the transition metals, bis(diphenylphosphino)methane has been shown to play a role in various organoaluminum catalytic systems.[6–8] While the organoaluminum chemistry of the dioxygen analogue of bis(diphenylphosphino)methane, bis(diphenylphosphinoyl)methane, remains largely unexplored, we have recently initiated an investigation into this chemistry.[9] Herein, we report the synthesis and molecular structure of $[Al(C_2H_5)][(Ph_2P(O))_2C]_2[Al(C_2H_5)_2]_2$, isolated from the reaction of triethylaluminum with bis(diphenylphosphinoyl)methane. The aluminum atom, situated at the core of the molecule, is five-coordinate residing in a trigonal bipyramidal environment.

EXPERIMENTAL

General

Standard Schlenk technique was employed in conjunction with an inert atmosphere dry box (Vacuum Atmospheres HE-43 Dri-Lab). Toluene and heptane were distilled

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under purified argon prior to use. Triethylaluminum, purchased from Aldrich Chemical Co., was used as received. Bis(diphenylphosphinoyl)methane was prepared in our laboratory. Single-crystal X-ray data were collected on a Nicolet R3m/V diffractometer. ^1H and ^{31}P NMR data were recorded on a JOEL-FX90 NMR spectrometer.

Synthesis of $[Al(C_2H_5)][(Ph_2P(O))_2C]_2[Al(C_2H_5)_2]_2$

In the drybox a 50 cm^3 reaction vessel was charged with bis(diphenylphosphinoyl)-methane (0.50 g, 1.2 mmol), triethylaluminum (0.33 cm^3, 2.4 mmol), and a toluene–heptane mixture (28 cm^3 and 2 cm^3, respectively). The reaction tube was removed from the drybox and heated in an oil bath (130°C) for 2 hrs. Upon cooling, a multitude of small, colourless, rectangular, air-sensitive, X-ray quality crystals resulted in quantitative yield (based on bis(diphenylphosphinoyl)methane), m.p. 205–206°C. ^1H NMR ($CDCl_3$): δ −0.15 and 1.16 (cm, 25 H, $Al(C_2H_5)$), 6.80–8.00 (m, 40 H, C_6H_5). ^{31}P NMR ($CDCl_3$): δ 34.76 (s, 4P, C–*P*(O)Ph_2).

Structural solution and refinement

A single crystal of $[Al(C_2H_5)][(Ph_2P(O))_2C]_2[Al(C_2H_5)_2]_2$ was mounted in a thin-walled glass capillary under an inert atmosphere of argon. Cell constants and an orientation matrix from the setting angles of 29 carefully centred reflections in the range $14.58 < 2\theta < 30.25°$ corresponded to a monoclinic cell with dimensions $a = 26.157(9)$, $b = 10.261(3)$, $c = 24.607(9)$ Å, $\beta = 120.48(2)$ Å^3, $V = 5691.65$ Å^3 and $\rho = 1.23$ g cm^{-3} for $Z = 4$. The space group was determined to be *C*2/*c*. The structure was solved by direct methods and refined, based on 2778 observed reflections ($I > 3\sigma(I)$), using SHELXTL.[10] Hydrogen atoms, located from difference Fourier maps, were placed in idealized positions with fixed isotropic tempera-

TABLE I
Summary of the crystallographic data for $[Al(C_2H_5)][(Ph_2P(O))_2C]_2[Al(C_2H_5)_2]_2$.

Empirical formula	$C_{60}H_{65}Al_3O_4P_4$
Molecular weight	1054.87
Colour; habit	colourless; rectangles
Space group	monoclinic; *C*2/*c*
a, Å	26.157(9)
b, Å	10.261(3)
c, Å	24.607(9)
β (deg)	120.48(2)
Cell volume, Å^3	5691.65
Z	4
ρ	1.23
Diffractometer	Nicolet R3m/V
Radiation	Mo-Kα (λ = 0.71073 Å)
Temperature	23°C
2θ Range, deg	3.50 to 45.0
Reflections collected	4078
Reflections observed	2778
GOF	1.81
R	0.051
R_w	0.068

ture factors. Atom A12 lies on a two-fold axis which generates the other half of the molecule; the ethyl group (atoms C30 and C31) bonded to Al2 is crystallographically disordered about the two-fold axis. Relevant crystallographic data are given in Table I.

RESULTS AND DISCUSSION

Our initial investigation into the organoaluminum chemistry of bidentate phosphine ligands concerned the reaction of trimethylaluminum with bis(diphenylphosphino)-

TABLE II

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å × 10^3) for $[Al(C_2H_5)][(Ph_2P(O))_2C]_2[Al(C_2H_5)_2]_2$.

Atom	*x/a*	*y/b*	*z/c*	*U*(eq)*
P(1)	4634(1)	1207(1)	8258(1)	53(1)
P(2)	3661(1)	997(1)	6838(1)	53(1)
Al(1)	3993(1)	2058(1)	5856(1)	62(1)
Al(2)	5000	2227(2)	7500	52(1)
O(1)	5241(1)	1930(3)	8480(1)	54(1)
O(2)	3614(1)	1561(3)	6239(1)	72(1)
C(1)	4827(2)	−368(4)	8633(2)	60(2)
C(2)	5143(2)	−1207(5)	8459(2)	72(2)
C(3)	5341(3)	−2398(5)	8741(3)	89(3)
C(4)	5214(3)	−2791(6)	9197(3)	109(4)
C(5)	4901(3)	−1995(6)	9369(3)	110(4)
C(6)	4702(2)	−784(5)	9093(2)	82(3)
C(7)	4258(2)	2080(5)	8591(2)	59(2)
C(8)	3722(2)	1626(6)	8508(2)	81(3)
C(9)	3424(3)	2354(8)	8729(3)	97(4)
C(10)	3641(3)	3506(8)	9022(3)	107(4)
C(11)	4162(3)	3994(6)	9099(3)	97(4)
C(12)	4474(2)	3265(5)	8885(2)	75(3)
C(13)	4335(2)	1254(4)	7475(2)	52(2)
C(14)	3066(2)	1749(4)	6899(2)	58(2)
C(15)	3111(2)	3079(5)	7035(2)	77(3)
C(16)	2672(3)	3701(5)	7083(3)	94(4)
C(17)	2181(3)	3042(7)	6999(3)	104(4)
C(18)	2130(2)	1748(6)	6862(3)	97(4)
C(19)	2572(2)	1089(5)	6813(3)	77(3)
C(20)	3456(2)	−709(5)	6674(2)	57(2)
C(21)	3047(3)	−1109(6)	6070(2)	92(3)
C(22)	2881(3)	−2421(7)	5946(3)	103(4)
C(23)	3130(3)	−3301(6)	6408(3)	94(4)
C(24)	3519(3)	−2930(6)	7007(3)	95(3)
C(25)	3685(2)	−1632(5)	7138(2)	79(3)
C(26)	3839(3)	3904(6)	5646(3)	134(4)
C(27)	3296(4)	4373(8)	5241(4)	184(7)
C(28)	3837(3)	880(8)	5162(3)	119(4)
C(29)	3283(5)	739(12)	4657(4)	263(10)
C(30)	5125(6)	4130(9)	7488(9)	61(7)
C(31)	4678(6)	4977(11)	7530(6)	104(8)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

methane. Although the simple 2:1 adduct $[Al(CH_3)_3]_2[Ph_2PCH_2]$[11] was the only product isolated, we thought that it might be possible to sufficiently modify the ligand so as to induce the normally inert central methylene unit of the ligand to react directly with an organoaluminum species. Thus, we endeavoured to examine the organoaluminum chemistry of the chalcogen derivatives of bis(diphenylphosphino)-methane.

Reaction of the dioxygen derivative bis(diphenylphosphinoyl)methane with triethylaluminum resulted in $[Al(C_2H_5)][(Ph_2P(O))_2C]_2[Al(C_2H_5)_2]_2$. The X-ray crystal structure of the title compound is shown in Figure 1. Final fractional atomic coordinates are given in Table II. Selected bond distances and angles are provided in Table III.

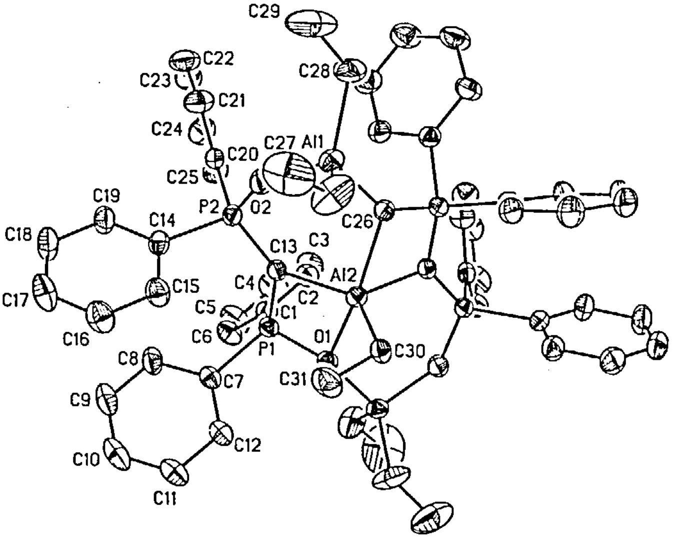

FIGURE 1 A view of the $[Al(C_2H_5)][(Ph_2P(O))_2C]_2[Al(C_2H_5)_2]_2$ molecule showing the atom labelling scheme. Thermal ellipsoids show 35% probability levels; hydrogen atoms have been omitted.

It is well-known that interactions of organoaluminum species with N–H amines result in alkane elimination (from cleavage of Al–R and N–H units) and Al–N cage products.[12] However, the literature reveals a paucity of similar studies involving Al–R and C–H fragments. As can be seen from Figure 1, the title compound consists of two bis(diphenylphosphinoyl)methanide units bridged by one ethylaluminum fragment and two diethylaluminum fragments. The reaction is given in Eq. (*1*).

$$2\,[(Ph_2P(O))_2CH_2]_2 + 3\,Al(C_2H_5)_3 \longrightarrow [Al(C_2H_5)][(Ph_2P(O))_2C]_2[Al(C_2H_5)_2]_2 + 4\,C_2H_6 \qquad (1)$$

The penta-coordination of the central aluminum atom Al2 is noteworthy. Indeed, this aluminum atom is bonded to the central methylene carbon atom, C13 and C13a, of each ligand, an oxygen atom from each ligand (O1 and O1a), in addition to a methylene carbon atom of an ethyl group (C30). The Al2, C13, C13a, and C30 atoms are coplanar while the two oxygen atoms, O1 and O1a, are in axial positions with respect to the AlC_3 plane. The O1–Al2–O1a bond angle is 163.9(2)° while the mean

TABLE III

Selected bond distances (Å) and angles (deg) for $[Al(C_2H_5)][(Ph_2P(O))_2C]_2[Al(C_2H_5)_2]_2$.

Atoms	Distance	Atoms	Distance
P(1)–C(1)	1.802(4)	P(1)–C(7)	1.806(6)
P(1)–C(13)	1.672(4)	P(2)–O(2)	1.530(4)
P(2)–C(13)	1.683(3)	P(2)–C(14)	1.809(5)
P(2)–C(20)	1.815(5)	Al(1)–O(2)	1.753(4)
Al(1)–C(26)	1.951(6)	Al(1)–C(28)	1.960(7)
Al(1)–O(1A)	1.839(2)	Al(2)–O(1)	2.182(3)
Al(2)–C(13)	1.979(5)	Al(2)–C(30)	1.983(10)
P(1)–O(1)	1.578(3)		

Atoms	Angle	Atoms	Angle
O(1)–P(1)–C(1)	105.9(2)	C(1)–P(1)–C(7)	106.7(2)
O(1)–P(1)–C(7)	107.1(2)	O(1)–P(1)–C(13)	100.7(2)
C(1)–P(1)–C(13)	117.5(2)	C(7)–P(1)–C(13)	117.7(2)
O(2)–P(2)–C(13)	111.8(2)	O(2)–P(2)–C(14)	105.4(2)
C(13)–P(2)–C(14)	113.2(2)	O(2)–P(2)–C(20)	106.3(2)
C(13)–P(2)–C(20)	114.2(2)	C(14)–P(2)–C(20)	105.1(2)
O(2)–Al(1)–C(26)	109.2(3)	O(2)–Al(1)–C(28)	111.4(3)
C(26)–Al(1)–C(28)	116.3(3)	O(2)–Al(1)–O(1A)	99.2(1)
C(26)–Al(1)–O(1A)	106.9(2)	C(28)–Al(1)–O(1A)	112.4(2)
O(1)–Al(2)–C(13)	73.8(1)	C(13)–Al(2)–C(30)	130.2(5)
O(1)–Al(2)–C(30)	101.3(6)	O(1)–Al(2)–O(1A)	163.9(2)
O(1)–Al(2)–C(13A)	98.0(1)	C(30)–Al(2)–O(1A)	94.5(6)
C(30)–Al(2)–C(13A)	110.4(5)	C(13)–Al(2)–C(13A)	119.4(3)
P(1)–O(1)–Al(1A)	142.4(2)	P(1)–O(1)–Al(2)	90.4(1)
P(2)–O(2)–Al(1)	146.8(2)	Al(2)–O(1)–Al(1A)	123.1(2)
P(1)–C(13)–Al(2)	95.1(2)	P(1)–C(13)–P(2)	136.5(3)
Al(1)–C(26)–C(27)	122.9(5)	P(2)–C(13)–Al(2)	126.7(3)
Al(2)–C(30)–C(31)	115.4(11)	Al(1)–C(28)–C(29)	121.1(7)

C–Al–C bond angle of the AlC_3 plane is 120.0(5)°. The coordination of Al2 may thus be described as trigonal bipyramidal. The Al2–O1 bond distance of 2.182(3) Å must be considered quite long while the Al2–C13 and Al2–C30 distances of 1.979(5) Å and 1.983(10) Å, respectively, are within the normal range for organoaluminum fragments. It is reasonable to assume resonance stabilized double bond character in P1–C13 and P2–C13 with distances of 1.672(4) Å and 1.683(3) Å, respectively. The core of the molecule is shown in Figure 2. As only the simple 1:2 addition product was observed when trimethylaluminum was allowed to react with bis(diphenylphosphino)methane[11] it is therefore logical that the observed lability of the central methylene hydrogen atoms of bis(diphenylphosphinoyl)methane is due to the increased acidity resulting from the two oxygen atoms.

In spite of the substantial steric demands of an ethylaluminum fragment and two diethylaluminum fragments, the general structure of the title compound and the methyl derivative[9] are quite similar. Indeed, crystals of the two compounds are isostructural, crystallizing in the same space group with nearly identical unit cell parameters. The axial O–Al–O bond angle of 163.9(2)° for the ethyl derivative reported herein is virtually identical to that of the methyl analogue (163.3(2)°).

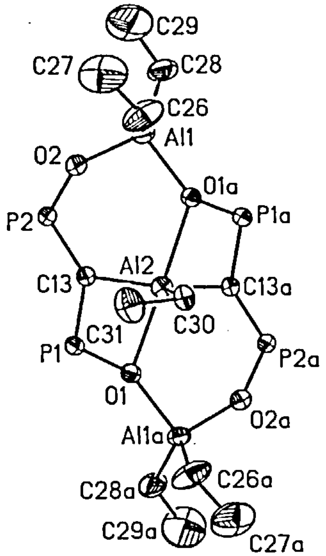

FIGURE 2 A view of the core of the $[Al(C_2H_5)][(Ph_2P(O))_2C]_2[Al(C_2H_5)_2]_2$ molecule.

Importantly, the Al2–C30 bond distance of 1.983(10) Å is within the expected range of other five-coordinate alkylaluminum fragments.[13–16] Indeed, this 1.983(10) Å distance is shorter than that reported for the methyl derivative (1.994(10) Å).

It has become increasingly obvious that the chalcogen derivatives of bis(diphenylphosphino)methane represents a rich and intriguing organoaluminum chemistry. Related studies are proceeding.

ACKNOWLEDGEMENTS

We are grateful to the National Science Foundation for support of this work to G.H.R. (RII-8520554).

SUPPLEMENTARY MATERIAL AVAILABLE

Tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters (8 pages) and a listing of observed and calculated structure factors (14 pages) are available from G.H.R.

REFERENCES

1. N. Van Order, Jr., *J. Am. Chem. Soc.*, **109**, 5680 (1987).
2. M.O. Albers, D.C. Liles, D.J. Robinson and E. Singleton, *Organometallics*, **6**, 2179 (1987).
3. B. Delavaux, B. Chaudret, G. Dahan and R. Pollblanc, *Organometallics*, **4**, 935 (1985).

4. B. Chaudret, F. Dahan and S. Saba, *Organometallics*, **4**, 1490 (1985).
5. J.A. Iggo, D.P. Markham, B.L. Shaw and M. Thornton-Pett, *Chem. Comm.*, 432 (1985).
6. H. Schmidbaur, S. Lauteschäger and G. Müller, *J. Organomet. Chem.*, **281**, 25 (1985).
7. T. Kagawa and H. Hashimoto, *Bull. Chem. Soc. Jpn.*, **45**, 1739 (1972).
8. T. Kagawa, Y. Inoue and H. Hasimoto, *Bull. Chem. Soc. Jpn.*, **43**, 1250 (1970).
9. G.H. Robinson, B. Lee, W.T. Pennington and S.A. Sangokoya, *J. Am. Chem. Soc.*, **110**, 6260 (1988).
10. G.M. Sheldrick, SHELXTL, Crystallographic Computing System, Revision 5.1, Nicolet Instruments Division: Madison, WI (1986).
11. G.H. Robinson, M.F. Self, S.A. Sangokoya and W.T. Pennington, *J. Crystallogr. Spectrosc. Res.*, **18**, 285 (1988).
12. A.W. Laubengayer, J.D. Smith, and G.G. Ehrlich, *J. Am. Chem. Soc.*, **83**, 542 (1961).
13. G.H. Robinson, F. Moise, W.T. Pennington and S.A. Sangokoya, *Polyhedron*, **8**, 1279 (1980).
14. G.H. Robinson, S.A. Sangokoya, F. Moise and W.T. Pennington, *Organometallics*, **7**, 1887 (1988).
15. G.H. Robinson and S.A. Sangokoya, *J. Am. Chem. Soc.*, **110**, 1494 (1988).
16. G.H. Robinson and S.A. Sangokoya, *J. Am. Chem. Soc.*, **109**, 6852 (1988).