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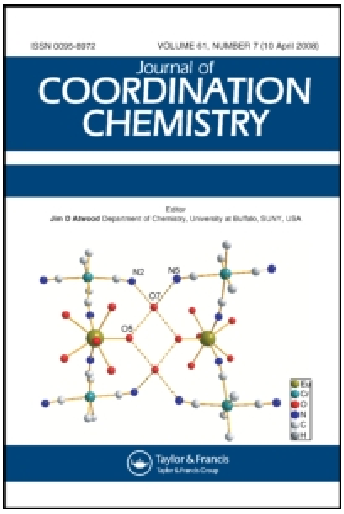

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REACTION OF DIISOBUTYLALUMINUM HYDRIDE WITH BIS(DIPHENYLPHOSPHINOYL)ETHANE. SYNTHESIS AND STRUCTURE OF $[Al(C_4H_9)_3]_2[dppe]$

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Reaction of an excess of diisobutylaluminum hydride with bis(diphenylphosphinoyl)ethane (dppe-O_2), the di-oxygen derivative of bis(diphenylphosphino)ethane (dppe), in heptane affords the crystalline product $[Al(C_4H_9)_3]_2[dppe]$. The title compound crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters $a = 9.514(3)$, $b = 10.417(4)$, $c = 13.364(4)$ Å, $\alpha = 97.67(3)$, $\beta = 102.09(2)$, $\delta = 95.49(3)°$, $V = 1273.1(7)$ Å^3, and $D_c = 1.04$ g cm^{-3} for $Z = 1$. Least-squares refinement based on 2455 observed reflections ($I > 3\sigma(I)$) converged at $R = 0.059$, $R_w = 0.070$. The title compound results from a unique reaction wherein dppe and triisobutylaluminum were generated *in situ* from dppe-O_2 and diisobutylaluminum hydride, respectively.

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

INTRODUCTION

Although the organo–transition metal chemistry of the bidentate phosphine ligands bis(diphenylphosphino)methane[1-6] and bis(diphenylphosphino)ethane has been extensively explored,[7-10] the corresponding organo–main group chemistry of these ligands has not developed in parallel. Moreover, the literature reveals a paucity of structural studies concerning the interactions of main group metals with chalcogen derivatives of these bidentate phosphine ligands. Herein we report the synthesis and structure of $[Al(C_4H_9)_3]_2[dppe]$ isolated from reaction of bis(diphenylphosphinoyl)-ethane (dppe-O_2), the di-oxygen derivative of bis(diphenylphosphino)ethane (dppe), with diisobutylaluminum hydride. The formation of $[Al(C_4H_9)_3]_2[dppe]$ is quite interesting in that the reaction of dppe and triisobutylaluminum, generated *in situ*, from dppe-O_2 and diisobutylaluminum hydride, respectively, resulted in the title compound.

EXPERIMENTAL

General

Owing to the extreme air- and water-sensitivity of both diisobutylaluminum hydride and the title compound, the exclusion of oxygen and moisture from the synthesis and subsequent manipulations was essential. To this end, standard Schlenk technique

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was employed in conjunction with an inert atmosphere drybox (Vacuum Atmospheres HE-43 Dri-Lab). Heptane was distilled from CaH_2 under an atmosphere of argon prior to use. Diisobutylaluminum hydride, purchased from Aldrich Chemical Co., was used as received. Bis(diphenylphosphinoyl)ethane was prepared in our laboratory.[11] X-ray diffraction data were collected on a Nicolet R3m/V diffractometer. NMR data were recorded on a JEOL FX-90Q spectrometer or on an IBM 200 MHz spectrometer as indicated.

Synthesis of $[Al(C_4H_9)_3]_2[dppe]$

A glass reaction vessel was charged with bis(diphenylphosphinoyl)ethane (1.16 mmol) and brought into the drybox where heptane (10 cm^3) was added. Diisobutylaluminum hydride (5.10 mmol) was slowly added *via* syringe. Reaction was immediate and quite exothermic resulting in a colourless homogeneous solution. The reaction vessel was removed from the drybox and heated in an oil bath at 150°C for 24 hours. After cooling, the solution was transferred, *via* cannula, to a 100 cm^3 Schlenk flask and concentrated under vacuum. Cooling to −15°C for 48 hours resulted in colourless, air-sensitive crystals (80% yield based on the phosphine ligand); m.p. 101–102°C. ^{1}H NMR (JEOL FX-90Q) ($CDCl_3$): δ 0.381 (d, 12H, Al-$C\mathit{H}_2$-$CH(CH_3)_2$), 0.834 (d, 36H, Al-CH_2-$CH(C\mathit{H}_3)_2$), 1.73 (m, 6H, Al-CH_2-$C\mathit{H}(CH_3)_2$), 2.16 (t, 4H, P-CH_2CH_2-P), 7.24 (m, 20H, C_6H_5). ^{31}P{H} NMR (IBM 200 MHz) ($CDCl_3$), H_3PO_4 external reference: δ −12.057 (s, P-CH_2CH_2-P).

TABLE I
Summary of the crystallographic data for $[Al(C_4H_9)_3]_2[dppe]$.

Empirical formula	$C_{50}H_{78}Al_2P_2$
Molecular weight	795.18
Colour; habit	colourless; parallelepiped
Size	0.50 × 0.30 × 0.25 mm
Space group	Triclinic, $P\bar{1}$
Unit cell dimensions	
a, Å	9.514(3)
b, Å	10.417(4)
c, Å	13.364(4)
α, deg	97.67(3)
β, deg	102.09(2)
γ, deg	95.49(3)
Cell volume, Å^3	1273.1(7)
Z	1
D_c/g cm^{-3}	1.04
Diffractometer	Nicolet R3m/V
Radiation	Mo-$K\alpha$ ($\lambda = 0.71073$)
Temperature	21°C
2θ range	3.50 to 45.0°
Reflections collected; unique	3579; 3355 ($R_{merge} = 0.038$)
Reflections observed	2455 ($I > 3\sigma(I)$)
GOF	2.21
R	0.059
R_w	0.070

TABLE II
Atomic coordinates (× 10^4) and equivalent isotropic thermal parameters ($Å^2$ × 10^3) for $[Al(C_4H_9)_3]_2[dppe]$.

	x/a	*y/b*	*z/c*	*U(eq)**
P(1)	3863(1)	450(1)	8467(1)	42(1)
Al(1)	3285(1)	−1779(1)	7300(1)	50(1)
C(1)	4565(4)	1788(4)	7883(3)	50(2)
C(2)	5983(5)	2354(5)	8154(4)	76(2)
C(3)	6450(7)	3324(6)	7650(5)	101(3)
C(4)	5510(9)	3736(6)	6861(5)	102(3)
C(5)	4118(8)	3191(6)	6606(4)	91(3)
C(6)	3641(6)	2227(5)	7098(3)	69(2)
C(7)	2362(4)	1072(4)	8945(3)	44(1)
C(8)	963(5)	473(5)	8512(4)	75(2)
C(9)	−178(5)	946(6)	8861(5)	99(3)
C(10)	46(6)	1964(6)	9650(4)	87(3)
C(11)	1415(6)	2550(5)	10088(4)	78(2)
C(12)	2571(5)	2114(5)	9730(3)	65(2)
C(13)	5253(4)	454(4)	9656(3)	48(2)
C(14)	2052(5)	−1355(5)	6021(3)	68(2)
C(15)	1515(12)	−2404(9)	5142(6)	223(6)
C(16)	418(9)	−1999(9)	4254(5)	192(5)
C(17)	1777(9)	−3635(7)	5036(5)	143(4)
C(18)	5255(5)	−2256(5)	7316(4)	73(2)
C(19)	6132(8)	−1853(11)	6629(8)	167(5)
C(20)	7565(6)	−2447(8)	6714(6)	141(4)
C(21)	6063(8)	−747(8)	6175(6)	139(4)
C(22)	2102(5)	−2792(5)	8083(4)	67(2)
C(23)	2187(5)	−4243(5)	8058(4)	69(2)
C(24)	821(6)	−4998(6)	8208(5)	107(3)
C(25)	3512(6)	−4494(6)	8867(4)	95(3)

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

Structural solution and refinement

A colourless parallelepiped crystal of $[Al(C_4H_9)_3]_2[dppe]$ was mounted in a thin-walled glass capillary under an inert atmosphere of argon. Cell dimensions and an orientation matrix for data collection, obtained from a least-squares refinement of the settings angles of 30 carefully centred reflections in the range $15.43 < 2\theta < 29.04°$, corresponded to a triclinic cell with parameters $a = 9.514(3)$, $b = 10.417(4)$, $c = 13.364(4)$ Å, $\alpha = 97.67(3)$, $\beta = 102.09(2)$, $\delta = 95.49(3)°$, $V = 1273.1(7)$ $Å^3$, and $D_c = 1.04$ g cm^{-3} for $Z = 1$. The space group was determined to be $P\bar{1}$ (No. 2). The structure was solved by direct methods and refined, based on 2455 observed reflections with intensities $I > 3\sigma(I)$, using SHELXTL.[12] Non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were located by standard difference Fourier techniques, and were included in the structure factor calculations at idealized positions ($d_{C-H} = 0.96$ Å). Isotropic group thermal parameters were refined for the phenyl and methylene bridge-head hydrogen atoms ($U_{iso} = 0.082(4)$), the isobutyl methylene hydrogen atoms ($U_{iso} = 0.13(1)$), the isobutyl methyne hydrogen atoms ($U_{iso} = 0.19(2)$), and the isobutyl methyl hydrogen atoms ($U_{iso} = 0.23(1)$). The weighting scheme was based on counting statistics and included a factor ($p = 0.0003$) to downweight the intense reflections. The maximum peaks on the final difference map correspond to 0.36 and −0.34 e/Å^3, respectively. Refinement converged at $R = 0.059$ ($R_w = 0.070$). Relevant crystallographic data are given in Table I. Final coordinates are given in Table II.

RESULTS AND DISCUSSION

The great versatility of the bidentate phosphine ligands bis(diphenylphosphino)-methane and bis(diphenylphosphino)ethane has long been recognized in transition metal chemistry.[1-10] Importantly, the organo–main group chemistry of these ligands, particularly that of their oxygen and sulfur derivatives, remains largely unexplored. This laboratory recently initiated investigations into the organo-aluminum chemistry of these ligands.

While our initial investigation into this chemistry described the synthesis and structure of the $[Al(CH_3)_3]_2[dppm]$ adduct, isolated from reaction of the bidentate phosphine ligand with trimethylaluminum,[13] subsequent experiments with oxygen and sulfur derivatives of dppm proved quite intriguing. We recently reported the synthesis and structure of $[Al(CH_3)][dppm\text{-}O_2]_2[Al(CH_3)_2]_2$, isolated from reaction of trimethylaluminum with dppm-O_2.[14] This product proved quite interesting in that, unlike the $[Al(CH_3)_3]_2[dppm]$ compound, condensation occurred as both methylene hydrogen atoms of the central carbon atom of each ligand were cleaved along with four Al–CH_3 bonds (thereby eliminating methane). This compound was also intriguing due to the penta-coordination of the central aluminum atom in the compound. The triethylaluminum analogue has recently been reported.[15] The isolation of these products further piqued our curiosity regarding the organoaluminum chemistry of the chalcogen derivatives of bidentate phosphine ligands and prompted us to examine the di-thio derivative of dppm, bis)diphenylthiophosphino)methane (dppm-S_2). Reaction of diisobutylaluminum hydride with dppm-S_2 afforded the novel $[Al(C_4H_9)]_2[dppm\text{-}S][Al(C_4H_9)_2S]_2$ product.[16] This compound, resulting from a unique condensation reaction involving the reduction of both P=S bonds and the subsequent cleavage of Al–H, Al–R, and S–P, and C–H bonds, contained a rare Al_2S_2 core.

In an effort to assess the effects of the hydrocarbon bridge in these systems ($-CH_2-$ *versus* $-CH_2CH_2-$) on the reactivity, diisobutylaluminum hydride was allowed to react with dppe-O_2; $[Al(C_4H_9)_3]_2[dppe]$ was the only product isolated. As can be seen from the X-ray crystal structure of $[Al(C_4H_9)_3]_2[dppe]$ (Figure 1), the title compound resides about a crystallographic inversion centre which lies at the centre of the C(13)–C(13a) bond. The independent Al(1)–P(1) bond distance of 2.560(2) Å is within the expected range for aluminum–phosphorus adducts.[13,16,17]

The mechanism leading to the title compound is worthy of note. It is proposed that the first step in the process involves reduction of both P=O fragments of the bidentate phosphine ligand by diisobutylaluminum hydride (Figure 2). The water generated reacts stoichiometrically with remaining diisobutylaluminum hydride to produce the organoaluminum–dioxygen dimer (A). Similar aluminum–oxygen Al_2O_2 dimeric species have been previously reported.[18,19] Indeed, the sulfur analogue of (A) has recently been observed in the condensation product of dppm-S_2 and diisobutyl-aluminum hydride.[16] It is reasonable that one alkyl group of each of the two four-coordinate aluminum atoms subsequently serves as an alkyl bridge to the two

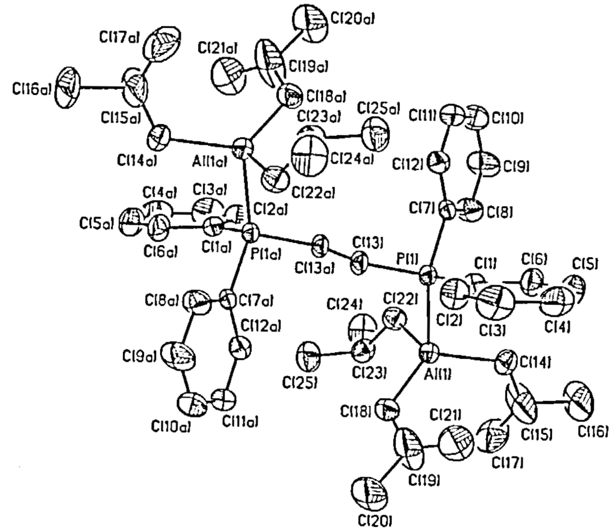

FIGURE 1 A view of the $[Al(C_4H_9)_3]_2[dppe]$ molecule showing the atom labelling scheme. Thermal ellipsoids show 30% probability levels; hydrogen atoms have been omitted. Selected bond distances (Å) and angles (deg): Al(1)–P(1), 2.560(2); Al(1)–C(14), 1.989(5); Al(1)–C(18), 1.982(5); Al(1)–C(22), 2.009(5); P(1)–C(1), 1.825(5); P(1)–C(7), 1.821(4); P(1)–C(13), 1.842(4); C(13)–C(13a), 1.518(8); Al(1)–P(1)–C(1), 115.2(1); Al(1)–P(1)–C(7), 116.2(1); Al(1)–P(1)–C(13), 112.6(1); C(14)–Al(1)–C(18), 121.0(2); C(14)–Al(1)–C(22), 111.3(2); C(18)–Al(1)–C(22), 116.3(2); P(1)–C(13)–C(13a), 111.9(3); C(1)–P(1)–C(7), 103.5(2); C(1)–P(1)–C(13), 104.3(2); C(7)–P(1)–C(13), 103.7(2).

$$Ph_2P(O)CH_2CH_2(O)PPh_2 \xrightarrow{(i\text{-}Bu)_2AlH} Ph_2PCH_2CH_2PPh_2 + 2H_2O$$

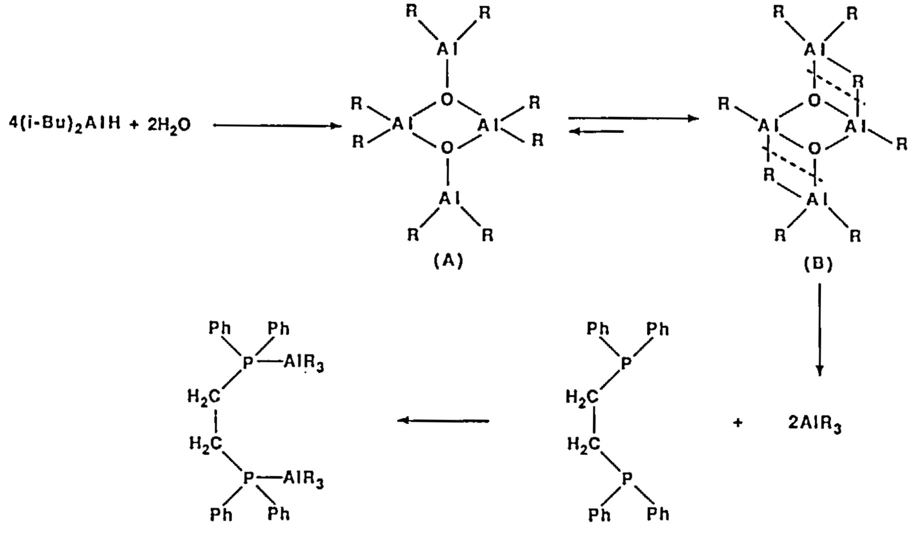

FIGURE 2 Proposed mechanism for the formation of $[Al(C_4H_9)_3]_2[dppe]$.

formerly three-coordinate aluminum atoms as indicated in (**B**). Bridge cleavage of the Al-O and Al-R fragments as indicated in (**B**) (dashed lines) would provide the required two units of triisobutylaluminum. Subsequent reaction of triisobutylaluminum with dppe would readily provide $[Al(C_4H_9)_3]_2[dppe]$.

It is evident that the oxygen and sulfur derivatives of bidentate phosphine ligands exhibit substantially different reactivities with organoaluminum species. Future contributions will further address the effects of the hydrocarbon bridge in these bidentate phosphine ligands.

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SUPPLEMENTARY MATERIAL AVAILABLE

Summary of data collection and refinement (4 pages), tables of atomic coordinates, bond distances and angles, thermal parameters (9 pages), and observed and calculated structure factors (12 pages) are available from the authors.

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