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Tris[*o*-((diphenylphosphino)methyl)phenyl]aluminum: An Unusual Organoaluminum Complex with Five-Coordinate (C_3P_2) Trigonal-Bipyramidal Aluminum

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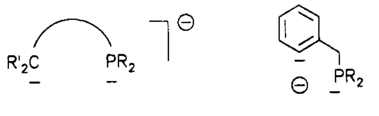
Summary: The organoaluminum complex Al[*o*-(Ph_2PCH_2)C_6H_4]$_3$ (Ph = phenyl) is obtained from $AlCl_3$ and the lithiated ligand in diethyl ether. As shown by ^{27}Al NMR spectroscopy, it exhibits a pentacoordinate aluminum center (δ(^{27}Al) = 131 ppm, $w_{1/2}$ = 12 kHz). An X-ray structure analysis reveals a trigonal-bipyramidal coordination at aluminum with a donor set comprised of three carbon atoms in the equatorial plane and two of the three phosphino functions in axial positions with exceedingly long Al–P bonds (2.676 (3)/2.782 (2) Å; $C_{57}H_{48}AlP_3$·1.25(toluene), triclinic, space group $P\bar{1}$ (No. 2), a = 12.482 (2) Å, b = 16.137 (3) Å, c = 17.144 (2) Å, α = 62.61 (1)°, β = 88.08 (1)°, γ = 67.28 (1)°, V = 2784.0 Å^3, R (R_w) = 0.094 (0.091), $w = 1/\sigma^2(F_o)$ for 463 refined parameters). The coordination geometry is achieved by two of the anionic phosphines acting as chelating ligands, spanning equatorial (C atom) and axial sites (P atom), while the third phosphine is only carbon-bonded. Al[*o*-(Ph_2PCH_2)C_6H_4]$_3$ is the first triorganoaluminum bis(phosphine) adduct where C_3P_2 pentacoordination at aluminum has been definitely proven for both the solution and the solid state.

Neutral pentacoordinate aluminum donor adducts of the type AlX_3L_2 (L = Lewis base; X = halogen, alkyl, hydrogen) are well established with donors containing "hard" donor sites, particularly nitrogen.[2,3] Well-characterized bis(phosphine) adducts seem to be limited to $AlCl_3(PMe_3)_2$.[4] Recently also stable 1:2 alane–phosphine adducts could be described for the first time.[5] Fivefold coordination in triorganoaluminum phosphine adducts has been claimed for 1:1 diphosphine adducts,[6] but recent evidence obtained on $Ph_2PCH_2PPh_2(AlMe_3)$ only points to a highly fluxional molecule in solution with tetracoordinate aluminum even at −80 °C.[7]

In contrast to neutral phosphines, anionic phosphines have been shown to be good phosphorus ligands even to p-block metals.[8] Phosphinomethanides, where the carbanionic function is directly connected to the phosphino group, have been successfully employed for this purpose and show a rich and varied coordination chemistry to main-group metals.[9] Far less is known about the complexation behavior of anionic phosphines of type A toward main-group elements (Chart I).[10,11] In A the carbanionic function is not directly connected to phosphorus, whereby the chelating ability of these P,C-difunctional ligands should be drastically improved, giving rise to the formation of novel heterocycles of different ring size. A particularly good candidate for main-group element complexation should be B, as these ligands are expected to form five-membered rings upon complexation. Ligands of type B were first introduced by Abicht and Issleib[12] and used mainly for the preparation of late-transition-metal complexes.[10,13,14] As the first results of an investigation of the complexation behavior of B toward group 13 elements we report here on an Al(III) complex of B (R = Ph).

Chart I



A B (R = Ph, Me)

Al[*o*-(Ph_2PCH_2)C_6H_4]$_3$ (2) may be prepared in 80.2% yield from $AlCl_3$ and the lithiated ligand 1 in a 1:3 molar ratio in diethyl ether at room temperature.[15] According to its NMR spectra (^{1}H, ^{13}C, ^{31}P), 2 is a highly fluxional molecule, giving rise to only one set of signals for the ligand atoms between 310 and 243 K. In particular, in the ^{31}P NMR spectrum a single line is observed in this temperature range (δ(^{31}P) = −13.5/−14.2 ppm at 310/243 K, re-

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[15] 2 is obtained as colorless crystals (from toluene); mp 373 K dec. *Selected NMR data* (ppm referred to internal $SiMe_4$ or external 85% H_3PO_4; benzene-d_6 or toluene-d_8; 310 K): 250-MHz ^{1}H NMR (Bruker WM 250) δ 3.7 (s, CH_2), 6.7–7.2 (m, phenyl H), 8.2 (d, ^3J(HH) = 6.8 Hz, H16, H26, H36; see Figure 1 for atom numbering); 100.6-MHz ^{13}C NMR (JEOL JNM GX400) δ 37.4 (s, CH_2), 125.5–145.8 (m, phenyl and cocrystallized toluene); 161.9-MHz ^{31}P NMR (Bruker AMX 400) δ −13.5 s (see text for low-temperature spectra). The 104.2-MHz ^{27}Al NMR spectra (Bruker AMX 400) are referenced to an external saturated solution of Al(acac)$_3$ in benzene-d_6. See text for details.

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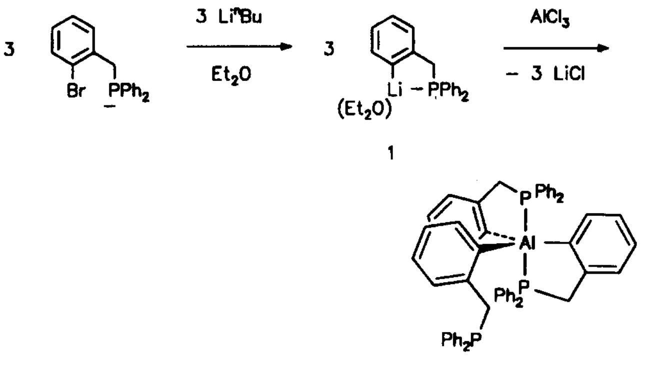

2

spectively). At T = 193 K this resonance splits up and two signal groups in an intensity ratio of 1:2 appear. A single broad line is observed at −12.3 ppm, while two broad, not entirely resolved lines are found at ca. −15.0 and −15.8 ppm.[16] From these data the free activation energy ($\Delta G^{\ddagger}$) of the exchange process may be estimated at 39 kJ/mol.[17] With $\delta(^{31}P)$ = −10.1 ppm at 193 K for uncomplexed diphenylbenzylphosphine, the shifts upon coordination[18] are −2.2 and −5.7 ppm for the low-temperature resonances of **2**, respectively. Small negative shifts upon coordination seem to be typical for the phosphorus resonances of phenyl- and benzylphosphines coordinated to trimethylaluminum.[19] Although this clearly points to two different types of phosphorus atoms in **2**, a conclusion about the actual number of coordinated phosphorus atoms is not unambiguous.[20]

This question is solved by means of ^{27}Al NMR spectroscopy. In toluene/toluene-d_8 at 368 K a broad ^{27}Al resonance at 131 ppm ($w_{1/2}$ = 12 kHz) is detectable. Shift and line width strongly indicate a 5-fold coordination at aluminum, which means that two of the three phosphino groups are metal-complexed. For dimeric diorganoaluminum compounds characteristic ^{27}Al shifts around 160 ppm have been previously observed for tetracoordinate aluminum; for aluminum with coordination number 5 the respective values are centered around 120 ppm, while octahedral complexes (with O-donor ligands) have shifts around 0 ppm.[21,22] The low solubility of **2** even at higher temperatures and large line widths due to the molecular dimensions make the recording of the ^{27}Al NMR spectra at higher temperatures mandatory.[23] Previous work amply demonstrates that $\delta(^{27}Al)$ clearly reflects the coordination number even at temperatures where for highly dynamic molecules like **2** ^{1}H and ^{13}C NMR spectra show only averaged signals.[21]

To our knowledge, **2** is the first pentacoordinate aluminum species with a donor set comprised of three carbon and two phosphorus atoms. Details of the coordination

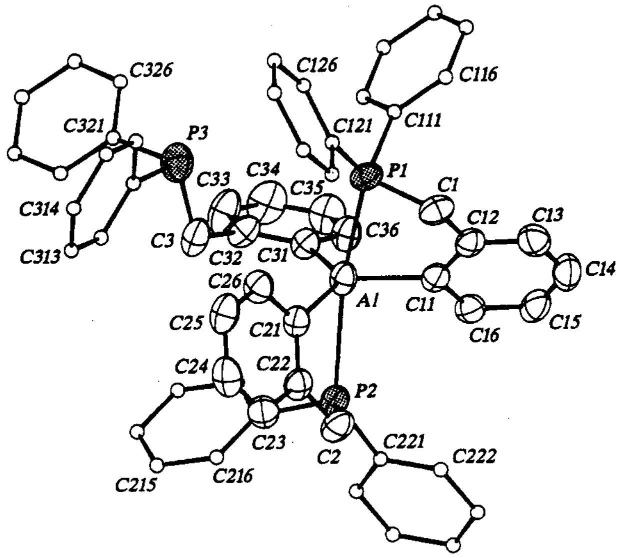

Figure 1. Molecular structure of **2** in the solid state and atomic numbering scheme adopted (ORTEP, displacement ellipsoids at the 50% probability level; P–phenyl carbon atoms with arbitrary radii for clarity; hydrogen atoms omitted). Important bond distances (Å) and angles (deg): Al–P1 = 2.676 (3), Al–P2 = 2.782 (2), Al···P3 = 4.440 (6), Al–C11 = 2.009 (6), Al–C21 = 2.029 (6), Al–C31 = 1.996 (6); P1–Al–P2 = 164.8 (1), C11–Al–C21 = 120.0 (2), C21–Al–C31 = 125.2 (2), C31–Al–C11 = 114.4 (2), Al–P1–C1 = 89.9 (2), Al–P2–C2 = 89.7 (2), P1–C1–C12 = 109.6 (5), P2–C2–C22 = 109.4 (3), P3–C3–C32 = 110.9 (4).

geometry at the aluminum center are given by an X-ray structure determination.[24] A trigonal-bipyramidal (tbp) aluminum coordination with three carbon atoms in the equatorial plane and two phosphorus atoms in axial positions is observed in the solid state. The third phosphino group remains uncoordinated. Thus, two of the *o*-(phosphinomethyl)phenyl ligands act as chelating ligands to aluminum with concomitant formation of five-membered rings, while the third one is only carbon-bonded. Slight deviations from an ideal tbp geometry may be accounted for by the five-membered-ring formation, in particular the intra-ring angles P–Al–C_{ipso} (79.2 (2)/76.8 (2)°) and subsequently also P1–Al–P2, which deviates noticeably from linearity (164.8 (1)°). The five-membered rings are in almost ideal envelope conformations, the envelope planes being Al, C11, C12, C1 (torsion angle 5.0 (3)°) and Al, P1, C1 for one ring and Al, C21, C22, C2 (torsion angle 1.8 (3)°) and Al, P2, C2 for the second ring. The respective dihedral

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[16] A possible coupling of the two inequivalent ^{31}P nuclei is probably hidden by the broad line widths.

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[23] At T = 353 K: $\delta(^{27}Al)$ = 130 ppm, $w_{1/2}$ = 13 kHz.

[24] Crystal structure data: Enraf-Nonius CAD4 diffractometer, Mo Kα radiation, λ = 0.710 69 Å, graphite monochromator, 298 K, **2**·1.25(toluene), $C_{57}H_{48}AlP_3 \cdot 1.25C_7H_8$, M_r = 968.098, triclinic, space group $P\bar{1}$ (No. 2), a = 12.482 (2) Å, b = 16.137 (3) Å, c = 17.144 (2) Å, α = 62.61 (1)°, β = 88.08 (1)°, γ = 67.28 (1)°, V = 2784.0 Å^3, D_c = 1.155 g/cm^3, μ(Mo Kα) = 1.5 cm^{-1}, F(000) = 1021. A total of 14 661 reflections were measured, 14 160 of which were unique and 8199 with $F_o \geq 6.0\sigma(F_o)$ were considered "observed" (R_{int} = 0.014, $((\sin\vartheta)/\lambda)_{max}$ = 0.703 Å^{-1}, hkl range ±17, ±22, −22, $\vartheta/2\vartheta$ scans, $\Delta\omega$ = 0.6 + 0.35 tan ϑ). Lorentz–polarization corrections were applied; corrections for crystal decay (−1.6%) and for absorption were not considered necessary. The structure was solved by direct methods (SHELXS-86). All H atoms were introduced at idealized geometrical positions; those at the heavily disordered cocrystallized toluene molecules were neglected, as were their methyl groups. R (R_w) = 0.094 (0.091) ($w = 1/\sigma^2(F_o)$) for 463 refined parameters (anisotropic, H atoms constant, P–phenyl rings as rigid, idealized hexagons, two of them with isotropic displacement parameters, SHELX-76). $\Delta\rho_{fin}$(max/min) = +0.96/−0.69 e/Å^3. The refinement was badly hampered by the severe disorder of the several incorporated, loosely packed toluene molecules and by a slight disorder of some of the phenyl rings which could not be resolved. The applied constrained refinement was necessary because of this disorder. Crystallization from other solvents failed. Apparently, the incorporation of toluene molecules is mandatory to obtain suitable single crystals (compare also the relatively low density of the crystals). See the note at the end of the paper for supplementary material.

angles are 137.5 and 137.7°. The observed envelope conformations are clearly a result of the exceedingly long Al–P bonds (2.676 (3)/2.782 (2) Å), which have no precedent in the literature.[25] Their slight but significant inequality reflects the steric congestion around the aluminum center, the effect of which should be especially pronounced because of the inherent weakness of the Al–P bonds. These weak Al–P bonds also account for the extremely rapid fluxionality of **2**.

In conclusion, all spectroscopic and structural results for **2** are consistent with C_3P_2 pentacoordination at aluminum both in solution as in the solid state. The structural details not only reveal a tbp geometry but also indicate a rather weak Al–P bonding.

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Supplementary Material Available: Complete tables of atomic coordinates, displacement parameters, and bond distances and angles (19 pages). Ordering information is given on any current masthead page.

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Articles

Kinetics and Mechanism of Biaryl Reductive Elimination from Electron-Poor $[(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2]Pt(Ar)_2$ Complexes

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The syntheses and elimination properties of electron-deficient (fluoroaryl)- and (fluoroalkyl)phosphine complexes of platinum are described. Treatment of (cod)$PtCl_2$ with $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (dfppe) or $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ (dfepe) at elevated temperatures gives the dichlorides (dfepe)$PtCl_2$ (**1**) and (dfppe)$PtCl_2$ (**2**) in high yield. The diaryls (dfppe)$Pt(Ph)_2$ (**3**) and (dfppe)Pt(*p*-tol)$_2$ (**4**) and the dialkyls (dfppe)$Pt(Me)_2$ (**5**) and (dfepe)$Pt(Me)_2$ (**6**) are prepared by metathesis of **1** or **2** with the appropriate Grignard reagent. Thermolysis of the diphenyl complex **3** cleanly yields biphenyl as the sole observed organic elimination product. No organic products derived from ancillary ligand degradation are observed. The fate of the released metal fragment is solvent-dependent, with the bis chelate $(dfppe)_2Pt$ (**7**) being the major product in noncoordinating aromatic solvents. The crystal structure of **7** has been determined. Crossover labeling studies for **3** and the regiospecific formation of 4,4′-dimethylbiphenyl from the thermolysis of **4** confirm that these elimination reactions proceed via an intramolecular 1,1′-coupling process. Elimination kinetics for **3** and **4** are conveniently followed by ^1H NMR spectroscopy. Decomposition rates follow first-order behavior in all solvents examined and are independent of added phosphine concentration. The rate of biphenyl reductive elimination from **3** is found to be inversely proportional to solvent polarity, varying by almost a factor of 10 between benzene ($\epsilon = 2.28$, $k = [2.44\ (5)] \times 10^{-4}\ s^{-1}$) and DMSO ($\epsilon = 45.0$, $k = [2.50\ (2)] \times 10^{-5}\ s^{-1}$) media at 100 °C. Entropies of activation obtained in benzene ($\Delta S^{\ddagger} = -1.5 \pm 1$ eu) and DMSO ($\Delta S^{\ddagger} = -1.7 \pm 2$ eu) are essentially equivalent and suggest that there is no significant solvent coordination along the elimination reaction coordinate. The mechanistic interpretation of these results and comparisons with prior group 10 elimination studies are discussed.

Introduction

Transition-metal-mediated carbon–carbon bond formation is a pivotal step in many organometallic transformations.[1] Accordingly, the elementary process of reductive elimination from late-transition-metal dialkyl and diaryl complexes has been the focus of numerous mechanistic[2-8] and theoretical[8,9] investigations. Despite the

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