Phosphorus–Carbon Compounds

Selective Preparation of the $[3,5\text{-}t\mathrm{Bu}_2\text{-}1,2,4\text{-}\mathrm{C}_2\mathrm{P}_3]^-$ Ion and Synthesis and Structure of the Cationic Species *nido*-$[3,5\text{-}t\mathrm{Bu}_2\text{-}1,2,4\text{-}\mathrm{C}_2\mathrm{P}_3]^+$, Isoelectronic with $[\mathrm{C}_5\mathrm{R}_5]^+$[**]

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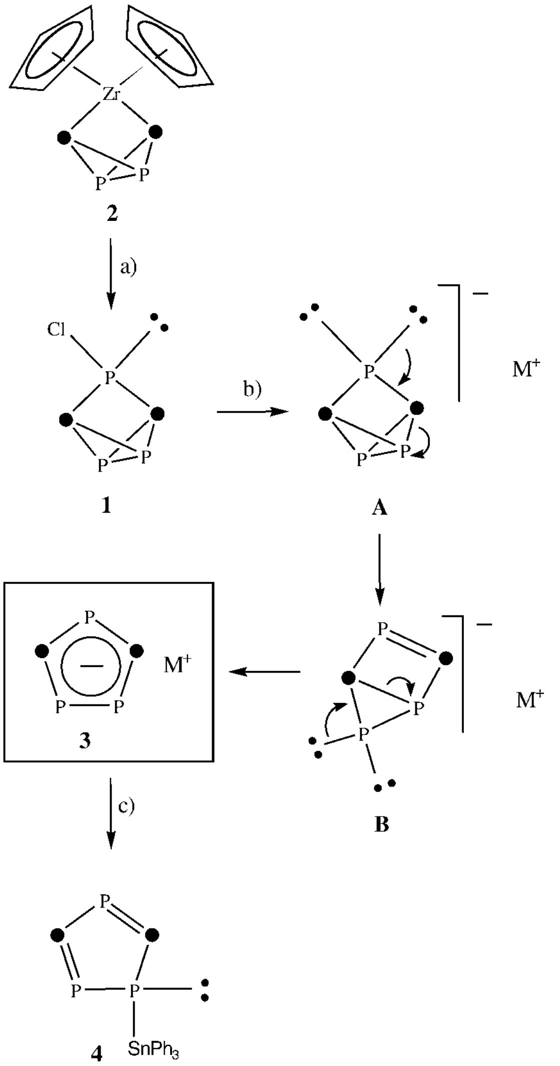
Dedicated to Professor Manfred Regitz

There has been significant progress in the chemistry of transition-metal complexes carrying the η^5-3,5-tBu$_2$-1,2,4-C$_2$P$_3$ ligand.[1] Although the isolobal relationship P↔CH and diagonal relationship P/C suggest that complexes carrying this ligand should behave like the corresponding η^5-cyclopentadienyl-substituted analogues, recent work has shown that the phosphorus-containing systems exhibit subtle differences in both bonding and reactivity.[2–4] This situation suggests that further investigations could be rewarding. In a new approach to this chemistry we focused on the reactivity of the interesting tricyclic C$_2$P$_3$ compound **1** (Scheme 1), first reported by Regitz et al.[5] First, we used this species as a convenient starting point for a new selective synthetic approach to the aromatic ion $[3,5\text{-}t\mathrm{Bu}_2\text{-}1,2,4\text{-}\mathrm{C}_2\mathrm{P}_3]^-$ (**3**). Second, and again reflecting on the consequences of replacing CH groups by isolobal P atoms, we explored the possibility of utilizing **1** as a precursor to cations $[\mathrm{C}_2t\mathrm{Bu}_2\mathrm{P}_3]^+$, isoelectronic with $[\mathrm{C}_5\mathrm{R}_5]^+$.

The published synthetic pathways to the anion **3**,[6–8] which derive from earlier work by Becker et al.,[9,10] involve reaction of P≡CtBu with alkali metals (M). However, this procedure is unselective, and to obtain pure **3** it is necessary to repeatedly recrystallize the moisture-sensitive alkali-metal salts to remove the second product of these reactions, the $[2,4,5\text{-}t\mathrm{Bu}_3\text{-}1,3\text{-}\mathrm{C}_3\mathrm{P}_2]^-$ ion. Therefore, we recognized that if the full potential of this area was to be realized, it was important to devise a more efficient and selective pathway to **3**. We reasoned that if the tricyclic compound **1**, which is readily formed in good to excellent yield by treating the readily accessible zirconium complex **2** with PCl$_3$,[5] was treated with an alkali metal in THF, the anionic species **A** should be generated (Scheme 1). We then hypothesized that such a species should undergo consecutive ring-opening reactions (**A**→**B**→**3**) and thus selectively provide the desired anion.



Scheme 1. a) PCl$_3$; b) M, THF, −MCl; c) Ph$_3$SnCl, −MCl (● = CtBu; ·· = lone pair; M = Li, Na.

Reaction (RT, 2 h, THF) of **1** with Li or Na metal leads to quantitative formation of the lithium or sodium salt of **3**, which confirms our ring-opening hypotheses. Both Li·**3** and Na·**3** react quantitatively with Ph$_3$SnCl to give the known compound 3,5-tBu$_2$-1-SnPh$_3$-1,2,4-C$_2$P$_3$ (**4**), which has been shown to be a valuable reagent for the syntheses of complexes of the η^5-C$_2$P$_3$ ligand.[7]

We believed that **1** might react with Lewis acids to provide an entry point to the cationic $[\mathrm{C}_2t\mathrm{Bu}_2\mathrm{P}_3]^+$ manifold, related to the isoelectronic pentamethylcyclopentadienyl cation, a species that has recently attracted considerable attention.[11–15] In particular, in view of the isolobal relationship P↔CH, and

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Stohrer and Hoffmann's conclusion[16] that a dynamic Jahn–Teller system of C_{2v} $[CH]_5^+$ ion geometries can be accessed by interaction of an empty p orbital centered on C(3) with the σ* levels of a tricyclo[2.1.0.0^{2,5}]pentane unit, abstraction of a chloride anion from the P–Cl bond of **1** might lead via a phosphenium cation to the formation of the unknown $[C_2tBu_2P_3]^+$ ions and potentially interesting structures.

Our attempt to achieve this by treating **1** with $SbCl_5$ was unsuccessful in that chlorination of the P–P bond occurred to give $SbCl_3$ and the known compound **5** (Scheme 2).[5] However, reaction (20 °C, CH_2Cl_2, 10 min) of **2** with a stoichiometric amount of $AlCl_3$ produced a colorless solution from which a small amount of white precipitate separated. This solid redissolved on gentle warming, and storage of the resulting solution at 20 °C for 24 h furnished colorless crystalline blocks. A single-crystal X-ray diffraction study of this compound showed it to have the Wadeian structure *nido*-$[3,5\text{-}t\mathrm{Bu}_2\text{-}1,2,4\text{-}C_2P_3]^+[AlCl_4]^-$ (**6**) (Figure 1). The molecule is essentially ion-separated, with $[AlCl_4]^-$ ions loosely linked by long-range Cl···P interactions (ranging from 3.37 to 3.58 Å) to a cluster cation that is isoelectronic with the hypothetical $[C_5Me_5]^+$ cation.

The cation consists of three phosphorus and two *t*BuC units arranged in a pseudo square-based-pyramidal geometry, consisting of a diamond-shaped P_2C_2 base (with alternating P and C units) capped by an apical four-coordinate P atom. This is a 14-electron *nido* cluster, based on an octahedron with one missing vertex, in which the carbon atoms occupy the sites of lowest connectivity. The basal P–C bonds are all approximately equal (ca. 1.80 Å), whereas the P–C bonds to the apical P atom are significantly longer (2.00 Å). The P-C-P angles in the basal unit are approximately 100°, whereas the C-P-C angles are considerably more compressed (79°). All the bond angles subtended at the apical phosphorus atom by adjacent basal atoms are extremely acute (ca. 50°).

The structure of **6** is an analogue of that predicted by Hoffmann[16] for the $[C_5H_5]^+$ ion and also to the species *nido*-2-*t*Bu-1,2-PCB_3H_5 prepared by the reaction of P≡C*t*Bu with

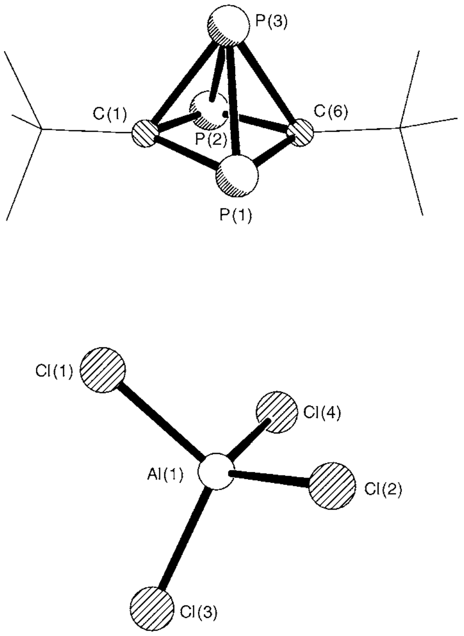
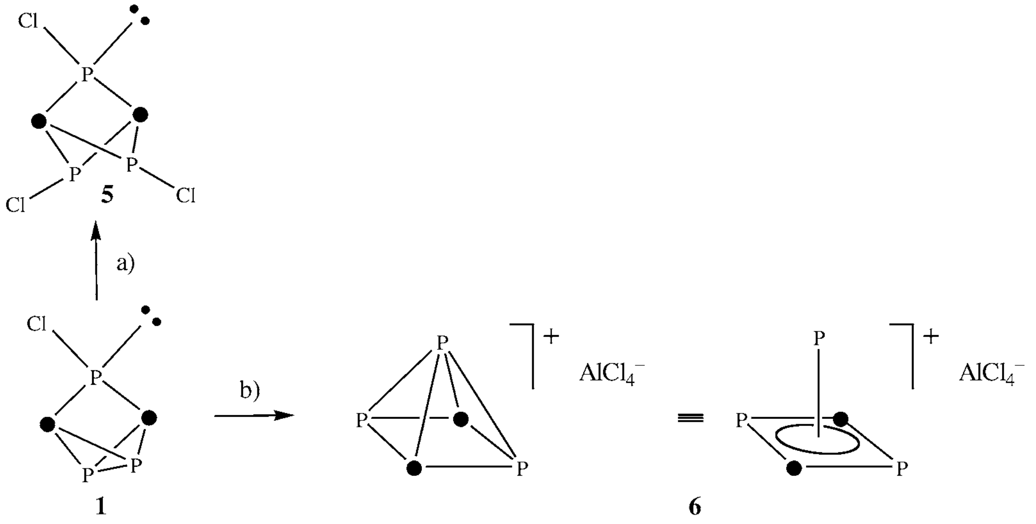


Figure 1. Crystal structure of **6**. H atoms have been omitted for clarity. Only one of the two independent molecules in the unit cell is shown. Selected bond lengths [Å] and angles [°]: P(1)–C(1) 1.8009(15), P(1)–C(6) 1.8037(15), P(1)–P(3) 2.2367(7), P(2)–C(1) 1.8011(15), P(2)–C(6) 1.8020(16), P(2)–P(3) 2.2517(8), P(3)–C(1) 1.9955(16), P(3)–C(6) 2.0022(15); C(1)-P(1)-C(6) 79.30(7), C(1)-P(1)-P(3) 58.04(5), C(6)-P(1)-P(3) 58.24(5), C(1)-P(2)-C(6) 79.34(7), C(1)-P(2)-P(3) 57.72(5), C(6)-P(2)-P(3) 57.93(5), C(1)-P(3)-C(6) 70.25(6), C(1)-P(3)-P(1) 49.97(4), C(6)-P(3)-P(1) 49.99(5), C(1)-P(3)-P(2) 49.73(5), C(6)-P(3)-P(2) 49.70(5), P(1)-P(3)-P(2) 75.93(2), P(1)-C(1)-P(2) 100.10(7), P(1)-C(1)-P(3) 71.99(6), P(2)-C(1)-P(3) 72.55(6). Selected bond lengths [Å] and angles [°] for the second independent molecule in the unit cell (P(6) is the apical phosphorus atom): P(4)–C(16) 1.7981(16), P(4)–C(11) 1.8013(16), P(4)–P(6) 2.2540(8), P(5)–C(16) 1.8018(16), P(5)–C(11) 1.8083(15), P(5)–P(6) 2.2287(7), P(6)–C(16) 1.9934(16), P(6)–C(11) 1.9955(16); C(16)-P(4)-C(11) 79.29(7), C(16)-P(4)-P(6) 57.63(5), C(11)-P(4)-P(6) 57.67(5), C(16)-P(5)-C(11) 79.01(7), C(16)-P(5)-P(6) 58.14(5), C(11)-P(5)-P(6) 58.13(5), C(16)-P(6)-C(11) 70.30(6), C(16)-P(6)-P(5) 50.14(5), C(11)-P(6)-P(5) 50.32(5), C(16)-P(6)-P(4) 49.63(5), C(11)-P(6)-P(4) 49.70(5), P(5)-P(6)-P(4) 76.19(2), P(4)-C(11)-P(5) 100.03(7), P(4)-C(11)-P(6) 72.63(6), P(5)-C(11)-P(6) 71.54(6).



Scheme 2. a) $SbCl_5$, CH_2Cl_2, $-SbCl_3$; b) $AlCl_3$, CH_2Cl_2 (● = C*t*Bu, ·· = lone pair).

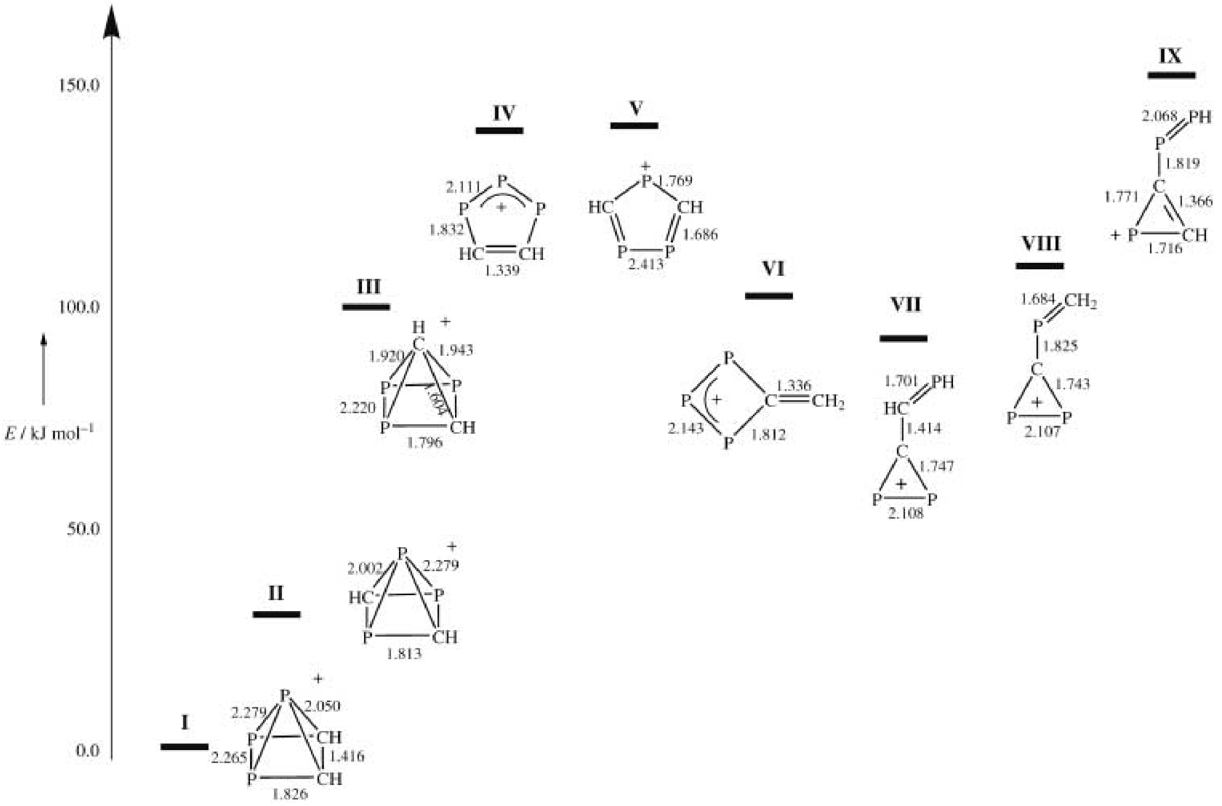


Figure 2. Optimized structural parameters and relative energies E of $[C_2H_2P_3]^+$ isomers.

B_4H_{10}.[17] Recent calculations have shown, however, that the vinylcyclopropenyl and cyclopentadienyl cations are more stable isomers of the $[C_5H_5]^+$ ion than a square-based-pyramidal structure.[18,19] These observations encouraged us to survey systematically the potential-energy surface (PES) of the model cation $[C_2H_2P_3]^+$ at the B3LYP/6-311G** level. Optimized structural parameters and relative energies of the most stable isomers are summarized in Figure 2. In contrast to the isomers of the $[C_5H_5]^+$ ion the most stable structures on the PES for $[P_3C_2H_2]^+$ ions are square-based pyramids, the lowest lying of which, **I**, has two basal phosphorus atoms in a 2,3-arrangement. Structure **II**, which has the same connectivity as **6**, is 24.4 kJ mol^{-1} higher in energy, and its optimized structural parameters are remarkably similar to those in the crystal structure of **6**. The third possible square-based pyramid, structure **III**, with a CH group in the apical position, is 99.8 kJ mol^{-1} higher in energy than **I**. A survey of species located on the PES of $[C_5H_5]^+$ led us to investigate additional isomers based on the cyclopentadienyl (**IV** and **V**) methylenecyclobutenyl (**VI**) and vinylcyclopropenyl (**VII**, **VIII**, and **IX**) structures.[*] However, even the most stable of these alternative structures (**VII**) lies 83.5 kJ mol^{-1} above the global minimum **I**. The calculations therefore imply that **6** is not the most stable isomer of the $[C_2tBu_2P_3]^+$ ion, despite the fact that it is formed in the experiment. We cannot rule out the possibility that **6** crystallized preferentially, and that analogues of **I** and **II**, undergoing rapid exchange, are present in our experiments. However, if one considers that **6** is formed by abstraction of a chloride anion from **1**, then it would be the kinetic product of the reaction. It might be possible to access structure **I** from **II** if **III** is invoked as an intermediate. However, the barrier for the conversion of **II** into **III** is calculated to be rather high (115 kJ mol^{-1}), and this implies that **6** is the only species of the $[P_3C_2R_2]^+$ manifold that is present.

Phosphorus compounds have a striking structural resemblance to carbon compounds. However, as is shown here and in valence isomers of tetraphosphabenzene and phosphorus analogues of amidinium salts, any isomers that are high in energy as a result of the constraint of bond angles (i.e., strain energy) will be much more stable on the hypersurface for the phosphorus analogues.[20] Most significantly, the stability of the planar cyclopentadienyl, methylenecyclobutenyl, and vinylcyclopropenyl analogues is much reduced in the phosphorus-containing systems because of the inefficient π–π overlap in double bonds involving atoms of the second period. As a result, there is a distinct switch in global minimum from cyclic unsaturated species to saturated cages with high connectivity.

The ^1H, ^{13}C, and ^{27}Al NMR spectra of **6** in CD_2Cl_2 solution are consistent with the solid-state structure. Curiously, however, no signals attributable to **6** could be observed in the ^{31}P NMR spectrum of **6** over the temperature range −100 to +30 °C. Further calculations shed some light on this rather

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[*] We considered many alternative linkage isomers of the methylenecyclobutenyl and vinylcyclopropenyl structures; only the most stable are shown in Figure 2.

puzzling observation. The NMR spectroscopic chemical-shift values of the ^{31}P nuclei in structure **II** were calculated to be $\delta = -532$ (apical) and $\delta = 246$ (basal) ppm. The value for the apical phosphorus atom is in good agreement with that found for *nido*-2-*t*Bu-1,2-PCB_3H_5.[17] The lack of signals at these chemical shifts in our spectra led us to conclude that a fluxional process was occurring, the result of which was to exchange the apical and basal phosphorus atoms. A similar process was predicted by Stohrer and Hoffmann[16] in their analysis of bond-stretch isomerism and polytopal rearrangements within the $[C_5H_5]^+$ manifold. Here, exchange of basal and apical carbon atoms is predicted to occur via a C_{2v} transition state. In the case of the $[P_3C_2H_2]^+$ manifold, a similar C_{2v}-symmetric transition state was located (one imaginary frequency), only 37.0 kJ mol^{-1} higher in energy than **II** and thus allowing facile exchange of apical and basal phosphorus atoms (Figure 3).

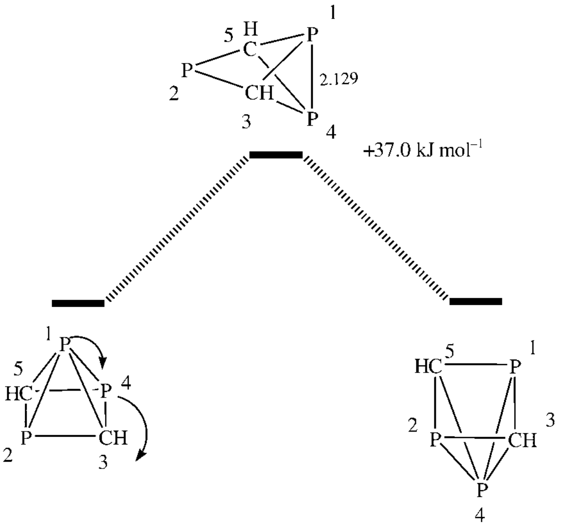

Figure 3. Facile exchange of apical and basal phosphorus atoms.

This result allowed us to calculate the rate constant for this exchange process for a range of temperatures, and ^{31}P NMR spectra were simulated using these data. At 298 K the simulated spectrum exhibited a single resonance at $\delta = -12$ ppm with a line width at half height ($\omega_{1/2}$) of about 3000 Hz, and at 183 K two peaks at $\delta = -532$ and 246 ppm were predicted, with a line width of about 100 Hz. The poor solubility of **6** and the calculated broadening of the signals provides an explanation for our inability to observe, even at low temperature, any signal in the ^{31}P NMR spectrum of this species. Consistent with this rapid exchange of apical and basal phosphorus atoms, signals arising from **6** in the ^{13}C NMR spectrum all show significant broadening.

From a synthetic standpoint, the synthesis of **6** by a Lewis acid promoted ring-opening reaction of **1** represents a new approach to phosphorus–carbon clusters. These compounds were previously prepared from P≡C*t*Bu, either by thermolysis or by reaction with various transition-metal species or Lewis acids,[21,22] synthetic approaches which have to date not provided access to molecules such as **6**. Interestingly, the cation of **6** obeys Wade's rules and is in fact the first example of a cationic phosphorus–carbon cluster.

In conclusion we have shown that the tricyclic C_2P_3 compound **1** can selectively ring open to give in high yield the anion **3** and the novel nido cation **6**.

Experimental Section

3·M: In a typical experiment, compound **1** (172 mg, 0.65 mmol) was dissolved in THF (5 mL) and added to a suspension of Na pieces (100 mg, 4.34 mmol) in THF (5 mL). The resulting mixture was stirred for 2 h, after which time it had turned deep red, which indicated formation of **2**: an NMR spectrum recorded at this time indicated that conversion into **2** was essentially quantitative. The solution was then filtered, cooled to −30 °C, and a solution of Ph_3SnCl (272 mg, 0.71 mmol) in THF (10 mL) added in portions, which caused an instant color change to yellow. Conversion into compound **4** was again quantitative, as shown by ^{31}P NMR spectroscopy.

The reaction with Li could be accomplished in the same manner by using an excess of Li metal that had been activated by sonication.

6: $AlCl_3$ (87 g, 0.65 mmol) was added to a stirred solution of **1** (172 mg, 0.65 mmol) in CH_2Cl_2 (5 mL). After stirring the mixture for 10 min, a white solid was observed to form in the colorless solution. The solid redissolved on gentle heating. Storage for 16 h at 20 °C yielded a good crop of colorless blocks of **6**. ^{1}H NMR (25 °C, 299.9 MHz, CD_2Cl_2): $\delta = 1.01$ ppm (s, $C(CH_3)_3$); ^{27}Al NMR (25 °C, 78.2 MHz, CD_2Cl_2): $\delta = 102.2$ ppm (s, $AlCl_4^-$); ^{13}C NMR (25 °C, 75.4 MHz, CD_2Cl_2): $\delta = 29.5$ (apparent q, 3.0 Hz, $C(CH_3)_3$), 31.2 (br, $C(CH_3)_3$); 32.8 ppm (br, P_3C_2tBu).

All density functional calculations were performed with the Gaussian 98 program.[23] The natures of the minima and transition states were confirmed by vibrational analysis (zero or one imaginary frequency, respectively). Shielding parameters σ were calculated by using the GIAO formalism,[24] and converted into chemical shifts δ by using $\delta = 328.5 - \sigma$ ppm, where 328.5 ppm is the absolute shielding parameter for the ^{31}P reference standard, 85 % H_3PO_4.[25]

Crystal structure for **6**: $C_{20}H_{36}Al_2Cl_8P_6$, $M_r = 799.87$, $T = 173(2)$ K, monoclinic, space group $P2(1)/n$, $a = 10.529(2)$, $b = 21.520(4)$, $c = 16.354(3)$ Å, $\beta = 95.95(3)°$, $V = 3685.6(13)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.442$ Mg m^{-3}, $\mu = 0.933$ mm^{-1}, $3.14 \leq 2\theta \leq 54.96°$. X-ray measurements were made using a Bruker APEX area-detector diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å)[26] on a single crystal of **6** of size 0.2 × 0.2 × 0.1 mm that was coated in perfluoropolyether oil and mounted on a glass fiber. Of the 25 669 reflections collected, 8453 were independent. Intensities were integrated[27] from several series of exposures, each exposure covering 0.3° in ω, and the total data set was a hemisphere. Absorption corrections were applied, based on multiple and symmetry-equivalent measurements.[28] The structure was solved by direct methods[29] and refined by least-squares methods on F^2 values for all reflections[30] with weighting $w^{-1} = \sigma^2(F_o^2) + (0.0267P)^2$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$, to final values of $R1 = 0.0256$ $[I > 2\sigma(I)]$ and $wR2 = 0.0575$ (all data). Largest peak and hole in the final difference map were 0.462 and −0.179 e Å^{-3}. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. All hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. CCDC-202457 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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