1,3,5-Triphosphabicyclo[3.1.0]hexene-η^3,η^1-diyl Hafnium Complexes: Structure and Reactivity

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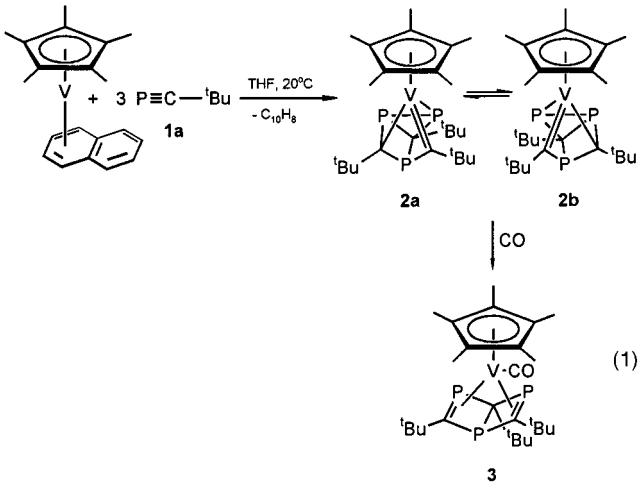
It is shown that the $(P{\equiv}C{-}t\mathrm{Bu})_3$ ligand found in the hafnium complex (COT)Hf$(P{\equiv}C{-}t\mathrm{Bu})_3$ **5** (COT = cyclooctatetraene), which we reported recently,[3] is also present in the new hafnium complex **12**, prepared by reaction of hexachloroethane with complex **5** in pentane, as well as in its trimethylphosphane adduct **14**. The structures of complexes **12** and **14** have been determined by X-ray crystallography and that of **5** by comparing its ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra with those of the complexes **12** and **14**. The organophosphorus ligand in all three complexes is a 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabicyclo[3.1.0]hexene-η^3,η^1-diyl. Hydrolysis of complexes **5** and **12** with water gives the new phosphorus heterocycle **15**, whereas the new heterocycles **16** and **17** are formed in an approximately 1:1 mixture using either silica gel containing 2% H_2O or $Na_2SO_4 \cdot 10\ H_2O$.

Introduction

Although numerous reactions are known where phosphaalkynes (**1**), e.g. *tert*-butylphosphaalkyne (**1a**), are cyclodimerized in the coordination sphere of a transition metal, the corresponding cyclotrimerizations are rare.[1] Until recently, the only example reported where it has been established unambiguously that **1a** is cyclotrimerized is the reaction to give the stable vanadium complexes **2** and **3**.[2]



(1)

Recently, we succeeded in preparing an η^8-cyclooctatetraene hafnium$-(PC-t\mathrm{Bu})_3$ complex **5** from **1a** and η^8-cyclooctatetraene-η^4-butadiene hafnium **4a** in high yield. Subsequent reaction of **5** with hexachloroethane afforded the new cyclotrimer 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene **6** (Eq. 2a).[3] An extensive NMR study of complex **5** showed that the trimeric phosphaalkyne unit in this hafnium complex is not bonded to the metal as a triphosphabenzene **6**, even though this species is liberated in subsequent displacement reactions. However, the NMR experiments did not permit a full description of the bonding situation.[3]

Slight modification of the cyclooctatetraene ligand in complex **4** (introduction of trimethylsilyl substituents → **4b**) led to another hafnium$-(PC-t\mathrm{Bu})_3$ complex (**7**), in which a 7-hafna-1,3,5-triphosphanorbornadiene appears to be formed. Free 1,3,5-triphospha-Dewar-benzene **8** could be obtained by displacement of the $(PC-t\mathrm{Bu})_3$ unit from **7**[3] (Eq. 2b).

In the last few years, two transition metal complexes have been reported where a 1,3-diphosphabenzene[4] (**9**) and a 1,3,5-triphosphabenzene[5] (**10**) are incorporated as η^6-coordinated ligands. However, it would seem very unlikely that the η^6-phosphabenzene molybdenumdicarbonyl complex **11** published much earlier[6] does indeed have the claimed structure.[7]

In this publication, we show that the $(P{\equiv}C-t\mathrm{Bu})_3$ ligand bonded to the hafnium in complex **5** as well as in the two new complexes **12** and **14** is a new type with a 1,3,5-triphosphabicyclo[3.1.0]hexene skeleton. This has been established by determining the structures of complexes **12** and **14** by X-ray crystallography. Supporting evidence comes from the observation that hydrolysis of complexes **5** and **12** yields the same phosphorus heterocycles **15**–**17**, indicating that the $(P{\equiv}C-t\mathrm{Bu})_3$ unit has the same structure in all three complexes **5**, **12**, and **14**.

Results and Discussion

As described previously,[3] triphosphabenzene **6** can be generated from the hafnium complex **5** in 53% yield by a redox reaction with hexachloroethane (Eq. 2). The "(COT)-

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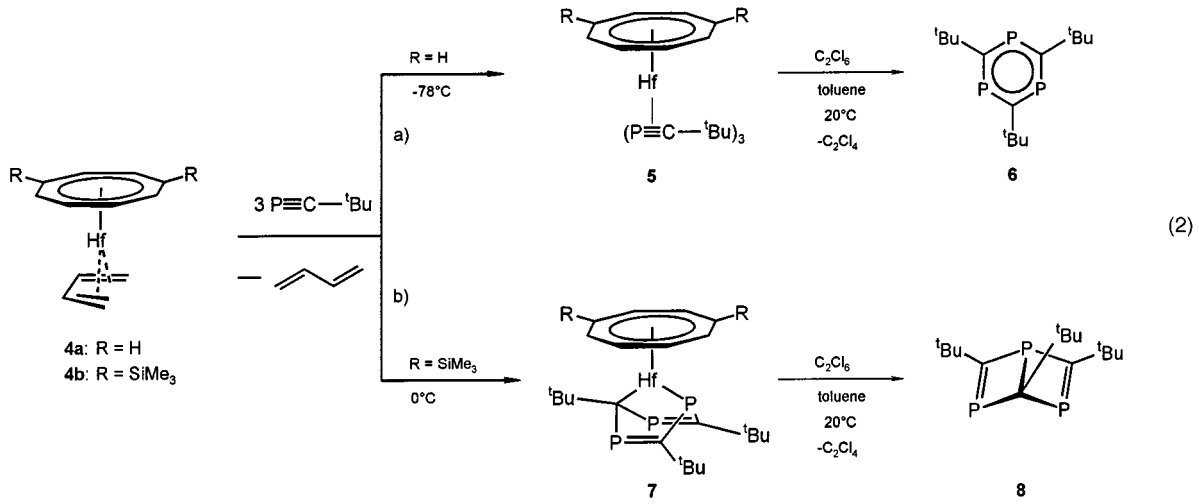
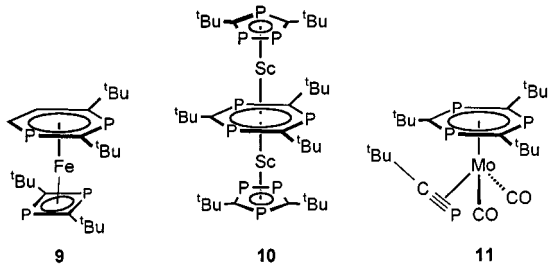
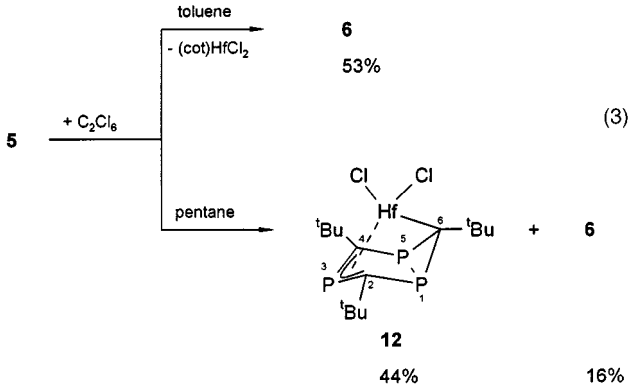




Scheme 1

hafnium(II)" fragment (COT = cyclooctatetraene) is oxidized to $(COT)HfCl_2$ and the hexachloroethane is reduced to tetrachloroethene. Unexpectedly, further studies revealed that the course of this reaction can be influenced by variation of the solvent. In our original experiments we had used toluene,[3] but replacing this by pentane led to an almost complete change in the reaction products. In the latter medium, the aforementioned redox reaction becomes merely a side reaction giving **6** only in ca. 16% yield, while the main product, 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabicyclo[3.1.0]-hexene-η^3,η^1-diylhafnium dichloride **12** is formed in ca. 44% yield. The fate of the cyclooctatetraene ligand is unknown.



The new hafnium complex **12** is a red solid. Crystals suitable for X-ray analysis could be obtained from pentane at −20°C.

X-ray structural analysis of **12** revealed that it is dimeric in the solid state and contains a μ-Cl_2 bridge. Molecular weight measurements showed the complex to be monomeric in solution, e.g. in toluene. The $(PC-tBu)_3$ moiety in **12** possesses a hitherto unknown structure for this ligand: it is linked to the metal as a 1,3,5-triphosphabicyclo[3.1.0]hexenediyl via a C1−Hf σ-bond and an η^3-allyl bond (C6, C11, and P1). The bicyclic ligand adopts a chair conformation, with an interplanar angle P2−C1−P3 and C6−C11−P2−P3 of 77.9°; P1 is bent away from the metal by 24.1°. The P−C and P−P σ-bond lengths in the bicyclic system lie in the normal ranges,[8] e.g. P2−C1 = 1.924(6), P3−C1 = 1.893(6), P3−C6 = 1.950(6), P2−C11 = 1.851(6) Å. The η^3-allylic nature of the C6−P1−C11 moiety is evident from the typical bond lengths Hf−C6 = 2.442(6), Hf−C11 = 2.358(6), Hf−P1 = 2.727(2) Å and from the P−C distances P1−C6 = 1.729(6) and P1−C11 = 1.752(6), which lie between those known for P−C single and P−C double bonds.[8] Similar P−C distances have been found in η^3-P−C−C and η^3-C−P−C allylic complexes of cobalt,[9] nickel,[10] and molybdenum.[11] The Hf−C1 σ-bond is reflected in a short distance of 2.081(6) Å.

As mentioned above, the hafnium complex **12** is monomeric in solution and is therefore electronically and coordinatively unsaturated. Thus, it can be expected to react readily with electron-donating ligands such as isocyanides and phosphanes. Indeed, even at −78°C, complex **12** takes up one equivalent of *tert*-butyl isocyanides or trimethylphosphane to give the new hafnium complexes **13** and **14**, respectively. No further reactions, e.g. displacement of the $(PC-tBu)_3$ unit, are observed when these ligands are use in excess.

Both complexes were isolated as dark-red microcrystals. Only those of **14** proved to be stable at room temperature and both complexes were found to be unstable in solution above 0°C. The trimethylphosphane complex **14** dissociates into complex **12** and free trimethylphosphane, while the isonitrile complex **13** rearranges into a complex of unknown structure that gives rise to two new signals in the

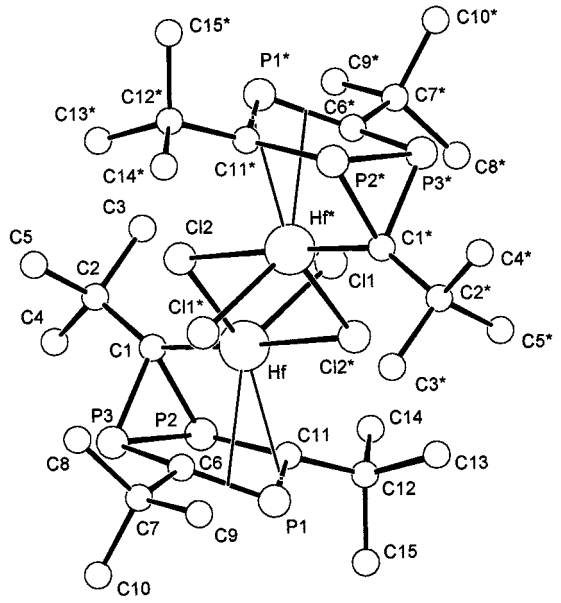
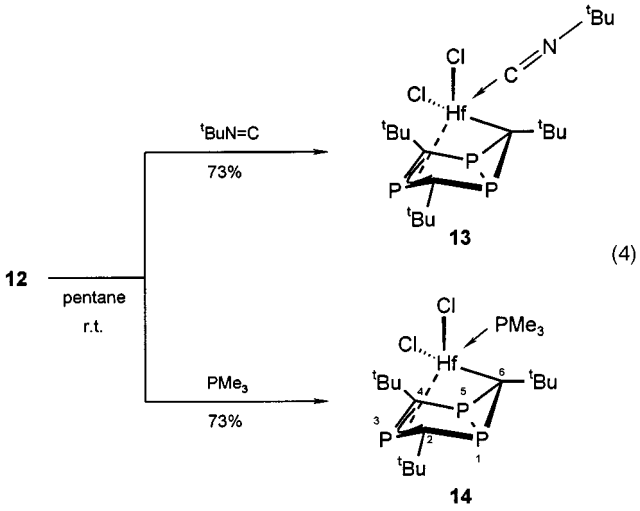


Figure 1. Molecular structure of **12**; selected bond lengths [Å] and angles [°]: Hf−Cl1 2.371(2), Hf−Cl2 2.489(1), Hf−P1 2.727(2), Hf−C6 2.442(6), Hf−C1 2.081(6), Hf−C11 2.358(6), P1−C6 1.729(6), P1−C11 1.752(6), P2−P3 2.213(2), P2−C1 1.924(6), P3−C1 1.893(6), P2−C11 1.851(6), P3−C6 1.950(6); P2−C1−P3 70.8(2), C1−P3−P2 55.2(2), C6−P3−P2 96.4(2), C6−P1−C11 98.9(3), P1−C6−P3 120.9(3)



(4)

^{31}P-NMR spectrum at δ = −163.8 and −100.4 in a 2:1 ratio.

X-ray analysis of crystals of **14**, obtained from pentane solution at −78°C, revealed that the complex is monomeric and contains a (PC−*t*Bu)$_3$ unit isostructural with that found in complex **12**. However, in view of the rather poor quality of the crystal structure analytical data, no further details will be discussed, neither here nor in the Experimental Section.

To gain insight into the structure of the [P_3C_3tBu$_3$] ligand of the complexes **5**, **12**, and **14** in solution, we examined their NMR spectra (^{1}H, ^{13}C, ^{31}P) in detail. In each case, the NMR spectra recorded at −30°C showed that a single complex of high symmetry was present. The similarity of the characteristic features of the spectra shows that the structure of the [P_3C_3tBu$_3$] ligand is the same in all three cases. For the three P and three C atoms of the [P_3C_3] unit, two signals are found in a 1:2 ratio in the ^{31}P- and ^{13}C-NMR spectra, respectively. In the ^{1}H-NMR spectra, two signals are observed in the same ratio due to the protons of the *tert*-butyl groups (see Table 1).

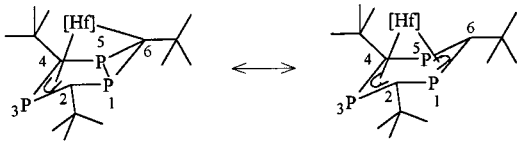
Although the ^{31}P-NMR spectra of the complexes are broadly similar, the positions of the signals differ somewhat depending on the nature of the other ligand bonded to the metal (e.g. **5**: δ = 357.1 and 17.3; **12**: δ = 410.2 and −45.6). Nevertheless, the P,P coupling constants remain almost unchanged (41.9−43.8 Hz). While the ^{13}C-chemical shifts of the three ring-carbon atoms of complexes **5**, **12**, and **14** differ considerably from compound to compound, the appearance of the multiplets and the magnitude of the coupling constants remains essentially the same.

For complex **12**, a detailed analysis of the ^{13}C multiplet at δ = 169.1 (C2 and C4) reveals that these carbon atoms constitute the X part of an AA′MX spin system (A, M = ^{31}P, X = ^{13}C). It consists of two AA′X subspectra, each of five signals, where the outer combination lines, just detectable above the noise, are split by $^1J_{P,C}$ = 73.4 Hz. Although an exact analysis is not possible, the spectrum allows adequately accurate estimates of $^1J_{P1,P5}$ (74 Hz), $^1J_{P3,C2}$ (73 Hz), $^1J_{P2,C2}$ (70 Hz), and $^3J_{P5,C2}$ (13 Hz) to be made. These values were confirmed by computer simulation. The interpretation of the magnitude of $J_{P1,P5}$ (74 Hz) is ambiguous: it appears to be rather small for a $^1J_{P,P}$ coupling, but large for a $^2J_{P,P}$ coupling (e.g. $^1J_{P,P}$ in complex **2a**, **b** = 219 Hz). On the basis of these NMR studies, we propose that the structure of the (P_3C_3tBu$_3$) ligand in complexes **5**, **12**, and **14** is best represented by the two canonical forms **a** and **b** (see Table 1).

Support for this interpretation of the NMR spectra is provided by the products of hydrolysis of complexes **5** and **12**. When the hafnium complex **5** is treated with an excess of water, the only metal-free reaction products obtained are the new bicyclic phosphorus heterocycle **15** (yield 55%) together with 10% of 1,3,5-triphosphabenzene **6**. Under milder and more controlled conditions, the addition of the second equivalent of water can be suppressed and the two new phosphorus heterocycles **16** and **17** are formed in almost equal amounts. Suitable reagents for this purpose are silica gel with a water content of 2% and the hydrate $Na_2SO_4 \cdot 10\ H_2O$. With these two reagents, both hafnium complexes **5** and **12** react to give 1,3,5-triphosphabicyclo[3.1.0]hex-2-ene **16** and 1,3,5-triphosphacyclohexa-1,4-diene **17** in yields of 83% and 90%, respectively. It is likely that **16** is an intermediate in the formation of **15** from complex **5**. The NMR spectra of **15**, **16**, and **17** indicate that only one isomer is formed in each case.

The structure determination of compounds **15**−**17** is based mainly upon their NMR data. The IR and mass spectra, as well as elemental analysis data support the proposed structures. The presence of a diphosphirane unit in compounds **15** and **16** is evident from the high field shifts of P1 and P5 [δ = −222.8 (s) in **15**; δ = −117.4 and −128.6

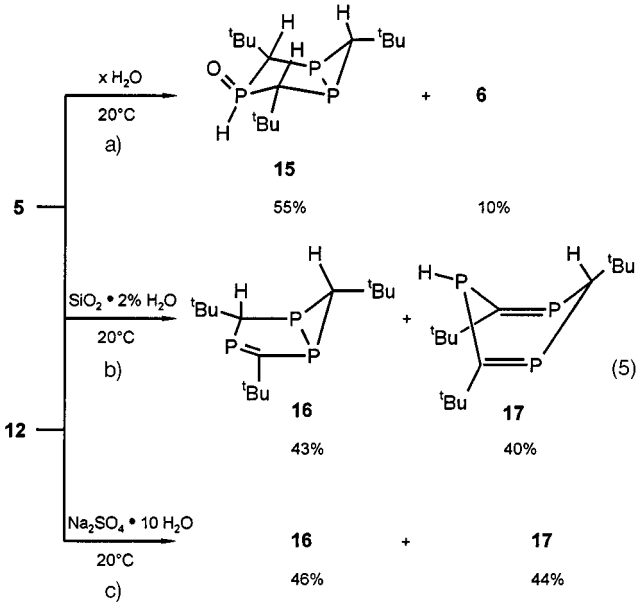
Table 1. Characteristic NMR data (^{1}H, ^{13}C, ^{31}P) of the [$P_3C_3tBu_3$] hafnium complexes **5**, **12**, and **14**



a b

	complex **5** [Hf] = (COT)Hf	complex **12** [Hf] = $HfCl_2$	complex **14** [Hf] = $HfCl_2(PMe_3)$
^{31}P NMR[a]	357.1 (t, $^2J_{P,P}$ = 43.8, P3) 17.3 (d, $^2J_{P,P}$ = 43.8, P1, P5)	410.2 (t, $^2J_{P,P}$ = 43.0, P3) −45.6 (d, $^2J_{P,P}$ = 43.0, P1, P5)	399.1 (dt, $^2J_{P,P}$ = 41.9, P3) 41.5 (dd, $^2J_{P,P}$ = 41.9, P1, P5)
^{1}H NMR[b]	0.81 (s, 9 H, *t*Bu at C6) 1.35 (s, 18 H, *t*Bu at C2, C4)	1.29 (s, 9 H, *t*Bu at C6) 1.42 (s, 18 H, *t*Bu at C2, C4)	1.49 (s, *t*Bu at C6) 1.41 (s, *t*Bu at C2, C4)
^{13}C NMR[c]	93.8 (t, $^1J_{C,P}$ = 59.4, C6) 139.3 (dt, $^1J_{C,P}$ = 74, 69.4, C2, C4)	176.3[d] (t, $^1J_{C,P}$ = 67.7, C6) 169.1[e] (dt, $^1J_{C,P}$ = 73.4, 83.0, C2, C4)	168.1 (br. m, C6) 165.1 (br. m, C2, C4)

[a] 162.0 MHz ([D_8]THF, −30°C, 85% H_3PO_4). − [b] 300 MHz ([D_8]THF, −30°C, TMS). − [c] 100.6 MHz ([D_8]THF, −30°C, TMS). − [d] A_2X spin system (A = ^{31}P, X = ^{13}C). − [e] AA′MX spin system (A,M = ^{31}P, X = ^{13}C).

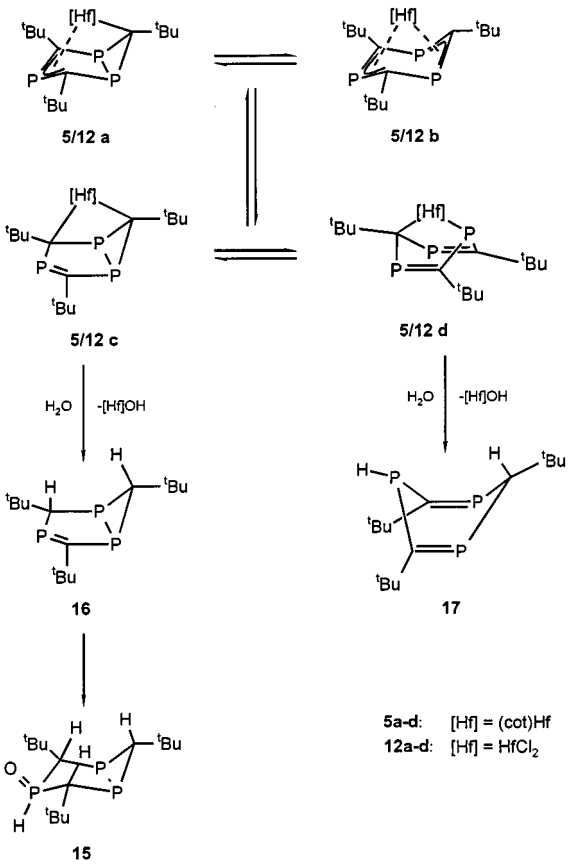


($^1J_{P,P}$ = 167.2 Hz) in **16**].[12] The proposed conformation of **15** shown in Eq. 5a is supported by the small magnitudes of the coupling constants between P1, P5 and 2-H and 4-H ($^3J_{P,H}$ = 3.5 Hz) and the high value of 16 Hz between P3 and 2,4-H, as well as by NOESY experiments. The presence of the PHO unit in **15** is indicated by its ^{31}P-NMR signal at δ = 39.4 with $^1J_{P,H}$ = 454.6 Hz and its IR absorptions at 2320 and 1183 cm^{-1}, which are typical for P−H and P=O bonds, respectively.[13] The small coupling constants between 4-H and the two adjacent P atoms reveal its *trans* orientation with respect to the lone pairs of these P atoms in compound **16**.[12] The high symmetry of 1,3,5-triphosphacyclohexa-1,4-diene **17** is reflected in its simple ^{31}P- and ^{13}C-NMR spectra, which feature only two sets of signals for the three P and C atoms of the six-membered ring and the three *tert*-butyl groups (^{31}P: δ = 241.3 and −24.9; ^{13}C: δ = 213.5 and 66.1) in a 2:1 ratio. The ^{1}H-, ^{13}C-, and ^{31}P-NMR chemical shifts are also consistent with the structure proposed for **17**. Analysis of the multiplets in the ^{13}C-NMR spectrum provides additional evidence for this structure. The signals attributable to C2, C4 and those of the *tert*-butyl groups linked to C2 and C4 all analyse as the X part of an AA′MX spin system (A, A′, M = ^{31}P, X = ^{13}C). The magnitude of the P1,P5 coupling constant, estimated as 10.5 Hz by simulation of the C2 multiplet, shows that P1 and P5 are not directly bonded.

The only difficulty in the interpretation of the ^{13}C-NMR spectrum of **17** was the finding that the signal of C6 at δ = 66.1 is a first-order triplet of doublets with a triplet splitting of $^1J_{P,C}$ = 51.5 Hz and a doublet splitting of $^3J_{P,C}$ = 42.2 Hz. While the value of $^1J_{P,C}$ is unremarkable, the magnitude of $^3J_{P,C}$ is unexpectedly large. In related organophosphorus compounds, a ^{31}P,^{13}C coupling constant of this order is more consistent with a one-bond coupling and we have not found any example of such a large coupling over three bonds in the literature. In order to show that P3 and C6 are not directly bonded and to confirm the connectivities in **17**, we determined the ^{13}C isotope shifts on the phosphorus chemical shifts. Analysis of the ^{13}C satellites in the ^{31}P-NMR spectrum showed that $^1\Delta^{31}P_1(^{13/12}C_6)$ amounts to −30.0 ppb, but that $^3\Delta^{31}P_3(^{13/12}C_6)$ is just −4.6 ppb. The latter is of a much smaller magnitude than is usually observed for $^1\Delta^{31}P(^{13/12}C)$ in similar compounds, confirming that P-3 and C-6 are not directly connected.[14] The observed ^{31}P,^{13}C and ^{31}P,^{1}H coupling constants are consistent with the electron pair on phosphorus and 6-H being *cis* to one another. The magnitude of ^3J(P-3,C-6) in compound **17** (42.2 Hz) is a further example illustrating the strong stereochemical dependence of $^3J(^{31}P,^{13}C)$[15,16] (for a full listing of NMR data, see Experimental Section).

As far as we are aware, the 1,3,5-triphosphabicyclo[3.1.0]hexane **15** and -hexene **16**, as well as the 1,3,5-triphosphacyclohexa-1,4-diene **17**, are the first examples of such phosphorus heterocycles to be reported. Their synthesis from the hafnium complexes **5** and **12** can be rationalized in terms of the hydrolysis of the two mesomeric forms **5c/12c** and **5d/12d**, which contain one P−M and one C−M σ-bond (see Scheme 2). In the presence of pure water, the

phosphorus heterocycle **16** adds a second equivalent of water to give compound **15**. In all these reactions, the hafnium part of the complexes **5** and **12** should be displaced as the corresponding hafnium dihydroxide, species that are known to be unstable.[17]



Scheme 2

In summary, we have determined the solid-state structures of the hafnium complexes **12** and **14** by X-ray analysis and have shown by extensive NMR studies and by hydrolysis of **5**, **12**, and **14** that all these hafnium complexes have the same structure in solution. By hydrolysis of **5** and **12** we have also been able to synthesize the new phosphorus heterocycles **15**, **16**, and **17**.

Experimental Section

General: All experiments were carried out under argon in anhydrous solvents. − MS: EI; Finnigan MAT 311 ADF. − ^{1}H- and ^{13}C-NMR: Bruker AC 200, AC 300, AMX 400, and DMX 600; chemical shifts were determined relative to solvent signals and converted to the TMS scale [$\delta(^1H)$ of C_6D_5H at 7.15; $\delta(^{13}C)$ of C_6D_6 at 128.0]. The ^{13}C multiplicities were confirmed by means of DEPT spectra. − ^{31}P-NMR: Bruker AC 200 (81.1 MHz) and AC 300 (121.5 MHz), external standard H_3PO_4. − Elemental analysis: Microanalytical laboratory, Dornis and Kolbe, Mülheim a.d. Ruhr. − Commercial chemicals: hexachloroethane, *tert*-butyl isocyanide (Aldrich); sodium sulfate decahydrate (Reininghaus). − (η^8-Cyclooctatetraene)(P≡C−*t*Bu)$_3$hafnium (**5**)[3] and trimethylphosphane[18] were prepared according to published procedures.

(2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabicyclo[3.1.0]hexene-η^3,η^1-diyl)hafnium Dichloride (12): Hexachloroethane (230 mg, 0.97 mmol) was added to a suspension of the hafnium complex **5** (480 mg, 0.82 mmol) in pentane (10 mL). The reaction mixture was stirred at room temperature for 12 h, in the course of which the colour changed from green to red and a brown precipitate was formed. After filtration through Celite and washing the solid with pentane (2 × 3 mL), the filtrate was concentrated to a volume of ca. 4 mL and cooled to −78°C. Red-violet crystals of complex **12** (210 mg, 44%) precipitated, which were isolated by filtration. Triphosphabenzene **6** (40 mg, 16%) could be isolated from the filtrate by column chromatography. Complex **12**: m.p. 172°C (dec.). − ^{1}H and ^{31}P NMR: See Table 1. − ^{13}C{^{1}H} NMR (100.6 MHz, [D$_8$]THF, −30°C): δ = 176.3 (A_2X spin system, A = ^{31}P, X = ^{13}C, t, $^1J_{C,P}$ = 67.7 Hz, C-6), 169.1 (AA′MX spin system, AA′ = ^{31}P-1 and ^{31}P-5, M = ^{31}P-3, X = ^{13}C-2,4, $J_{M,X}$ = 73.4, $J_{A,A}$ = 73.7, $|J_{A,X}$ = 70|, $J_{A',X}$ = 13 Hz , values checked by simulation, C-2 and C-4), 42.8 [t, $^2J_{C,P}$ = 7.6 Hz, *C*(CH$_3$)$_3$ at C-6], 33.2 [C(*C*H$_3$)$_3$ at C-6], 41.8 [*C*(CH$_3$)$_3$ at C-2 and C-4], 36.4 [C(*C*H$_3$)$_3$ at C-2 and C-4]. − MS (EI, 70 eV); *m/z* (%): 550 (28) [M$^+$], 450 (17) [M − PC*t*Bu$^+$], 300 (12) [(PC*t*Bu)$_3^+$], 169 (31) [PC$_2$(*t*Bu)$_2^+$], 41 (100). − $C_{15}H_{27}P_3Cl_2Hf$ (549.7): calcd. C 32.78, H 4.95; found C 32.75, H 4.90.

***tert*-Butyl Isocyanide Adduct 13 of Complex 12:** *tert*-Butyl isocyanide (0.8 g, 9.6 mmol) was added to a cooled (−78°C) solution of the hafnium complex **12** (300 mg, 0.55 mmol) in pentane (5 mL) and the reaction mixture was stirred for 12 h. The solvent and excess isocyanide were then evaporated off at 0.5 bar and the residue was taken up in pentane (2 mL). At −78°C, dark-red microcrystals separated, which were collected by filtration and dried at −78°C and 0.5 bar to yield 150 mg (44%) of the isocyanide adduct **13**. Complex **13** was found to be unstable at room temperature and thus had to be stored at −78°C. − ^{1}H NMR (200.1 MHz, [D$_8$]toluene, 30°C): δ = 1.52 (s, 27 H, *t*Bu at C2, C4 and C6), 0.77 (s, *t*Bu at N). − ^{13}C{^{1}H} NMR (50.1 MHz, [D$_8$]toluene, 30°C): δ = 188.5−187.0 (br. m, C-2, C-4, C-6), 150.1 (m, C=N), 54.6 [br. s, *C*(CH$_3$) at N], 33.9 [dt, $J_{C,P}$ = 10.7 and 9.8 Hz, *C*(CH$_3$) at C-2, C-4 and C-6], 33.3 [t, $J_{C,P}$ = 7.9 Hz, C(*C*CH$_3$) at C-6], 30.3 [d, $J_{C,P}$ = 7.8 Hz, C(*C*H$_3$) at C-2 and C-4], 27.6 [s, C(*C*H$_3$) at N]. − ^{31}P NMR (81.1 MHz, [D$_8$]toluene, 30°C): δ = 315.1 (t, $J_{P,P}$ = 5.0 Hz, P-3), −24.1 (d, $J_{P,P}$ = 5.0 Hz, P-1 and P-5).

Trimethylphosphane Adduct 14 of Complex 12: Trimethylphosphane (0.1 mL, 0.8 g, 10.5 mmol) was added to a solution of the hafnium complex **12** (300 mg, 0.55 mmol) in pentane (5 mL), cooled to −78°C. After stirring for 2 h, all volatile components were removed at 0°C and 0.5 mbar and the red oily residue was redissolved in pentane (2 mL) at −10°C. At −78°C dark-red crystals of complex **14** (250 mg, 73%) suitable for X-ray analysis were obtained. The product was isolated by filtration and dried at 0.5 mbar. − ^{1}H and ^{31}P NMR: See Table 1. − ^{13}C{^{1}H} NMR (100.6 MHz, [D$_8$]THF, −30°C): δ = 168.1 (m, C-6), 165.1 (m, C-2 and C-4), 40.6 [t, $^2J_{P1,C}$ = $^2J_{P5,C}$ = 7.9 Hz, *C*(CH$_3$) at C-6], 40.1 [td, $^2J_{P3,C}$ = 16.6 Hz, $^2J_{P1,C}$ = $^3J_{P5,2}$ = 10.4 Hz, *C*(CH$_3$) at C-2 and C-4], 36.1 [s, C(*C*H$_3$) at C-2 and C-4], 32.4 [s, C(*C*H$_3$) at C-6], 13.0 [d, $^1J_{P,C}$ = 10.4 Hz, P(*C*H$_3$)$_3$].

2,4,6-Tri-*tert*-butyl-1,3,5-triphospha-3-oxobicyclo[3.1.0]hexane (15) from Hydrolysis of Hafnium Complex 5: To a green solution of complex **5** (300 mg, 0.51 mmol) in diethyl ether (5 mL) at 0°C was added water (1 mL, 5.56 mmol). After stirring for 10 h at room temperature, a brownish solid precipitated from the yellow solution. The precipitate was removed by filtration through Celite and all volatiles were distilled off from the filtrate at 20°C and 0.5 mbar.

Chromatographic separation of the solid residue on silica gel gave triphosphabenzene **6** (15 mg, 10%) as a first fraction on eluting with pentane, followed by compound **15** (90 mg, 55%) on eluting with THF. The latter was isolated by concentrating the THF fraction to 5 mL, adding pentane (5 mL), and cooling to −78°C, whereupon **15** precipitated as colourless needles; m.p. 198°C. − ^{1}H NMR ([D$_8$]THF, 400 MHz, 30°C): δ = 6.10 (dtt, $^1J_{P3,H}$ = 454.6 Hz, $^3J_{P1,H}$ = $^3J_{P5,H}$ = 2.0 Hz, $^3J_{2\,H,H}$ = $^3J_{4\,H,H}$ = 9.2 Hz, 3-H), 1.94 [t(d), $^2J_{P1,H}$ = $^2J_{P5,H}$ = 4.1 Hz, $^4J_{P3,H}$ ≈ 1.4 Hz, 6-H], 1.73 (dd/pseudo t, $^2J_{P3,H}$ = 16.0 Hz, $^2J_{P1,H}$ + $^3J_{P5,H}$ = 6.8 Hz, $^3J_{3\,H,H}$ = 9.2 Hz, 2-H and 4-H), 1.30 [s, 18 H, C(CH$_3$)$_3$ at C-2 and C-4], 0.94 [t, 9 H, $^4J_{P1,H}$ = $^4J_{P5,H}$ < 1 Hz, C(CH$_3$)$_3$ at C-6]. − ^{13}C NMR ([D$_8$]THF, 100.1 MHz, 30°C): δ = 51.1 [dtd(A$_2$MX), $^1J_{C,H}$ = 155, $^1J_{P1,C}$ = $^1J_{P5,C}$ = 47.3, $^3J_{P3,C}$ = 6.5 Hz, C-6], 47.3 [tdd(AA′MX), $^1J_{C,H}$ = 140, $^1J_{P3,H}$ = 54.9, $J_{P1,C}$ + $J_{P5,C}$ = 52.0 Hz, C-2 + C-4], 34.1 [dt(AA′MX), $J_{P1,C}$ + $J_{P5,C}$ = 17.6, $^2J_{P3,C}$ = 0.9 Hz, *C*(CH$_3$)$_3$ at C-2 and C-4], 33.5 [dt(A$_2$MX), $^2J_{P1,C}$ = $^2J_{P5,C}$ = 11.8, $^4J_{P3,C}$ = 6.0 Hz, *C*(CH$_3$)$_3$ at C-6], 30.3 [tq(A$_2$MX), $^1J_{C,H}$ = 126, $^3J_{P1,C}$ = $^3J_{P5,C}$ = 5.9 Hz, C(*C*H$_3$)$_3$ at C-6], 30.1 [dtt(AA′MX), $^1J_{C,H}$ = 126, $J_{P1,C}$ + $J_{P5,C}$ = 10.7, $^3J_{P3,C}$ = 5.6 Hz, C(*C*H$_3$)$_3$ at C-2 and C-4]. − ^{31}P NMR ([D$_8$]THF, 30°C, 81.1 MHz): δ = 39.4 (s, P-3), −222.8 (s, P-1 and P-5). − IR (KBr): $\tilde{\nu}$ = 2961 (*t*Bu), 2320 (P−H), 1393, 1363 (*t*Bu), 1138 cm^{-1} (P=O). − MS (EI, 70 eV): *m/z* (%): 320 (100) [M$^+$], 305 (47) [M − CH$_3^+$], 263 (72) [(M − *t*Bu$^+$], 251 (60), 57 (50) [*t*Bu$^+$]. − $C_{15}H_{31}OP_3$ (320.3): calcd. C 56.24, H 9.75; found C 56.18, H 9.68.

2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabicyclo[3.1.0]hex-2-ene (16) and 2,4,6-Tri-*tert*-butyl-1,3,5-triphosphacyclohexa-1,4-diene (17): (a) By Hydrolysis of Hafnium Complex 5 with Hydrated Silica Gel: Silica gel (63−100 μm, Merck AG, dried at 150°C for 12 h and then deactivated with 2% water) was added to a suspension of complex **5** (300 mg, 0.55 mmol) in pentane (10 mL). Immediately, a colour change from green to yellow was observed. After stirring for 15 min, the reaction mixture was extracted with pentane. The combined extracts were concentrated to one-third of the original volume and crystallization at −78°C yielded **17** (60 mg, 40%) as a pale-yellow powder. Column chromatography (glass column, ∅ = 2 cm, 15 cm silica gel, argon pressure) of the mother liquor and evaporation of pentane from the appropriate fraction furnished **16** (67 mg, 43%) as a pale-yellow powder.

(b) By Hydrolysis of Hafnium Complex 12 with $Na_2SO_4 \cdot 10\ H_2O$: $Na_2SO_4 \cdot 10\ H_2O$ (156 mg, 1.10 mmol) was added to a solution of hafnium complex **12** (300 mg, 0.55 mmol) in diethyl ether (5 mL). After stirring the mixture for 12 h at room temperature, its colour changed from red-violet to yellow and a brownish precipitate was formed. Pentane (5 mL) was then added to complete the precipitation. The reaction mixture was filtered through Celite and compounds **16** and **17** were separated from the filtrate as described above. **16** (77 mg, 46%) and **17** (72 mg, 44%) were obtained as pale-yellow powders.

Compound 16: ^{1}H NMR (C$_6$D$_6$, 300.1 MHz, 30°C): δ = 2.92 (dd, $^2J_{P,H}$ = 4.2 and 1.1 Hz, 4-H), 2.57 (dd, ^2J = 9.3, 6.9 Hz, 6-H), 1.51 [d, $^4J_{P3,H}$ = 1.8 Hz, C(CH$_3$)$_3$ at C-2], 1.15 [s, C(CH$_3$)$_3$ at C-4], 0.95 [t, $^4J_{P,H}$ = 0.8 Hz, C(CH$_3$)$_3$ at C-6]. − ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75.5 MHz, 30°C): δ = 230.8 (ddd, $^1J_{P3,C}$ = 74.5, $^1J_{P1,C}$ = 58.8, $^2J_{P5,C}$ = 2.5 Hz, C-2), 70.6 (t, $^1J_{P,C}$ = 53.0 Hz, C-6), 61.4 (ddd, $^1J_{P,C}$ = 48.5, 44.1, $^2J_{P,C}$ = 6.4 Hz, C-4), 43.1 [dd, $^2J_{P,C}$ = 20, 18 Hz, *C*(CH$_3$)$_3$ at C-2], 34.2 [dd, $^2J_{P,C}$ = 15.2, $^4J_{P,C}$ = 2.0 Hz, *C*(CH$_3$)$_3$ at C-6], 36.0 [dd, $J_{P,C}$ = 15.3, 2.8 Hz, *C*(CH$_3$)$_3$ at C-4], 33.6 [dd, $^3J_{P,C}$ = 14.6, 9.0 Hz, C(*C*H$_3$)$_3$ at C-2], 30.6 [t, $^3J_{P,C}$ = 5.5 Hz, C(*C*H$_3$)$_3$ at C-6], 30.0 [dd, $^3J_{P,C}$ = 10.5, 8.5 Hz, C(*C*H$_3$)$_3$ at C-4]. − ^{31}P NMR (C$_6$D$_6$, 121.5 MHz, 30°C): δ = 311.8 (dd, $^2J_{P1,P3}$ = 36.5, $^2J_{P3,P5}$ = 13.0 Hz, P-3), −117.4 (dd, $^1J_{P1,P5}$ = 167.2, $^2J_{P1,P3}$ = 36.5 Hz, P-1), −128.6 (dd, $^1J_{P1,P5}$ = 167.2, $^2J_{P3,P5}$ = 13.0 Hz, P-5). − MS (EI, 70 eV): *m/z* (%): 302 (96) [M$^+$], 245 (12) [M − *t*Bu$^+$], 231 (14), 175 (100) [M − CH*t*Bu$^+$], 162 (29), 131 (53) [P$_2$C*t*Bu$^+$], 113 (21), 100 (19) [PC*t*Bu$^+$], 69 (29), 57 (38) [*t*Bu$^+$]. − $C_{15}H_{29}P_3$ (302.3): calcd. C 59.60, H 9.67; found C 59.87, H 9.61.

Compound 17: ^{1}H NMR (C$_6$D$_6$, 400.1 MHz, 30°C): δ = 6.40 (dt, $^1J_{P,H}$ = 227.7, $^3J_{P,H}$ = 6.4 Hz, 3-H), 1.98 (dt, $^2J_{P,C}$ = 9.6 Hz, $^4J_{P,C}$ = 5.2 Hz, 6-H), 1.41 [s, C(CH$_3$)$_3$ at C-6], 1.35 [br. s, C(CH$_3$)$_3$ at C-2 and C-4]; structure established by NOESY. − ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz, 30°C): δ = 213.5 (AA′MX spin system, $^1J_{P,C}$ = 40.8 and 50.0 Hz, C-2 and C-4), 66.1 (dt, $^1J_{P,C}$ = 51.5, $^3J_{P,C}$ = 42.2 Hz, C-6), 43.2 [AA′MX spin system, *J* not resolved, *C*(CH$_3$)$_3$ at C-2 and C-4], 34.2 [dt, $^2J_{P,C}$ = 15.3, $^4J_{P,C}$ = 2.5 Hz, *C*(CH$_3$)$_3$ at C-6], 32.7 [AA′MX spin system, $^3J_{P,C}$ = 14.1 and 3.5 Hz, $^5J_{P,C}$ = 0.8 Hz, C(*C*H$_3$)$_3$ at C-2 and C-4], 31.2 [td, $^3J_{P,C}$ = 9.5 Hz, $^5J_{P,C}$ = 0.9 Hz, C(*C*H$_3$)$_3$ at C-6]. − ^{31}P{^{1}H} NMR (C$_6$D$_6$, 162.0 and 243.0 MHz, 30°C): δ = 241.3 (t, $^2J_{P,P}$ = 5.5 Hz, P-1 and P-5), −249 (t, P-3). − IR (KBr): $\tilde{\nu}$ = 2957, 2898 (*t*Bu), 2329 cm^{-1} (P−H). − MS (EI, 70 eV): *m/z* (%): 302 (22) [M$^+$], 211 (11), 231 (5), 175 (23), 155 (21), 131 (22), 113 (7), 99 (100), 69 (33), 57 (84). − $C_{15}H_{29}P_3$ (302.3): calcd. C 59.60, H 9.67; found C 59.55, H 9.63.

X-ray Crystal Structure Analysis of 12:[19] Siemens SMART diffractometer (Mo-K_α radiation), T = 100 K; structure solution by heavy atom method (SHELXS-86[20]) and refinement by SHELXL-93;[21] monoclinic, space group *C*2/*c*; lattice constants a = 9.943(2), b = 18.315(4), c = 22.456(5) Å; β = 90.66(3)°, V = 4089.1(14) Å^3, Z = 8, μ(Mo-K_α) = 5.591 mm^{-1}, crystal size 0.46 × 0.39 × 0.21 mm, θ_{max} = 33.16°; 7591 independent reflections (R_{int} = 0.0680); 22971 measured reflections, of which 5300 were considered observed with $I > 2\sigma(I)$; empirical absorption correction; min./max. transmission 0.168/0.318; max./min. residual electronic density −5.883 and −3.151 e/Å^3 (less then 1 Å from Hf). 190 parameters [C, Cl, Hf, and P anisotropic; the positions of the H atoms were calculated for idealized distances (d_{C-H} = 0.980 Å)]; R_1 = 0.0590; wR^2 = 0.1340.

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[1] J. F. Nixon, *Chem. Rev.* **1988**, *88*, 1327−1362; M. Regitz, P. Binger, *Angew. Chem.* **1988**, *100*, 1541−1565; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1484−1508; P. Binger in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme Verlag, **1990**, p. 90−107; J. F. Nixon, *Coord. Chem. Rev.* **1995**, *145*, 201−258; K. B. Dillon, F. Mathey, J. F. Nixon, *Phosphorus: The Carbon Copy*, Wiley, **1998**, p. 347−355.
[2] R. Milczarek, W. Rüsseler, P. Binger, K. Jonas, K. Angermund, C. Krüger, M. Regitz, *Angew. Chem.* **1987**, *99*, 957−958; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 908−909.
[3] P. Binger, S. Leininger, J. Stannek, B. Gabor, R. Mynott, J. Bruckmann, C. Krüger, *Angew. Chem.* **1995**, *107*, 2411−2414; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2227−2230.
[4] D. Böhm, F. Knoch, S. Kummer, U. Schmidt, U. Zenneck, *Angew. Chem.* **1995**, *107*, 251−253; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 198−201.
[5] P. L. Arnold, F. G. N. Cloke, P. B. Hitchcock, J. F. Nixon, *J. Am. Chem. Soc.* **1996**, *118*, 7630−7631.
[6] A. R. Barron, A. H. Cowley, *Angew. Chem.* **1987**, *99*, 956; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 907−908.
[7] [7a] J. Haas, Diplomarbeit, Universität Bonn, **1988**. − [7b] P. Binger, J. Haas, J. Stannek, S. Stutzmann, C. Krüger, *Eur. J.*

Inorg. Chem. **1999**, 83−86. − [7c] M. Scheer, J. Krug, *Z. Anorg. Allg. Chem.* **1998**, *624*, 399−405.
[8] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1987**, 1.
[9] R. Appel, W. Schuhr, F. Knoch, *Angew. Chem.* **1985**, *97*, 421−422; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 420−421; F. Mercier, C. Hugel-Legoff, L. Richard, F. Mathey, *J. Organomet. Chem.* **1990**, *389*, 389−397.
[10] R. Appel, W. Schuhr, F. Knoch, *J. Organomet. Chem.* **1987**, *319*, 345−350.
[11] C. Hugel-Legoff, F. Mercier, L. Richard, F. Mathey, *J. Organomet. Chem.* **1989**, *363*, 325−333.
[12] D. G. Gorenstein, D. O. Shah in *Phosphorus-NMR, Principles and Application* (Ed.: D. G. Gorenstein), Academic Press, **1984**, p. 549−591.
[13] L. C. Thomas, *Interpretation of the IR Spectra of Organophosphorus Compounds*, Heyden, London, **1974**.
[14] For the nomenclature of the isotope effect, see W. Gombler, *J. Am. Chem. Soc.* **1982**, *104*, 6616.
$^{j}\Delta^{k}X(^{llm}Y) = \delta_{X}(^{l}Y) - \delta_{X}(^{m}Y)$
where $^{j}\Delta$ is the isotope shift over *j* bonds observed for nucleus ^{k}X caused by the isotopes ^{l}Y and ^{m}Y (where *l* has the higher mass number). A shift to higher NMR frequency is positive.
[15] [15a] G. Heckmann, E. Fluck, *Magn. Res. Chem.* **1995**, *33*, 553. − [15b] W. Buchner, W. Ries, W. Malisch, *Magn. Res. Chem.* **1990**, *28*, 515. − [15c] Unpublished observations.
[16] R. Mynott, P. Phillips, manuscript in preparation for submission to *Magn. Res. Chem.*
[17] [17a] P. C. Wailes, R. S. P. Coutts, H. Weigold, *Organometallic Chemistry of Titanium, Zirconium and Hafnium*, Academic Press, New York, **1974**. − [17b] G. L. Hillhouse, J. E. Bercaw, *J. Am. Chem. Soc.* **1984**, *106*, 5472−5478 and references cited therein.
[18] W. Wolfsberger, H. Schmidbaur, *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 149.
[19] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101625. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (0)1223/ 336033; e-mail: deposit@chemcrys.cam.ac.uk].
[20] G. M. Sheldrick, *SHELXS-86*, *Program for Crystal Structure Solution*, Universität Göttingen, **1986**.
[21] G. M. Sheldrick, *SHELXL-93*, *Program for Crystal Structure Solution*, Universität Göttingen, **1993**.

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