# Synthesis, Structure, and Chemical Reactivity of a Stable $C_5Me_5$-Substituted Phosphanylium Ion: (Pentamethylcyclopentadienyl)(t-butylamino)-phosphanylium Tetrachloroaluminate†

**Dietrich Gudat, Martin Nieger, and Edgar Niecke***
*Anorganisch-Chemisches Institut der Universität Bonn, Gerhard-Domagk-Strasse 1, 5300 Bonn 1, Federal Republic of Germany*

Stable phosphanylium salts of $[P(NHBu^t)(C_5Me_5)]^+$ (**4**) were obtained *via* different routes, *viz.* (*i*) $Al_2Cl_6$-promoted halide abstraction from a chlorophosphane precursor, (*ii*) displacement of chloride by the nucleofugic anion, $OSO_2CF_3^-$, and (*iii*) protonation of an iminophosphane precursor. A crystalline product was isolated in case of the tetrachloroaluminate of (**4**), and its structure was investigated by X-ray diffractometry. The results confirm the presence of discrete cations, featuring $\eta^2$ attachment of the $C_5Me_5$ ligand to phosphorus in the solid state. In solution, according to the results of n.m.r. spectroscopic studies, the cation exhibits a fluxional structure with all five ring atoms becoming equivalent. Investigations of the chemical reactivity of (**4**) include acid–base reactions and studies of the co-ordination chemistry. In addition to activity as both Lewis acid and base, which is a common feature for phosphanylium ions, (**4**) is the first two-co-ordinate phosphorus cation which was shown to react as a Brønsted acid. Deprotonation initially gives the iminophosphane, $P(=NBu^t)(C_5Me_5)$, which further reacts with (**4**) to yield a polycyclic cation, (**14**), the structure of which was determined by X-ray diffraction. Reactions of (**4**) with transition metals involve oxidative addition of complex metal hydrides and co-ordination to reactive metal centres to give cationic complexes which are isolobal to transition metal carbene complexes. No evidence was obtained in these reactions to indicate any activation of the $C_5Me_5$–phosphorus bonds.

Compared with diamino- and amino-substituted phosphanylium ions (1) and (2), pentamethylcyclopentadienyl-substituted derivatives (3) were found to be adequately stable. Cowley and
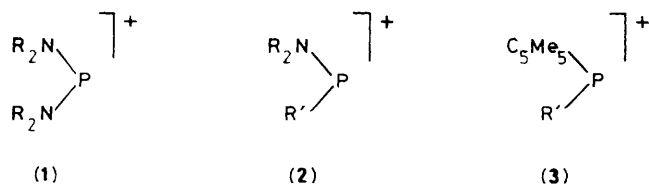


co-workers[1,2] reported the generation of phosphanylium ions of the general formula $[PR'(C_5Me_5)]^+$ [$R' = NMe_2$, $CMe_3$, or $CH(SiMe_3)_2$]. None of the products could be isolated, but nevertheless they were unequivocally characterized by means of n.m.r. spectroscopy and even when $R' = $ alkyl were found to be stable for some time. Based on spectroscopic evidence and molecular orbital calculations, the stabilization caused by the $C_5Me_5$ was attributed to multihapto-bonding between the $C_5Me_5$ moiety and phosphorus, giving rise to a delocalization of the positive charge on the ring.[1] Results of semiempirical calculations on cations $[PR'(C_5H_5)]^+$ ($R' = NH_2$ or Me),[1,2] as well as an *ab initio* study on $[P(C_5H_5)_2]^+$,[3] both imply that $\eta^2$- or $\eta^3$-co-ordination of the ring is energetically favoured compared with $\eta^5$ attachment, which has been verified for metallocenes of the elements Si, Ge, or Sn.[4]

Apart from the bonding situation of the $C_5Me_5$ substituent, $C_5Me_5$-substituted two-co-ordinate phosphorus compounds are of considerable interest because of the ability of the ligand to

behave as a functional group. Thus, nucleophilic substitution of $C_5Me_5$ has been reported for a diphosphene, $(C_5Me_5)P=P(C_5Me_5)$,[5] and activation of the $P-C_5Me_5$ bond by transition metals gives simple access to transition-metal substituted phospha-alkenes[6] and iminophosphanes.[7]

In this paper we report on the synthesis, structure, and reactivity of the first isolated $C_5Me_5$-substituted phosphanylium salt, $[P(NHBu^t)(C_5Me_5)][AlCl_4]$. The cation is unique in that it features not only a potentially reactive $P-C_5Me_5$ unit, but also a primary amino ligand. In addition to reactivity as both Lewis acid and base, which is well established for the amino-substituted cations (1) and (2),[8] $[P(NHBu^t)(C_5Me_5)]^+$ (**4**) is also the conjugate acid of the corresponding iminophosphane, $P(=NBu^t)(C_5Me_5)$ (**5**), and is therefore expected to behave as a Brønsted acid.

Several reactions of (**4**) with different bases were studied. Further investigations of the chemical behaviour of (**4**) were centred on the attempt to activate the $P-C_5Me_5$ bond, yielding transition-metal substituted phosphanylium ions.

## Results and Discussion

*Preparation of* $[P(NHBu^t)(C_5Me_5)]^+$ (**4**).—Three different routes have been followed for the preparation of $[P(NHBu^t)-(C_5Me_5)]^+$. The first [method (*a*), Scheme 1], which is established as a general synthetic route to phosphanylium ions,[8] involves $Al_2Cl_6$-promoted halide ion abstraction from the corresponding chlorophosphine precursor, (**6**). Pure (**4**) was isolated as the tetrachloroaluminate in 70—85% yield after recrystallization from $CH_2Cl_2$–hexane at 0 °C.

Following an alternative procedure, displacement of the chloride in (**6**) was achieved by reaction with silver trifluoromethanesulphonate, yielding the phosphanylium salt and AgCl [method (*b*), Scheme 1].

Proton attack on the P=C double bond in the phospha-

alkene $P[=C(OSO_2CF_3)_2](C_5Me_5)$ using trifluoromethane-sulphonic acid has been reported to result in formation of the corresponding cation, $[P\{CH(OSO_2CF_3)_2\}(C_5Me_5)]^+$.[6] We also investigated the analogous reactivity of the iminophosphane $P(=NBu^t)(C_5Me_5)$, (5)[9] [method (c), Scheme 1]. [31]P N.m.r. spectroscopic monitoring of the reaction of a $CH_2Cl_2$ solution of (5) with one equivalent of $CF_3SO_3H$ at $-78$ °C revealed that (4) is indeed the major reaction product ($>60\%$ from integration of the n.m.r. spectrum). However, attempts to purify the product failed due to the occurrence of unidentified by-products, which could not be separated.

*Spectroscopic Characterization.*—Spectroscopic data are given in Table 1. Salts of $[AlCl_4]^-$ were evidenced by the [27]Al



**Scheme 1.**
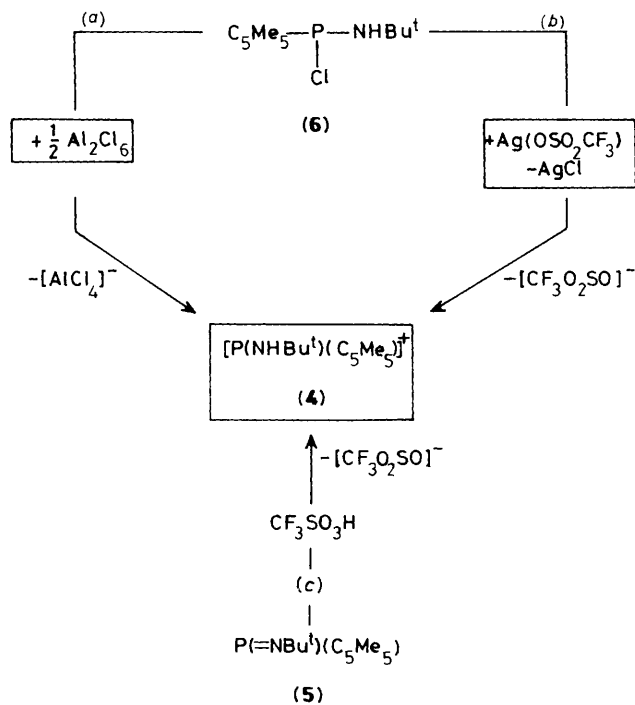
n.m.r. spectra, which show a sharp singlet at $\delta$ 103 p.p.m. ($\Delta v_{\frac{1}{2}}$ 3 Hz) characteristic of the $[AlCl_4]^-$ ion. In the [31]P n.m.r. spectrum, (4) gives rise to a single resonance which is shifted to higher field compared with the chlorophosphane precursor (6). A similar chemical shift variation, being of opposite sign to that found for amino-substituted phosphanylium ions,[8] has also been observed for $[P(NMe_2)(C_5Me_5)]^+$[1] and is attributable to multihapto-bonding between $C_5Me_5$ and P. The phosphorus chemical shift further depends on the counter ion, which may be explained in terms of an equilibrium between a two-co-ordinate cation and a covalent compound,[10] Scheme 2.
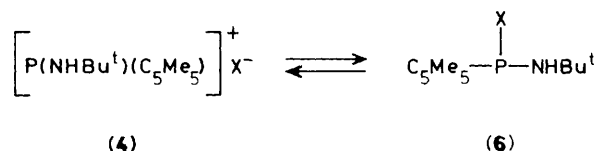


**Scheme 2.** $X = OSO_2CF_3$; Cl ($AlCl_3$ adduct in the case of the anion)

Hence, according to [31]P n.m.r. data, a considerable amount of the covalent species is present for $X = OSO_2CF_3$, while in the case of $X = AlCl_4$ exclusive occurrence of the ionic species follows from the [27]Al n.m.r. data.

Both salts of (4) display the equivalence of all five ring carbon atoms and corresponding methyl groups. Compared with the neutral compounds $(C_5Me_5)P=P(C_5Me_5)$,[5] $P[=C(OSO_2-CF_3)_2](C_5Me_5)$,[6] and $P(=NBu^t)(C_5Me_5)$,[9] deshielding of both the ring carbon and methyl proton resonances is observed, which implies considerable delocalization of positive charge on the ring and confirms the stabilizing effect of the $C_5Me_5$ substituent. The signal due to the NH proton in (4) is found as a very broad resonance at $\delta$ 6.4 p.p.m. A downfield shift of more than 3.5 p.p.m. relative to the corresponding signal of the chlorophosphine (6) may be understood as a result of P–N multiple bond character, leading to a significant bond anisotropy as well as to further charge delocalization to nitrogen. Variable-temperature studies on $CH_2Cl_2$ solutions of (4) further revealed that the degeneracy in the ^{1}H and [13]C n.m.r. spectra persists down to $-78$ and $-70$ °C, respectively, with a significant broadening being observed for the resonance of the

**Table 1.** Analytical and physical data

| Compound[a] | M.p./°C | Yield (%) | N.m.r. data[b] $\delta$(^{31}P) p.p.m. | $J$/Hz | $\delta$([27]Al) p.p.m. | I.r. data[c] $v$(NH)/cm$^{-1}$ | Analysis (%)[d] C | H | N |
|---|---|---|---|---|---|---|---|---|---|
| (4) | 123 | 87 | 106.7 | | 102.0 | 3 315m | 39.25 (41.30) | 6.85 (6.90) | 3.35 (3.45) |
| (4)[e] | | | 135.0 | | | | | | |
| (7) | | | 54.4, 21.2 | 382 (PP) | 103.0 | | | | |
| (9) | 112 | 93 | 16.2 | | 102.8 | 3 372m | | | |
| (10) | | | 63.0, 30.5 | 307 (PP) | 103.0 | 3 308m | | | |
| (13) | | | 46.2, 39.4 | 23 (PP) | 102.9 | | | | |
| (14)·0.5CH$_2$Cl$_2$ | 158 | 33 | 72.4, 15.7 | 36 (PP) | 102.8 | 3 320m | 48.75 (49.85) | 7.65 (7.35) | 4.25 (4.10) |
| (15) | | | $-9$, $-14$ | 223 (PP) | 103.0 | | | | |
| (16) | 153 | 88 | 21.2 | 225 (WP) | 102.9 | 3 350m | | | |
| (17a) | 112—119[f] | | 297.9 | 404 (WP) | 102.9 | 3 280m | | | |
| (17b) | 126—129[f] | 47 | 268.3 | 583 (WP) | 103.0 | 3 285m | 32.60 (34.30) | 4.00 (4.45) | 6.65 (7.30) |

[a] As $[AlCl_4]^-$ salts unless otherwise stated. [b] Recorded on a Varian FT-80-A spectrometer in $CD_2Cl_2$ or $CDCl_3$; standards were 85% $H_3PO_4$ and $[Al(OH_2)_6]^{3+}$; ^{1}H and ^{13}C data are given in the Experimental section. [c] Recorded from Nujol mulls between KBr pellets on a Perkin-Elmer 298 grating spectrometer. [d] Required values are given in parentheses. [e] As $[OSO_2CF_3]^-$ salt. [f] With decomposition.
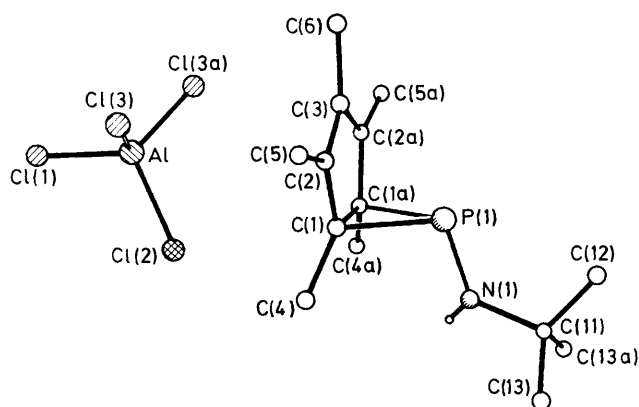
**Figure 1.** Plot of the crystal structure of [P(NHBu$^t$)(C$_5$Me$_5$)][AlCl$_4$]. Important bond lengths (Å) and angles (°): P(1)–N(1) 1.620(2), P(1)–C(1) 1.990(2), C(1)–C(2) 1.440(3), C(2)–C(3) 1.396(3), P(1)–N(1)–C(11) 127.7(3), N(1)–P(1)–C(1) 105.1(1), C(2)–C(1)–C(1a) 105.9(1), C(1)–C(2)–C(3) 109.6(2), C(2)–C(3)–C(2a) 108.9(3)

**Scheme 3.** Y = thf, NEt$_3$, N(CH$_2$CH$_2$)$_3$N, C$_5$H$_5$N, MeCN, or PPh$_3$

ring carbon atoms. These results clearly rule out static η$^5$ attachment of the C$_5$Me$_5$ ligand to phosphorus, but indicate a fluxional molecule, which exhibits a sequence of degenerate [1.5]sigmatropic rearrangements[11] involving species of lower hapticity. As this process is still rapid on the n.m.r. time-scale at −70 °C, which suggests a very low barrier to migration, unequivocal assignment of the bonding situation in solution is not feasible; however, data are similar to the findings of Cowley and co-workers[1,2] on [PR(C$_5$Me$_5$)]$^+$ ions, and are consistent with higher co-ordination at the phosphorus centre featuring η$^2$- or η$^3$-bonding to the C$_5$Me$_5$ ligand rather than σ-co-ordination.[1]

*Crystal Structure of* [P(NHBu$^t$)(C$_5$Me$_5$)][AlCl$_4$].—Crystalline [P(NHBu$^t$)(C$_5$Me$_5$)][AlCl$_4$] consists of discrete cations and [AlCl$_4$]$^-$ anions, with no significant interactions between the different ions. The cation (Figure 1) exhibits crystallographic mirror symmetry, with the mirror plane passing through C(6), C(3), P(1), N(1), C(11), and C(12), and bisecting C(1)–C(1a). The cyclopentadienyl ligand is η$^2$ bound to the phosphorus atom, with the P(1)–C(1,1a) distance of 1.990(2) Å showing considerable elongation with respect to the normal single bond distance.[12] The five-membered ring is planar within experimental error, and C–C distances are similar to those found for η$^2$-C$_5$Me$_5$ substituted compounds of Ge$^{II}$[13] and Sn$^{II}$.[14] Also, only small distortions of the C(ring)–C(methyl) bonds out of the ring plane, lying between 0° [at C(2) and C(3)] and 15.5° [at C(1)], are observed, thus suggesting[13,14] nearly ideal sp$^2$ hybridization for all five ring carbon atoms. The angle between the adjacent three- and five-membered rings, which amounts to 90.7°, is widened with respect to the analogous Ge[13] and Sn compounds,[14] revealing a lower tendency of the smaller P atom towards adopting a high co-ordination number. The t-butyl-amino ligand is oriented in such a way as to minimize steric interactions between the substituents. The P(1)–N(1) distance of 1.620(2) Å is similar to those found for diaminophosphanylium ions[8] and is indicative of substantial multiple bond character.[8] The position of the hydrogen atom has been located and confirms a planar co-ordination geometry around nitrogen; the low steric demand of hydrogen is reflected by the C(11)–N(1)–P(1) angle of 127.7 (3)°, which is considerably widened with respect to the value of 120° expected for sp$^2$ hybridization at nitrogen. In contrast, the low value of 106.2° for the bond angle at P(1) [defined as A–P(1)–N(1) where A = point bisecting C(1)–C(1a)] is attributable to a high *p* character of the
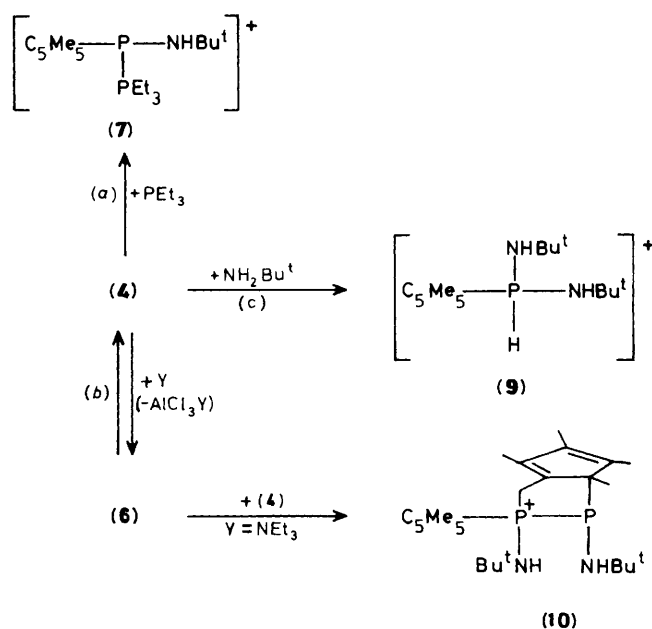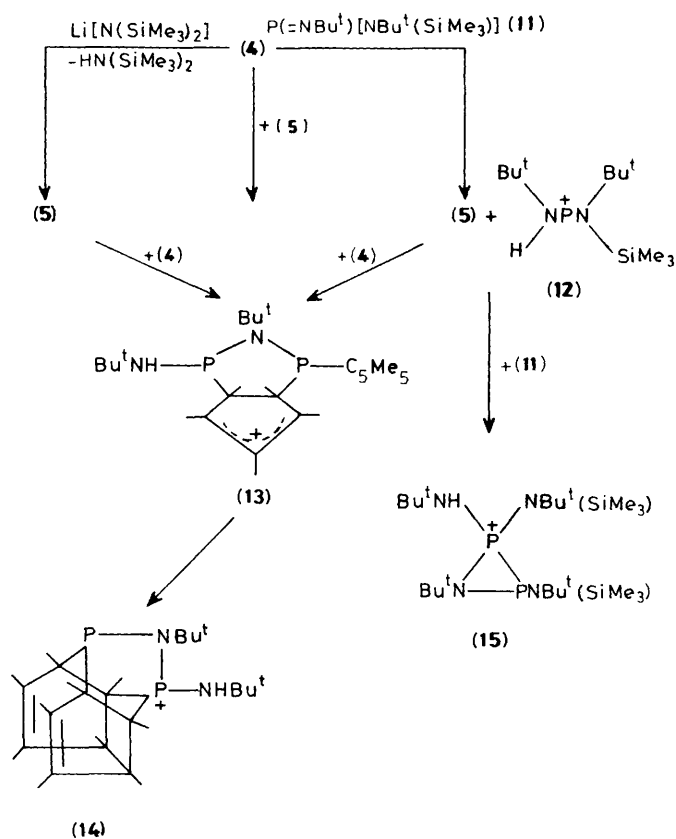
P(1)–C(1,1a) bonds, and corresponds with the apparent sp$^2$ hybridization of the ring atoms. On the whole, the structural parameters of [P(NHBu$^t$)(C$_5$Me$_5$)][AlCl$_4$] are in good agreement with description of the η$^2$-C$_5$Me$_5$–phosphorus bonding situation as a 'π-complex of a main group element'.[4]

*Chemical Reactivity.*—(a) *Acid–base reactions.* The Lewis and Brønsted acid behaviour of (4) was studied in reactions with different types of bases. 'Monofunctional' donors include neutral molecules possessing a single basic site, centred at an oxygen (tetrahydrofuran), nitrogen [NEt$_3$, N(CH$_2$CH$_2$)$_3$N, C$_5$H$_5$N, NH$_2$Bu$^t$, or MeCN], or phosphorus (PEt$_3$ or PPh$_3$) atom, and the anionic Li[N(SiMe$_3$)$_2$]. Ambivalent basicity is expected for the aminochlorophosphine (6) and iminophosphanes P(=NR′)R, which exhibit different nucleophilic sites at P and N. Typically, reactions were performed by adding the base to CH$_2$Cl$_2$ solutions of (4) at 0 °C, and the products were identified by their $^{31}$P and $^{27}$Al n.m.r. spectra. The results confirm that reactions proceed via either formation of Lewis acid–base adducts or deprotonation of cation (4), thus establishing the expected ambivalent behaviour.

Lewis acid–base reactions were observed with neutral donors (see Scheme 3). However, only with soft bases is a complex between (4) and the donor formed [route (*a*)], while in the case of hard donors the [AlCl$_4$]$^-$ anion can compete as a base, and the reaction proceeds via chloride transfer to (4), yielding (6), and a donor stabilized AlCl$_3$ adduct [route (*b*)]. The composition of the reaction products follows from $^{31}$P and $^{27}$Al n.m.r. data. Difficulties were found for the chlorophosphane (6) and donors of rather low basicity. In the first case, fast exchange of a chloride ion is observed between (4) and (6), leading to coalescence of the n.m.r. signals of both species. Addition of weak donors MeCN or PPh$_3$ to solutions of (4) only produces a change in $^{31}$P chemical shift, which is accompanied by some line broadening. Formation of a definite acid–base adduct is not observed, and the findings may be interpreted as an equilibrium between the unperturbed molecules and a weak donor–acceptor complex.[10] Interaction of (4) with t-butylamine proceeds via oxidative addition into a N–H bond to yield the phosphonium ion PH(NHBu$^t$)$_2$(C$_5$Me$_5$)$^+$ (9), which was unequivocally

Li[N(SiMe₃)₂]     P(=NBuᵗ)[NBuᵗ(SiMe₃)] (11)
───────────────  (4) ───────────────
-HN(SiMe₃)₂



Figure 2. Plot of the crystal structure of the cation (14). Important bond distances (A) and angles (°): P(1)–N(1) 1.627(4), P(1)–N(2) 1.668(3), P(2)–N(2) 1.755(4), P(1)–C(2) 1.826(4), P(1)–C(7) 1.818(4), P(2)–C(1) 1.893(4), P(2)–C(6) 1.896(4), C(3)–C(8) 1.646(6), C(4)–C(5) 1.325(6), C(9)–C(10) 1.310(6), N(2)–P(1)–N(1) 121.6(2), C(7)–P(1)–N(2) 103.0(2), C(7)–P(1)–C(2) 96.6(2), C(2)–P(1)–N(2) 102.9(2), P(2)–N(2)–P(1) 101.0(2), C(11)–N(1)–P(1) 140.1(3), C(1)–P(2)–N(2) 92.7(2), C(6)–P(2)–N(2) 93.3(2)

**Scheme 4.**

characterized by spectroscopic data. Although no intermediate could be detected by n.m.r. spectroscopy, formation of a Lewis acid–base adduct of (4) and the amine may be postulated as the initial step of the reaction.

The reaction of (4) and triethylamine further differs from the general scheme in that (6) and a stable AlCl₃-amine adduct are not formed, but instead a mixture of [NHEt₃][AlCl₄] and a product which is formulated as the phosphonium ion (10) on the basis of ³¹P, ¹³C, and ¹H n.m.r. data. Generation of (10) may be explained by formation of (6) and an AlCl₃-amine adduct in the first step, which then reacts with a second cation of (4) to yield the final products. Although spectroscopic detection of (6) was not feasible in this case, further findings corroborate the proposed reaction mechanism: (i) formation of (10) was also observed when a 1:1 mixture of (4) and (6) was treated with a solution containing one equivalent of Al₂Cl₆ and triethylamine, indicating the instability of the AlCl₃-amine adduct in this case; (ii) reaction of (4) with the conjugate base (5) was found to give a different product (see below), thus ruling out deprotonation of (4) by NEt₃ as the first step, and (iii) completion of the reaction was observed after half an equivalent of NEt₃ was added.

A different mechanism was established for the interaction of (4) with Li[N(SiMe₃)₂] and the aminoiminophosphane (11), respectively (see Scheme 4). ³¹P N.m.r. spectroscopic monitoring indicated formation of an identical transient intermediate in both cases, which subsequently rearranged to give a final product identified as the polycyclic cation (14). As formation of both (14) and its precursor were also observed in the reaction of (4) with the iminophosphane (5), without an additional base being present, occurrence of (5) as a common intermediate is assumed in all three cases, thus confirming the first example of a phosphanylium ion reacting as a Brønsted acid. For the further course of the reaction, formation of a Lewis
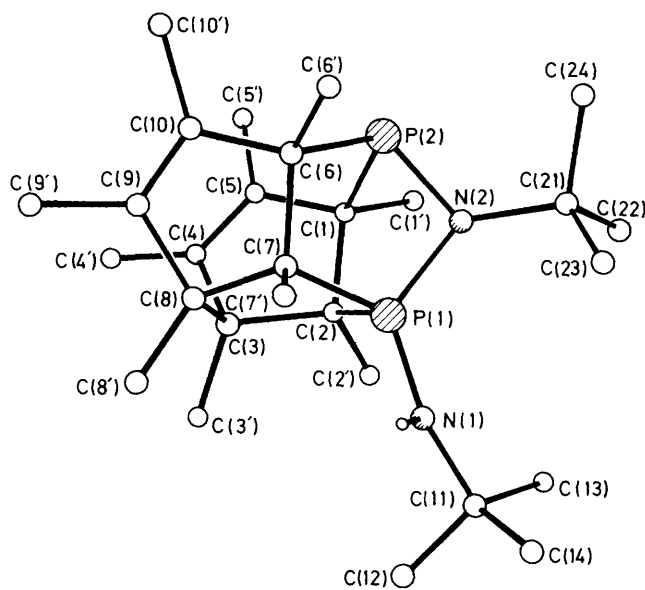
acid-base complex is proposed via interaction of the imino-nitrogen of (5) with the electrophilic phosphorus centre of the cation. Intramolecular stabilization of positive charge in the initial adduct may be achieved by interaction of the cationic centre with one of the cyclopentadienyl rings, so that on the basis of the ³¹P n.m.r. data (AB pattern, δₐ 46.2, δ_B 39.4 p.p.m., J_AB 23 Hz) the resulting intermediate is tentatively formulated as an allyl cation (13). Finally, (14) is formed via electrocyclic rearrangement of (13). The formation of (13) during the reaction of (4) with (11) was accompanied by formation of an additional product, which was detected by ³¹P n.m.r. spectroscopy. Both the characteristic AB pattern (δₐ −9, δ_B −14 p.p.m., J_AB 223 Hz) and the stoicheiometry of the reaction provide evidence that its formation must arise from interaction of (11) with a phosphanylium ion, (12), resulting from proton transfer from (4) to (11) (Scheme 4). As comparable reactions of phosphanylium ions with organic or inorganic multiple bonds are known to give rise to three-membered ring systems,[8] the reaction product was tentatively formulated as the cation (15) (Scheme 4).[15]

Isolation of pure, crystalline (14) was most easily achieved from the direct reaction of (4) with (5), and its formulation ascertained by analytical and spectroscopic data (³¹P, ¹³C, ¹H n.m.r., i.r.) as well as an X-ray crystal structure determination, the results of which are depicted in Figure 2. Solid (14), which was found to contain half a molecule of CH₂Cl₂ solvent per formula unit, consists of discrete cations and [AlCl₄]⁻ anions. Both P–N and P–C bond distances at the four-co-ordinate phosphorus, P(1), are significantly shortened with respect to the corresponding bond distances involving P(2). Co-ordination geometry around both nitrogen atoms is planar, with the P(1)–N(1)–C(11) angle of 140.1(3)° at the exocyclic nitrogen being considerably opened with respect to the expected value of 120°. Both cyclopentenyl rings feature significant deviations from planarity and display an 'envelope' conformation, thus enabling minimization of the electron repulsion of the two

double bonds. As a further consequence of repulsion of both the double bond π electrons and the two methyl substituents at C(3) and C(8), which are forced into an eclipsed configuration due to the rigidity of the ring skeleton, considerable elongation of the central C(3)–C(8) bond [1.646(6) Å] occurs with respect to an expected C–C-distance of 1.54 Å for a regular single bond.

Summarising the results of reactions of (4) with various bases, it can be concluded that the initial step may in general be identified as either a Lewis or Brønsted type interaction. Formation of cation (14) as the final product, following deprotonation of (4) implies that interaction of (4) and (5) must proceed significantly faster than the proton transfer itself. Further studies on this type of reaction are necessary to decide whether this surprising effect arises from the unique qualities of the $C_5Me_5$ ligand, or may be established as a general feature of deprotonation reactions of phosphanylium ions. Furthermore, the proton transfer reaction between (4) and (11) is of considerable interest, as it also renders possible a comparison of the basicity of the two iminophosphanes, viz. (5) and (11). The aminoiminophosphane (11) was shown to be the stronger base, which is consistent with a more effective stabilization of positive charge in the corresponding acid, (12), and once more confirms the extraordinary stability of diamino-substituted phosphanylium ions.

(b) *Reactions with transition metal complexes.* For conversion of the phosphanylium ion (4) into transition metal substituted derivatives two different approaches seemed possible, viz. (i) displacement of the amino ligand via reaction of (4) with complex metal hydrides,[16] and (ii) activation of the $C_5Me_5$ ligand by insertion of a reactive transition metal precursor.[6,7] In order to test the applicability of (i) and (ii) to the synthesis of metallated phosphanylium ions, reactions of (4) with $[W(CO)_3H(C_5H_5)]$ and $[W(CO)_3(MeCN)_3]$ were studied as representative examples. However, in no case was any evidence for the formation of metallated phosphanylium ions obtained.

While reaction of $[W(CO)_3H(C_5H_5)]$ with aminophosphine precursors was reported to give neutral phosphido complexes $[W(CO)_3(PR_2)(C_5H_5)]$ via elimination of amine,[16] the analogous reaction of (4) exclusively yields the phosphonium cation (16) as the product of an oxidative addition reaction of (4) into the W–H bond (Scheme 5). Attempts to achieve subsequent reductive elimination of either $C_5Me_5H$ or t-butyl-amine by thermolysis or base-catalysed elimination were unsuccessful, and only decomposition of (16) was observed. Reaction of (4) with $[W(CO)_3(MeCN)_3]$ at −20 °C in $CH_2Cl_2$ cleanly yielded the cationic phosphido complex (17a) via displacement of one of the co-ordinated nitrile ligands. Decomposition occurred gradually on increasing the temperature to 20 °C, and a new complex, (17b), was formed by substitution of the *trans*-CO ligand by MeCN, which was liberated previously. Direct formation of (17b) was observed in the reaction of (4) with $[W(CO)_3(MeCN)_3]$ in acetonitrile at 60 °C. In contrast to the reported syntheses of transition-metal substituted phospha-alkenes and iminophosphanes, for which comparable products were detected as transient intermediates,[6,7] (17a) and (17b) proved to be stable with respect to further elimination of nitrile ligands and transfer of the $C_5Me_5$ ligand from phosphorus to the metal, and except for partial decomposition no definite reaction was observed on prolonged heating in toluene or acetonitrile.

The formulations of (16), (17a), and (17b) were confirmed by analytical and spectroscopic data. For (16) the presence of a P–H bond follows from the large coupling of 539 Hz observed in the proton-coupled ^{31}P spectrum. According to ^{1}H and [13]C n.m.r. data, the $C_5Me_5$ ligand adopts a static σ configuration, and different resonances are found for all five carbon atoms and methyl groups, respectively, due to the presence of a chiral centre at phosphorus. The i.r. spectrum displays three bands in
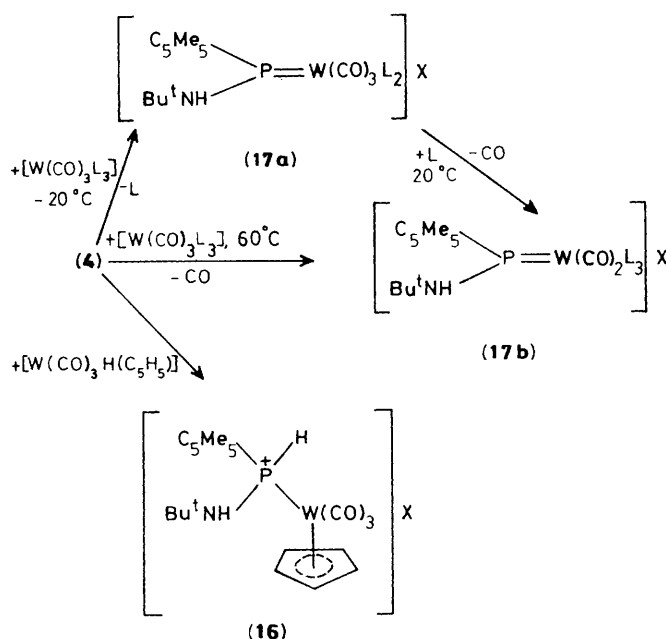


Scheme 5. L = MeCN, X = $AlCl_4$

the CO stretching region, the positions of which are in accord with a cationic complex of type $[W(CO)_3L(C_5H_5)]^+$. The ^{31}P chemical shifts of complexes (17a) and (17b) are found in a low-field region characteristic for most neutral and cationic phosphanylium complexes.[8] The large value of $^1J_{WP}$ implies significant π character of the phosphorus–metal bond,[16] confirming a close similarity of (17a) and (17b) with transition-metal carbene complexes, which may be explained in terms of an isolobal analogy.[17] The [13]C n.m.r. of both complexes exhibits three resonances for the $C_5Me_5$ ring carbons, confirming σ attachment of the ligands in this case. In the i.r. spectra, in addition to three [(17a)] or two [(17b)] intense bands in the CO stretching region, two weak bands are observed between 2 278 and 2 320 $cm^{-1}$, which may be attributed to CN stretching vibrations of co-ordinated nitriles. In the case of (17b), a small splitting observed for both carbonyl bands indicates the presence of conformational isomers. Compared with the tris-(acetonitrile) complex $[W(CO)_3(MeCN)_3]$, both absorptions are shifted to higher energy, thus indicating enhanced π acidity of cation (4) as a ligand in comparison with CO. Hence, the ease of displacement of the *trans*-carbonyl in (17a) may be attributed to stabilization of the metal–phosphorus back bonding due to the substitution of the *trans*-CO by the weaker π-acid MeCN, which is also reflected by the significant enhancement of the value of $^1J_{WP}$ for (17b). The considerable electronic stabilization, which is expected as a result of the formation of a formal metal–phosphorus double bond [16] in (17b), provides an explanation for the preference of the ligand-exchange reaction compared with migration of the $C_5Me_5$ ligand being favoured for co-ordinated phospha-alkenes and iminophosphanes.[6,7,11]

## Experimental

Operations were performed under dry argon. Solvents were dried over $CaH_2$ (methylene chloride) or sodium–benzophenone ketyl (ethers or hydrocarbons) and distilled under argon before use. [1]H N.m.r. spectra were recorded on a Varian EM 390 or Bruker AM 300 and [13]C n.m.r. spectra (δ/p.p.m. on a Varian FT80A spectrometer (in $CD_2Cl_2$ or $CDCl_3$). I.r. spectra were recorded from Nujol mulls between KBr pellets on a Perkin-

**Table 2.** Crystal data, structure analysis and refinement

| Compound | $[P(NHBu^t)(C_5Me_5)]$-$[AlCl_4]$ | $[AlCl_4]^-$ salt of (14) |
|---|---|---|
| Formula | $[C_{14}H_{25}NP]^+$ $[AlCl_4]^-$ | $[C_{28}H_{49}N_2P_2]^+$ $[AlCl_4]^-\cdot$ $0.5CH_2Cl_2$ |
| $M$ | 407.1 | 686.9 |
| Crystal system | Monoclinic | Triclinic |
| Space group | $C2/m$ | $P\bar{1}$ |
| $a$/Å | 15.257(7) | 9.632(3) |
| $b$/Å | 10.674(6) | 11.893(4) |
| $c$/Å | 14.434(10) | 16.019(4) |
| $\alpha$/° | 90 | 102.72(2) |
| $\beta$/° | 112.91(4) | 97.85(2) |
| $\gamma$/° | 90 | 94.41(3) |
| $U$/nm$^3$ | 2.165 | 1.762 |
| $Z$ | 4 | 2 |
| $D_c$/g cm$^{-3}$ | 1.25 | 1.29 |
| $F(000)$ | 848 | 724 |
| $\mu$/mm$^{-1}$ | 0.66 | 0.55 |
| Crystal size (mm) | $0.5 \times 0.6 \times 0.6$ | $0.4 \times 0.5 \times 0.6$ |
| Colour | Yellow | Colourless |
| Number of reflections measured ($2\theta_{max.} = 50°$) | 6 064 | 8 978 |
| Symmetry-independent | 1 963 | 6 198 |
| 'Observed' with $|F| > 4\sigma(F)$ | 1 730 | 4 502 |
| Parameters | 112 | 350 |
| $R$ | 0.048 | 0.066 |
| $R'$ $[w^{-1} = \sigma^2(F) + gF^2]$ | 0.050 | 0.067 |
| $g$ | 0.0002 | 0.0005 |

**Table 3.** Atomic co-ordinates ($\times 10^4$) for $[P(NHBu^t)(C_5Me_5)][AlCl_4]$

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Al | 1 819(1) | 0 | 2 525(1) |
| Cl(1) | 624(1) | 0 | 2 938(1) |
| Cl(2) | 3 062(1) | 0 | 3 896(1) |
| Cl(3) | 1 813(1) | 1 643(1) | 1 700(1) |
| P(1) | 5 961(1) | 0 | 2 421(1) |
| N(1) | 6 856(2) | 0 | 3 497(2) |
| C(11) | 7 882(2) | 0 | 3 685(3) |
| C(12) | 7 997(3) | 0 | 2 695(3) |
| C(13) | 8 319(2) | 1 171(3) | 4 289(2) |
| C(1) | 4 881(1) | 693(2) | 2 703(2) |
| C(2) | 4 312(1) | 1 064(2) | 1 686(2) |
| C(3) | 3 974(2) | 0 | 1 091(2) |
| C(4) | 5 118(2) | 1 523(2) | 3 603(2) |
| C(5) | 4 137(2) | 2 390(2) | 1 333(2) |
| C(6) | 3 378(3) | 0 | −11(3) |

**Table 4.** Atomic co-ordinates ($\times 10^4$) for the $[AlCl_4]^-$ salt of (14)

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Cl' | −1 099(5) | 5 768(4) | 9 997(3) |
| C' | −602(37) | 4 695(29) | −363(19) |
| P(1) | 1 940(1) | 8 238(1) | 7 182(1) |
| P(2) | 3 446(1) | 9 304(1) | 8 694(1) |
| N(1) | 978(4) | 8 023(3) | 6 231(2) |
| C(11) | −545(5) | 7 719(4) | 5 804(3) |
| C(12) | −805(6) | 6 416(4) | 5 443(3) |
| C(13) | −1 558(5) | 8 125(5) | 6 425(3) |
| C(14) | −708(6) | 8 331(5) | 5 054(3) |
| N(2) | 2 121(4) | 9 517(3) | 7 893(2) |
| C(21) | 1 502(5) | 10 652(4) | 7 894(3) |
| C(22) | 152(7) | 10 638(5) | 8 286(4) |
| C(23) | 1 244(7) | 10 850(5) | 6 985(3) |
| C(24) | 2 551(7) | 11 643(4) | 8 467(4) |
| C(1) | 2 454(5) | 7 911(4) | 8 789(3) |
| C(2) | 1 742(4) | 7 204(3) | 7 858(3) |
| C(3) | 2 764(5) | 6 239(3) | 7 597(3) |
| C(4) | 3 411(5) | 6 116(4) | 8 494(3) |
| C(5) | 3 338(5) | 7 044(4) | 9 112(3) |
| C(6) | 4 663(5) | 8 796(3) | 7 886(3) |
| C(7) | 3 746(4) | 8 022(3) | 7 032(3) |
| C(8) | 3 972(5) | 6 737(3) | 7 095(3) |
| C(9) | 5 418(5) | 6 937(4) | 7 657(3) |
| C(10) | 5 719(5) | 8 002(4) | 8 125(3) |
| C(1') | 1 421(6) | 8 337(4) | 9 413(3) |
| C(2') | 232(5) | 6 694(4) | 7 850(3) |
| C(3') | 1 947(5) | 5 085(4) | 7 055(3) |
| C(4') | 4 029(7) | 5 035(5) | 8 650(4) |
| C(5') | 3 999(6) | 7 278(5) | 10 049(3) |
| C(6') | 5 413(5) | 9 933(4) | 7 768(3) |
| C(7') | 4 119(5) | 8 341(4) | 6 207(3) |
| C(8') | 3 994(6) | 5 946(4) | 6 199(3) |
| C(9') | 6 363(5) | 5 972(4) | 7 637(4) |
| C(10') | 6 975(5) | 8 474(5) | 8 824(3) |
| Al | 6 747(2) | 2 501(1) | 6 521(1) |
| Cl(1) | 7 167(2) | 827(1) | 5 896(1) |
| Cl(2) | 7 882(2) | 3 739(1) | 6 032(1) |
| Cl(3) | 7 367(3) | 2 824(2) | 7 868(1) |
| Cl(4) | 4 570(2) | 2 635(2) | 6 261(2) |

Details of the crystal data, structure analysis and refinement are given in Table 2 and atomic co-ordinates in Tables 3 and 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

*Preparation of* $[P(NHBu^t)(C_5Me_5)][AlCl_4]$.—The aminochlorophosphane (6)[9] (6.83 g, 25 mmol) was dissolved in $CH_2Cl_2$ (15 cm$^3$) and added slowly to a vigorously stirred, ice-cooled suspension of $Al_2Cl_6$ (3.33 g, 25 mmol) in $CH_2Cl_2$ (50 cm$^3$). After the addition was complete, the light yellow solution was warmed to ambient temperature and concentrated *in vacuo* to a final volume of 25 cm$^3$. Addition of hexane (75 cm$^3$) produced a yellow precipitate, which was collected by filtration. Recrystallization was from $CH_2Cl_2$–hexane. [13]C N.m.r.: δ 130.2 (d, 10.2 Hz, C (ring)), 58.3 (d, 4.3 Hz, NC), 31.1 (d, 8.8 Hz, $NCMe_3$), 10.4 (Me (ring)). [1]H N.m.r.: δ 6.4 (broad, 1 H, NH), 2.07 (d, 3.4 Hz, 15 H, Me (ring)), 1.36 (d, 1.7 Hz, 9 H, $NCMe_3$).

*Preparation of* $[P(NHBu^t)(C_5Me_5)][OSO_2CF_3]$.—*Method A*. Compound (6) (550 mg, 2 mmol) was added to a stirred suspension of $Ag(OSO_2CF_3)$ (510 mg, 2 mmol) in $CH_2Cl_2$ or $CD_2Cl_2$ (4 cm$^3$). After stirring for 30 min, precipitated AgCl was separated by centrifugation and the product characterized by ^{31}P, ^{1}H, and [13]C n.m.r. spectroscopy.

Elmer 298 grating spectrometer. Microanalyses were performed by the microanalytical laboratories of the Universities of Bielefeld and Bonn.

Crystal structures of the tetrachloroaluminates of (4) and (14) were determined with a Nicolet $R3m$ diffractometer (ω scan mode, Mo-$K_\alpha$ radiation, λ = 0.710 69 Å), and solved and refined with SHELX 76 and SHELXTL.[18] The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically [solvent C atom of (14) with site occupancy factor = 0.5 isotropically]. Hydrogen atoms were localized by difference electron-density determination; N hydrogen atoms were refined free, and all others by using a 'riding' model.

*Method B.* $CF_3SO_3H$ (157 mg, 1 mmol) was added to a solution of (5) (237 mg, 1 mmol) at $-78\,^{\circ}C$. The reaction mixture was investigated by $^{31}P$ n.m.r. ($\delta$ 135 p.p.m.). The $^{13}C$ and $^1H$ n.m.r. were identical with (4).

*Reactions of* (4) *with Bases.—General method.* An ice-cooled solution of $[P(NHBu^t)(C_5Me_5)][AlCl_4]$ (410 mg, 1 mmol) in $CH_2Cl_2$ (4 cm³) was treated with one equivalent of the corresponding base. In the case of tetrahydrofuran (thf) and pyridine, up to five equivalents of the base were added portionwise, and the reaction monitored by $^{27}Al$ n.m.r. spectroscopy after each step. The products were characterized by $^{31}P$ and $^{27}Al$ n.m.r. spectroscopy.

*Reaction with thf.* $^{31}P$ N.m.r.: $\delta$ 139.7 $PCl(NHBu^t)(C_5Me_5)$; $^{27}Al$ n.m.r.: $\delta$ 102.0 $[AlCl_4]^-$, 89.4 $[AlCl_3(thf)]$, 65.7 $[AlCl_3(thf)_2]$ (8a).[19a]

*Reaction with* 1,4-*diazobicyclo[2.2.2]octane.* $^{31}P$ N.m.r.: $\delta$ 139.7 $PCl(NHBu^t)(C_5Me_5)$; $^{27}Al$ n.m.r.: no resonance observed due to insolubility.

*Reaction with pyridine* (py). $^{31}P$ N.m.r.: $\delta$ 139.7 $PCl(NHBu^t)(C_5Me_5)$; $^{27}Al$ n.m.r.: $\delta$ 101.0 $[AlCl_4]^-$, 25.0 $[AlCl_2(py)_4]^+$ (8b).[19b]

*Reaction with* $PCl(NHBu^t)(C_5Me_5)$. $^{31}P$ n.m.r.: $\delta$ 128.4 (broad singlet); $^{27}Al$ n.m.r.: $\delta$ 102.7 $[AlCl_4]^-$.

*Reaction with* $NH_2Bu^t$. The amine $NH_2Bu^t$ (365 mg, 5 mmol) was added *via* a syringe to a solution of $[P(NHBu^t)(C_5Me_5)][AlCl_4]$ (2.03 g, 5 mmol) in $CH_2Cl_2$ (10 cm³). The volume of the colourless solution was reduced to 5 cm³ *in vacuo*, and hexane (15 cm³) was added. The product was precipitated as a colourless, microcrystalline solid. Filtration and drying *in vacuo* gave pure (9). $^{13}C$ N.m.r.: $\delta$ 143.4 (d, 8.3 Hz, C=C ring), 132.4 (d, 3.9 Hz, C=C ring), 56.6 (d, 64.5 Hz, PC), 54.6 (d, 5.1 Hz, NC), 30.8 (d, 4.5 Hz, $NCMe_3$), 15.2 (d, 1.8 Hz, $PCMe$ ring), 10.4 (=$CMe$ ring); $^1H$ n.m.r.: $\delta$ 7.18 (dt, $^1J_{PH}$ 539 Hz, $^2J_{HH}$ 8.1 Hz, 1 H, PH), 2.46 (broad t, $^2J_{PH} = {}^2J_{HH}$ 8 Hz, 2 H, NH); 1.97 (6 H) and 1.90 (d, 4.3 Hz, 6 H) (=$CMe$ ring); 1.42 (d, 23.0 Hz, 3 H, $PCMe$ ring), 1.34 (d, 1.4 Hz, 18 H, $NCMe_3$).

*Reaction with* $NEt_3$. After evaporation of all volatiles *in vacuo*, a pale yellow, oily residue remained, which was shown to consist of a mixture of (10) and $[NHEt_3][AlCl_4]$ by means of n.m.r. spectroscopy. $^{13}C$ N.m.r.: $[NHEt_3]^+$: $\delta$ 46.8 (NC), 9.6 (NCC); (10): $\delta$ 145.4 (dd, $\Sigma J_{PC}$ 12.5 Hz), 143.5 (dd, $\Sigma J_{PC}$ 10 Hz), 139.4 (dd, $\Sigma J_{PC}$ 8.0 Hz), 138.9 (dd, $\Sigma J_{PC}$ 14 Hz), 137.5 (dd, $\Sigma J_{PC}$ 8.0 Hz), 136.2 (d, 9.0 Hz), 134.9 (dd, $\Sigma J_{PC}$ 6.0 Hz), and 132.8 (d, 1.0 Hz) (C=C ring); 60.9 (dd, $\Sigma J_{PC}$ 19 Hz) and 59.2 (dd, $\Sigma J_{PC}$ 35 Hz) (PC ring); 54.6 (dd, $\Sigma J_{PC}$ 15 Hz) and 53.0 (dd, $\Sigma J_{PC}$ 22 Hz) (NC); 32.1 (d, 3.0 Hz) and 32.0 (dd, $\Sigma J_{PC}$ 8.0 Hz) ($NCMe_3$); 24.5 (d, 20 Hz, $PCH_2$); 16.1 (dd, $\Sigma J_{PC}$ 39 Hz) and 15.9 (dd, $\Sigma J_{PC}$ 2.0 Hz) ($PCMe$ ring); 12.6 (dd, $\Sigma J_{PC}$ 4.0 Hz), 12.3, 11.8 (d, 3.0 Hz), 11.7 (dd, $\Sigma J_{PC}$ 4.0 Hz), 11.4 (d, $\Sigma J_{PC}$ 2.0 Hz), 11.1 (dd, $\Sigma J_{PC}$ 2.0 Hz), and 10.8 (d, $\Sigma J_{PC}$ 1.0 Hz) ($Me$ ring). $^1H$ N.m.r.: $[NHEt_3]^+$: $\delta$ 10.54 (broad, 1 H, NH), 3.14 (dq, $^3J_{HH}$ 6 and 8 Hz, 6 H, $NCH_2$), 1.37 (t, 8 Hz, 9 H, NCMe); (10): $\delta$ 8.31 (broad, 1 H) and 2.57 (broad d, 3 Hz, 1 H) (NH), 3.48 (d, 16 Hz, 1 H, $PCH_2$) (part of an AB spin system; the second resonance is masked under the $CH_2$ resonance of $[NHEt_3]^+$), 2.03—1.67 (m, 27 H, CMe ring); 1.28 (9 H) and 1.10 (d, 1.0 Hz, 9 H) ($NCMe_3$).

*Reaction with* $Li[N(SiMe_3)_2]$. Solid $[P(NHBu^t)(C_5Me_5)][AlCl_4]$ (410 mg, 1 mmol) was stirred for 2 h with a solution of $Li[N(SiMe_3)_2]$ (170 mg, 1 mmol) in toluene (4 cm³).

*Reaction with* $P(=NBu^t)(C_5Me_5)$ (5). Compound (5) (1.19 g, 5 mmol) was added *via* a syringe to a solution of $[P(NHBu^t)(C_5Me_5)][AlCl_4]$ (2.04 g, 5 mmol) in $CH_2Cl_2$ (10 cm³). Quantitative formation of (13) after 10 min was indicated by $^{31}P$ n.m.r. spectroscopy. After 2 h additional stirring, the volume was reduced *in vacuo* to 5 cm³, and hexane (15 cm³) was added. The precipitate was filtered off and recrystallized twice from $CHCl_3$-hexane. After drying *in vacuo*, pure (14) was

obtained as colourless crystals. $^{13}C$ N.m.r.: $\delta$ 139.4 (dd, 10.8 and 4.6 Hz), 129.8 (dd, 8.9 and 3.9 Hz) (C=C); 67.3 (d, 19.3 Hz, C allyl); 60.8 (dd, 18.1 and 10.9 Hz) and 59.6 (d, 86.4 Hz) (PC); 58.3 (d, 9.7 Hz) and 58.0 (d, 10.2 Hz) (NC); 32.7 (dd, 8.1 and 2.2 Hz) and 33.4 (d, 2.8 Hz) ($NCMe_3$); 20.6 (d, 26.1 Hz), 19.1, 16.5, 14.3, and 11.6 (*CMe*). $^1H$ n.m.r.: $\delta$ 3.06 (broad, 1 H, NH); 1.66 (d, 0.6 Hz, 9 H) and 1.53 (d, 1.4 Hz, 9 H) ($NCMe_3$); 1.57 (d, 2.0 Hz, 6 H), 1.51 (6 H), 1.27 (d, 16.0 Hz, 6 H), 1.26 (d, 17.8 Hz, 6 H), and 1.17 (d, 1.0 Hz, 6 H) (CMe).

*Tricarbonyl($\eta^5$-cyclopentadienyl)[($\sigma$-pentamethylcyclo-pentadienyl)(t-butylamino)phosphonio]tungsten(0) Tetrachloro-aluminate,* (16).—A solution of $[W(CO)_3H(C_5Me_5)]$ (1.00 g, 3 mmol) in $CH_2Cl_2$ (5 cm³) was added dropwise to an ice-cooled solution of $[P(NHBu^t)(C_5Me_5)][AlCl_4]$ (1.22 g, 3 mmol) in $CH_2Cl_2$ (5 cm³). After warming to room temperature, the solvent was evaporated *in vacuo*. The residue was dissolved in $CH_2Cl_2$ and precipitated by addition of hexane. Filtration and drying *in vacuo* afforded 1.95 g (88%) of (16) as a bright yellow solid.[13] $^{13}C$ N.m.r.: $\delta$ 217.4 (d, 2.7 Hz), 214.3 (d, 26.7 Hz), and 212.1 (d, 21.9 Hz) (CO); 144.1 (d, 8.6 Hz, 142.0 (d, 6.9 Hz), 138.6, and 134.0 (d, 3.4 Hz) (C=C); 93.3 ($C_5H_5$), 62.9 (d, 15.2 Hz, PC), 55.3 (d, 12.1 Hz, NC), 31.5 (d, 2.8 Hz, $NCMe_3$); 17.9 (d, 5.9 Hz), 13.0, 11.9, 11.3 (d, 1.8 Hz), and 10.9 (d, 1.3 Hz) (Me ring); $^1H$ N.m.r.: $\delta$ 7.43 (dd, $^1J_{HP}$ 392 Hz, $^3J_{HH}$ 11.3 Hz, 1 H, PH), 5.97 (5 H, $C_5H_5$); 1.96 (3 H), 1.80 (d, 5.1 Hz, 3 H), 1.75 (3 H), 1.74 (d, 6.7 Hz, 3 H), and 1.50 (d, 17.0 Hz, 3 H) (Me ring), 1.41 (9 H, $NCMe_3$). I.r.: $v(CO)$ at 2 046s, 1 980s, and 1 960vs cm⁻¹.

*Preparation of Complex* (17a).—The compound $[W(CO)_3(MeCN)_3]$ (391 mg, 1 mmol) was treated with a solution of $[P(NHBu^t)(C_5Me_5)][AlCl_4]$ (406 mg, 1 mmol) in $CH_2Cl_2$ (4 cm³) at $-20\,^{\circ}C$. After stirring the deep red solution for 1 h at $-20\,^{\circ}C$, volatiles were evaporated *in vacuo*, to give (17a) as a red microcrystalline solid. $^{13}C$ N.m.r. ($-40\,^{\circ}C$): $\delta$ 206.1 and 205.5 (d, 9.3 Hz) (CO); 139.7 (d, 3.4 Hz) and 137.1 (C=C); 128.1 (CN), 76.6 (broad, PC), 56.1 (d, 1.2 Hz, PNC), 30.3 (d, 4.3 Hz, $CMe_3$), 16.7 (d, 11 Hz, $PCMe$ ring); 10.4 and 10.3 (=$CMe$ ring); 3.9 (NCMe). $^1H$ N.m.r.: $\delta$ 6.06 (d, 10.2 Hz, 1 H, NH), 2.58 (6 H, $CH_3CN$), 1.85 (broad, 15 H, Me ring), 1.29 (9 H, Me ring). $^{27}Al$ N.m.r.: $\delta$ 102.9. I.r.: $v_{CN}$ 2 320w, 2 278w; $v_{CO}$ 2 008s, 1 935m, and 1 890s cm⁻¹.

*Preparation of Complex* (17b).—(a) A $CH_2Cl_2$ solution of (17a) was allowed to warm to 20 $^{\circ}C$ and kept at this temperature for several days. Conversion to (17b) was monitored by $^{31}P$ n.m.r. spectroscopy.

(b) A solution of $[P(NHBu^t)(C_5Me_5)][AlCl_4]$ (1.01 g, 2.5 mmol) and $[W(CO)_3(MeCN)_3]$ (0.97 g, 2.5 mmol) in acetonitrile (25 cm³) were refluxed for 2 h until a deep red solution was formed and evolution of CO had ceased. After cooling to room temperature, the solvent was evaporated *in vacuo*. Recrystallization of the red, oily residue from toluene at $-20\,^{\circ}C$ gave a pink, microcrystalline powder, which was once more recrystallized from a $CHCl_3$-hexane mixture, to give (17b) as red needles. $^{13}C$ N.m.r.: $\delta$ 217.4 (d, 16.9 Hz, CO); 139.5 and 137.9 (C=C); 125.2 and 124.8 (MeCN); 80.5 (broad, PC), 53.6 (PNC), 31.8 (d, 1.3 Hz, ($NCMe$)$_3$), 18.4 (broad, $PCMe$ ring), 10.9 (broad, =$CMe$ ring); 4.6 and 4.3 (MeCN). $^1H$ N.m.r.: $\delta$ 6.37 (d, 5.9 Hz, 1 H, NH); 2.62 (3 H) and 2.48 (6 H) (MeCN); 1.84 (broad, 15 H, Me ring), 1.26 (9 H, Me ring). $^{27}Al$ N.m.r.: $\delta$ 103.0. I.r.: $v_{CN}$ 2 316w, 2 286w cm⁻¹; $v_{CO}$ 1 929s, 1 922s, 1 852s, and 1 840s cm⁻¹.

# References

1 S. G. Baxter, A. H. Cowley, and S. K. Mehrotra, *J. Am. Chem. Soc.*, 1981, **103**, 5572.
2 A. H. Cowley and S. K. Mehrotra, *J. Am. Chem. Soc.*, 1983, **105**, 2074.
3 T. J. Lee, H. F. Schaefer III, and E. A. Magnusson, *J. Am. Chem. Soc.*, 1985, **107**, 7239.
4 P. Jutzi, *Adv. Organomet. Chem.*, 1986, **26**, 217 and refs. therein.
5 P. Jutzi, U. Meyer, B. Krebs, and M. Dartmann, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 919.
6 D. Gudat, E. Niecke, B. Krebs, and M. Dartmann, *Chimia*, 1985, **39**, 277.
7 D. Gudat and E. Niecke, *J. Chem. Soc., Chem. Commun.*, 1987, 10.
8 A. H. Cowley and R. A. Kemp, *Chem. Rev.*, 1985, **85**, 367 and refs. therein.
9 D. Gudat, E. Niecke, B. Krebs, and M. Dartmann, *Organometallics*, 1986, **5**, 2376.
10 O. Dahl, *Tetrahedron Lett.*, 1982, **23**, 1493.
11 R. F. Childs, *Tetrahedron*, 1982, **38**, 567.
12 D. E. C. Corbridge, 'The Structural Chemistry of Phosphorus,' Elsevier, Amsterdam, 1974.
13 P. Jutzi, B. Hampel, K. Stroppel, C. Krüger, K. Angermund, and P. Hofmann, *Chem. Ber.*, 1985, **118**, 2789; P. Jutzi, B. Hampel, M. B. Hursthouse, and A. J. Howes, *J. Organomet. Chem.*, 1986, **299**, 19; P. Jutzi, B. Hampel, M. B. Hursthouse, and A. J. Howes, *Organometallics*, 1986, **5**, 1944.
14 F. X. Kohl, E. Schlüter, P. Jutzi, C. Krüger, G. Wolmershäuser, P. Hofmann, and P. Stauffert, *Chem. Ber.*, 1984, **117**, 1178.
15 E. Niecke, D. Gudat, and E. Symalla, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 834.
16 E. Groß, K. Jörg, K. Fiederling, A. Göttlein, W. Malisch, and R. Boese, *Angew. Chem., Int. Ed. Engl.*, 1984, **24**, 738.
17 R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 711.
18 G. M. Sheldrick, SHELX 76, A program for structure determination, University of Cambridge, 1976; G. M. Sheldrick, SHELXTL, An integrated system for solving, refining and displaying crystal structures from diffraction data, University of Göttingen, 1978.
19 (*a*) H. Nöth, R. Rurländer, and P. Wolfgardt, *Z. Naturforsch., Teil B*, 1982, **37**, 29; (*b*) P. Pallmann, K. Hensen, and J. W. Bats, *ibid.*, p. 1312.