Syntheses of Phosphinine-Based Tripodal Ligands

Ute Rhörig,[a] Nicolas Mézailles,[a] Nicole Maigrot,[a] Louis Ricard,[a] François Mathey,*[a] and Pascal Le Floch*[a]

Keywords: Phosphorus heterocycles / Phosphinines / Cycloadditions / Tungsten / Tripodal ligands

The syntheses of several tripodal phosphinine-based ligands are presented. 1,3,2-Diazaphosphinine **(1)** undergoes Diels–Alder reactions with tris-(propynyl)phenylsilane to yield tris-(1,2-azaphosphinine)phenylsilane **6**. This intermediate serves as precursor for the preparation of two tripodal ligand. First, tris(phosphinine)phenylsilane **(7)** is obtained from the reaction with trimethylsilylacetylene. Under more drastic conditions, compound **6** reacts with 4-octyne to yield the tripodal ligand **8** containing six *n*-propyl groups. Reaction of **8** with $[W(CO)_5(THF)]$ affords the corresponding $W(CO)_3$ complex **9** whose structure was confirmed by an X-ray crystallographic study. The synthesis of two extended tripodal ligands **12** and **13** containing three phosphinine units each connected to the same CH linker by dimethylsilyl groups was also studied. As a prerequisite, the precursor tris(propynyldimethylsilyl)methane **(10)** was synthesized by reaction of three equivalents of propynyllithium with tris(bromodimethylsilyl)methane. Reaction of excess **1** with **10** yielded the corresponding tris(dimethylsilyl-1,2-azaphosphinine)methane **(11)** as an intermediate. The formation of ligands **12** and **13** was achieved by reacting **11** with trimethylsilylacetylene or 4-octyne, respectively, in excess. The reaction of ligand **13** with $[W(CO)_5(THF)]$ in toluene yielded the corresponding $W(CO)_3$ complex **14** which was structurally characterized.

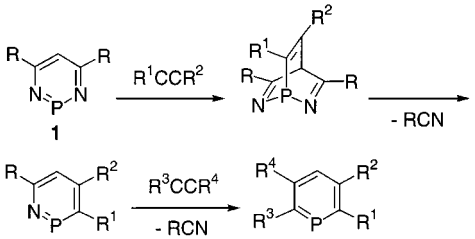
Introduction

Polydentate phosphane ligands continue to attract a lot of interest from both coordination and organometallic chemists. This is mainly due to their unique structural and electronic properties which allow the stabilization of many metallic centers with various oxidation states and geometries.[1] Furthermore, transition metal complexes of such ligands have shown an interesting potential in many catalytic processes of importance. Indeed, tripodal systems have been successfully used in the hydrogenation of alkynes, alkenes and nitriles, hydroformylation and isomerization reactions of alkenes, oligomerization and polymerization of alkynes,[2] C−H activation of unsaturated substrates[3] and, very recently, Bianchini et al. have reported the use of soluble metal complexes for hydrogenation, hydrogenolysis and desulfurization of thiophenic substrates.[4] For synthetic reasons most of these ligands usually bear *P*-alkyl or *P*-aryl groups as binding sites and tripodal structures incorporating strong π-acceptor phosphane groups are still rather rare.[5]

In the course of our studies on phosphinines we became interested in synthesizing analogs of these tripodal ligands. Phosphinines are known to be excellent π-acceptor ligands which significantly increase the Lewis-acidity of the metal centers to which they are coordinated.[6] Furthermore, they have shown a strong ability to stabilize very electron-rich metallic centers,[7] and recently, the synthesis of a remarkably stable gold(0) complex in which a phosphinine-based macrocycle acts like a "CO matrix" was reported.[8] Though some sp^2-based tridentate ligands with phosphaalkenes[9] and phosphinines[10] are known, tri- or tetrapodal ligands including P=C bonds are still unknown. Herein we wish to report on a simple synthetic methodology which allows the assembly of these phosphinine-based tripodal structures.

Results and Discussion

Synthetic approaches allowing the connection of phosphinines are rare and often require multi-step sequences. To circumvent this limitation, we developed a simple strategy relying on the reactivity of 1,3,2-diazaphosphinines.[11] As shown below, these heterocycles react with one equivalent of alkyne to give 1,2-azaphosphinines, which can subsequently be transformed into phosphinines at higher temperatures when a second equivalent of alkyne is reacted (Scheme 1). These thermally promoted transformations involve two successive [4+2] cycloaddition/cycloreversion sequences with the concomitant release of two molecules of nitrile. In a series of articles we showed that this approach was indeed particularly efficient for building sophisticated



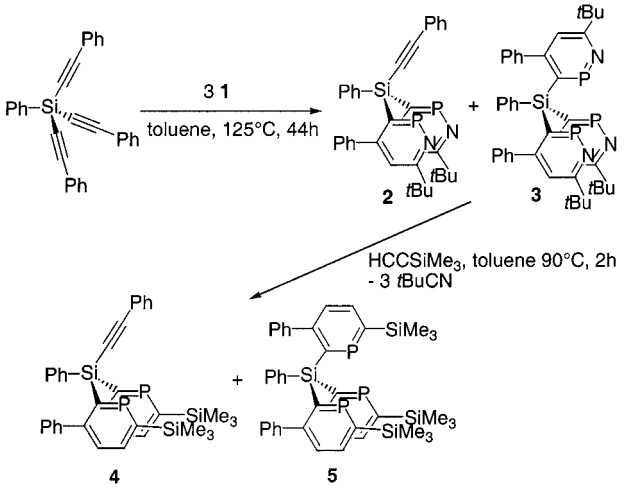
Scheme 1. Reactivity of 1,3,2-di- and 1,2-azaphosphinines towards alkynes

[a] Laboratoire "Héteroéléments et Coordination", UMR CNRS 7653, Ecole Polytechnique,
91128 Palaiseau Cedex, France
E-mail: lefloch@poly.polytechnique.fr

  1434−1948/00/1212−2565 $ 17.50+.50/0

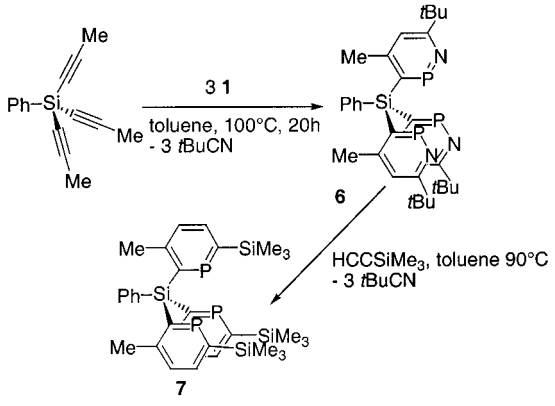
structures such as 2,3,5,6-tetrafunctionalized rings,[10] bis- and tris-phosphinines and phosphinine-based macrocycles.[12]

Quite logically we attempted to see whether this method could be transferred to the synthesis of tripodal structures with triynes. In all our experiments, the readily available 4,6-di-*tert*-butyl-1,3,2-diazaphosphinine **(1)** was used as precursor.[11] As the regioselectivity in the cycloaddition reaction can be a problem, we focused on silyl-substituted alkynes which usually react regiospecifically. Previous studies have indeed shown that the silyl-substituted carbon atom of the alkyne reacts exclusively at phosphorus, and therefore the silicon group is always located at the α-carbon atom in the final compound.[10–12] A first series of experiments demonstrated that the bulkiness of the alkyne is of utmost importance. Thus, the reaction of tris(phenylethynyl)phenylsilane with four equivalents of **1** in toluene at 125 °C yields a mixture of two compounds whose structures were ascribed, on the basis of their ^{31}P NMR spectroscopic data, to the bis(1,2-azaphosphinine)silane **(2)** (80%) (δ = 308.3) and the expected tris(1,2-azaphosphinine)silane **(3)** (20%) (δ = 307.5). Whatever the experimental conditions used (temperature, ratio of precursors, heating time), the formation of **3** never exceeded 20%: the presence of a phenyl group at the β-position of the phosphinine very likely hampers the third cycloaddition leading to **3**. To confirm our hypothesis about the structures of **2** and **3**, trimethylsilylacetylene was reacted with the mixture of compounds. After two hours of heating at 90 °C in toluene, the bis(phosphinine)phenylethynylsilane **(4)**, the desired tripodal ligand **5** and traces of the 2,6-bis(trimethylsilyl)phosphinine[11] resulting from the reaction of the excess of **1** with the alkyne were formed. Whereas this latter could easily be eliminated by chromatographic purification, complete separation of **4** and **5** turned out to be impossible and only compound **4** was isolated in pure form. Nevertheless, mass spectroscopy measurements carried out on a mixture of both compounds allowed us to confirm the proposed structure for ligand **5** {*m*/*z* (%) = 823 (10) [M]} (Scheme 2).



Scheme 2. Synthesis of ligands **4** and **5**

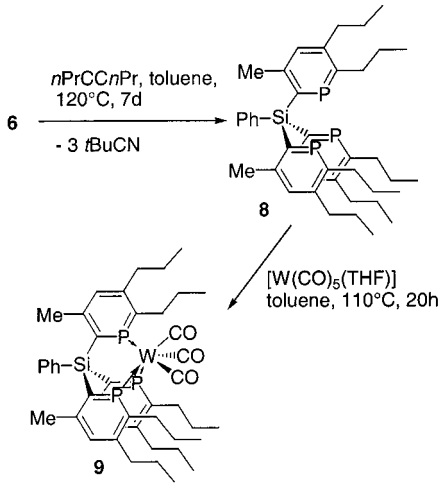
Better results were obtained simply by replacing the phenyl group of the alkyne moiety by a methyl group. Tris(propynyl)phenylsilane reacts with four equivalents of **1** to yield, after 20 hours at 100 °C, a mixture of **1** and a compound which gives a singlet in the ^{31}P NMR spectrum at δ = 308.0. On the basis of this chemical shift, which compares well with those of other 3-silyl-substituted-1,2-azaphosphinines, its formula was ascribed to that of the expected intermediate, the tris(1,2-azaphosphinine)phenylsilane **(6)**. In a subsequent step, **6** was reacted with trimethylsilylacetylene in excess. After 2 hours at 90 °C, the tripodal ligand **7** was formed together with traces of the 2,6-bis(trimethylsilyl)phosphinine.[11] The formulation of **7** was elucidated by conventional NMR spectroscopy and mass spectrometry. A significant piece of information is found in the ^{13}C NMR spectrum of **7**: the signal of the C2-carbon atom appears as a doublet of triplets due to the coupling to the neighboring P atom (^1J = 87.5 Hz) and to the two other magnetically equivalent P atoms of the other rings (^3J = 5.5 Hz) (Scheme 3).



Scheme 3. Synthesis of ligand **7**

Unfortunately, although somewhat predictably, the presence of three peripheral silyl groups in ligand **7** preclude complexation to non-sterically demanding $M(CO)_3$ fragments {M = Cr, Mo, W, with $[Cr(CO)_4(CH_3CN)_2]$, $[Mo(CO)_4(nbd)]$, $[W(CO)_5(THF)]$ or $[W(CO)_4(CH_3CN)_2]$ as precursors}. To alleviate the steric bulk around the cavity, we therefore decided to replace these silyl substituents by alkyl groups. To avoid the formation of many isomers, we decided to use the symmetrical 4-octyne. As previously observed, the use of a nonpolar alkyne dramatically decreases the rate of the reaction and seven days of heating at 120 °C were necessary to ensure the complete formation of ligand **8**, which was isolated as a yellow oil in 76% yield (Scheme 4).

Unequivocal evidence for the proposed structures were provided by NMR spectroscopy and mass spectrometry. As a result of alkyl substitution, the ^{31}P NMR chemical shift of **8** appears at rather high field (δ = 247.0) compared to that of phosphinine **7** (δ = 272.6). As postulated, the introduction of smaller groups at the α-positions frees the access to the cavity and complexation can now be achieved. Reaction of $[W(CO)_5(THF)]$ with **8** yields the expected $W(CO)_3$



Scheme 4. Synthesis of ligand **8** and complex **9**

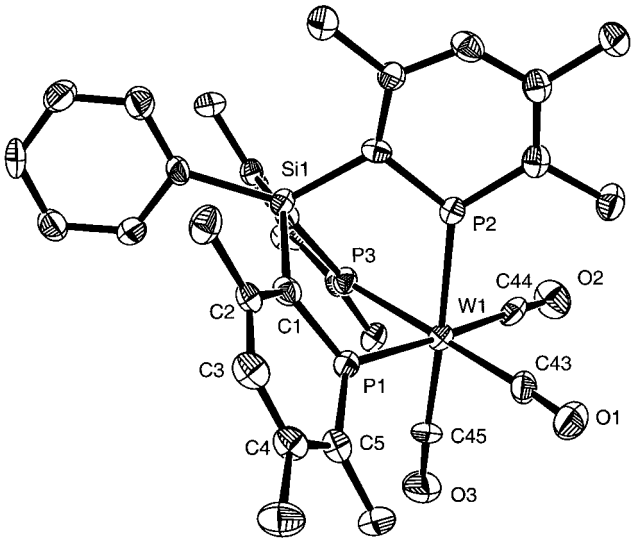
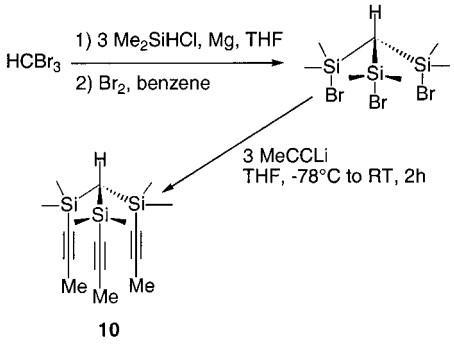


Figure 1. ORTEP drawing of **9** as determined by a single-crystal X-ray diffraction analysis; ellipsoids are drawn to enclose 50% of the electron density; the hydrogen atoms of the CH_2CH_3 grouping of the *n*-propyl substituent have been omitted for clarity[a]
[a] Selected bond lengths [Å] and angles [°]: W−P1 2.437(2), W−P2 2.502(2), W−P3, 2.427(2), W−C43, 2.00(1), W−C44, 2.02(1), W−C45 1.998(8), Si1−C1, 1.907(8), P1−C1 1.723(8), C1−C3, 1.40(1), C2−C3, 1.39(1), C3−C4 1.39(1), C4−C5 1.38(1), C5−P1 1.733(8), P1−W−P2, 84.76(7), P1−W−P3 84.56(7), P3−W−P1, 88.47(6), P1−W−C44 176.8(2), P2−W−C45 177.3(3), P3−W−C43 179.3(3), C5−P1−C1, 107.4(4), C6−C16 131.24(3), C1−C16, 100.93(3), C11−C16 101.62(3)

complex **9** after refluxing for 20 hours in toluene (Scheme 4).

Complex **9** was characterized by conventional NMR techniques, IR spectroscopy and elemental analysis. As frequently observed with phosphinines, coordination to a tungsten carbonyl fragment induces a significant upfield shift ($\delta = 213.1$, $\Delta\delta = -34$). In the ^{13}C NMR spectrum, the very characteristic doublet of triplets at $\delta = 210$, assignable to three magnetically equivalent carbonyl ligands, is found. Indeed, each carbonyl group is located *trans* to one phosphorus atom ($^2J = 29.0$ Hz) and *cis* to the other two ($^2J = 7.0$ Hz). Finally, as expected for strong π-acceptor ligands, the bands in the IR spectrum are shifted towards higher frequencies (1950 and 1875 cm^{-1}) than for "analogous" phosphane complexes[13a] {1930 and 1834 in $[MeC(CH_2PPh)_3W(CO)_3]$}.[13b] Slow diffusion of methanol (or pentane) into a dichloromethane solution of **9** furnished crystals suitable for an X-ray study. An ORTEP view of the structure is shown in Figure 1. The crystallographic labelling used is arbitrary and differs from the numbering utilized for NMR spectral assignments. As expected from NMR and IR spectroscopic data, the tripodal ligand occupies one face of the octahedron leaving three structurally equivalent carbonyls ligands. As previously observed in the X-ray structure of $[W(CO)_3$(silacalix-3-phosphinine)],[12a] a strain is found in the coordination sphere of tungsten, and the P−W−P angles are slightly smaller than the ideal value of 90° [ranging from 84.46(7) to 88.47(6)]. On the other hand, the internal bond lengths in the three phosphinine subunits are close to those recorded for free 2-substituted silylphosphinines,[12] thus indicating that aromaticity is not significantly perturbed. A similar observation has been made for $[W(CO)_5$(2-chlorophosphinine)].[14] The most surprising feature concerns the geometry around the silicon atom, where a significant deviation from the ideal tetrahedral geometry can be observed. Whereas four C−Si−C angles are "normal" [100.9(3) to 103.2(3)°], C1−Si1−C6 [119.3 (3)°] and C16−Si1−C11 [131.2(3)°] are strongly widened. This phenomenon very likely reflects a strong steric crowding between the hydrogen atoms of the phenyl substituent and those of the three methyl groups which point towards the top of the ligand. With this particular arrangement, the shortest through-space H(phenyl)−H(methyl) interaction measured is 2.29 Å.

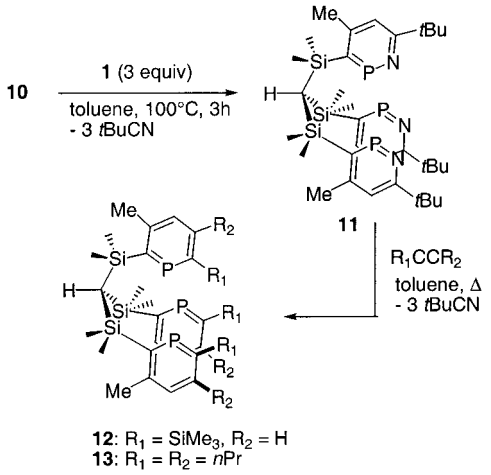
Being encouraged by these first results, we then attempted to enlarge the scope of our method to the preparation of more sophisticated polydentate species, such as extended tripodal ligands. We selected tris(propynyldimethylsilane)methane **(10)** as the starting material. Preparation of this molecule was readily achieved by reaction of three equivalents of propynyllithium with one equivalent of tris(bromodimethylsilyl)methane, whose synthesis was reported by Gade and Becker (Scheme 5).[15]



Scheme 5. Synthesis of triyne **10**

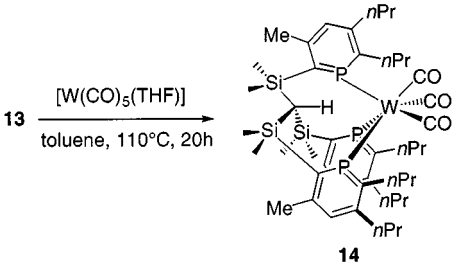
Reaction of this precursor with an excess of **1** for 30 hours at 100 °C yields intermediate **11**, which was characterized by ^{31}P NMR spectroscopy only ($\delta = 305.8$). Subsequent reaction with trimethylsilylacetylene in a large ex-

cess then led to the desired ligand **12** which was formed together with the 2,6-bis(trimethylsilyl)phosphinine as by-product. These two compounds were readily separated by column chromatography, and **12** was isolated as a white solid. All NMR spectroscopic data, as well as mass spectrometry, confirm the proposed structure. Despite the extension of each arm of the tripod resulting, supposedly, both in a larger size of the cavity and a greater flexibility, ligand **12** has the same coordinating behavior as **7**: the three $SiMe_3$ groups prevent the approach of $M(CO)_3$ fragments. Following the above-mentioned strategy we investigated the replacement of bulky $SiMe_3$ groups by linear alkyl groups. As shown in Scheme 6, the intermediate **11** can be reacted with 4-octyne in excess to yield ligand **13**. Heating at 120 °C for 13 days was necessary to ensure complete consumption of **11**. This very long heating period was somewhat detrimental to the overall yield (35%). All NMR spectroscopic data, as well as mass spectroscopy, confirm the proposed structure. The ^{31}P NMR chemical shift is found at δ = 242.6 as expected for an α-alkyl-substituted phosphinine.



Scheme 6. Syntheses of ligands **12** and **13**

As expected, the reaction of this extended tripod with $[W(CO)_5(THF)]$ in toluene at 110 °C for 20 h yield complex **14** as a red oil which slowly crystallizes (Scheme 7). Coordination to tungsten is obvious in the ^{31}P NMR spectrum. Coupling of ^{183}W (14% abundance) with three magnetically equivalent phosphorus atoms gives rise to the expected satellites at δ = 211.6 ($^1J_{P,W}$ = 227.7 Hz). In the ^{13}C NMR, the signal of the three carbonyl ligands appears as a "doublet of triplets" because each CO couples with one *trans* ($^2J_{P,C}$ = 21.2 Hz) and two *cis* ($^2J_{P,C}$ = 9.2 Hz) phosphorus atoms. The most surprising feature is found in the ^1H NMR spectrum. Whereas the signal for the H−C in the free ligand appears at about δ = 0 as a broad singlet, it is found in the complex at δ = +6 as a quadruplet ($^4J_{H,P}$ = 8.5 Hz). Surprisingly, no such effect in the chemical shift of the C−H was observed in the ^{13}C NMR spectrum. It thus seems that the strong downfield shift of the hydrogen results from a geometrical constraint. This hydrogen must be located in the anisotropy cone created by the three aromatic phosphinine moieties. This blocked conformation is also responsible for the magnetic inequivalence of the two methyl groups of the $SiMe_2$ linkers. The difference in their chemical shift of 0.5 ppm clearly shows that they have a very different electronic environment. In order to verify these assumptions, an X-ray crystal study was carried out.



Scheme 7. Complexation of ligand **13** with $[W(CO)_5(THF)]$

The complex crystallized as red blocks of almost millimeter size from a diffusion of MeOH into a chloroform solution of **14**. An ORTEP plot of the structure is shown in Figure 2. A number of very peculiar features are found in the structure. First, the apex carbon appears very flattened. The three Si−C−Si angles range between 114.93 and 118.17°. The sum of these angles at C (349.76°) is much closer to a C sp^2 hybridized than expected. Second, confirming the NMR findings, the hydrogen atom is located inside the cavity. This very peculiar arrangement prompted us to have a closer look at the bond lengths between C−H and H···W. In fact the C−H bond length is not elongated (0.979 Å) and the H···W distance of 2.683 Å indicates only a weak interaction between the metal center and the hydrogen. As expected for a coordinatively saturated metallic center there is no indication of an agostic interaction.

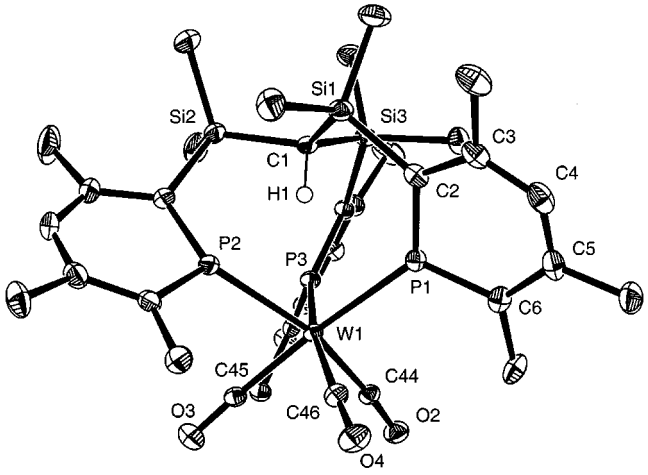


Figure 2. ORTEP drawing of **14** as determined by a single-crystal X-ray diffraction analysis; ellipsoids are drawn to enclose 50% of the electron density; the hydrogen atoms of the CH_2CH_3 grouping of the *n*-propyl substituents have are omitted for clarity[a]
[a] Selected bond lengths [Å] and angles [°]: W1−P1 2.5551(8), W1−P2 2.559(1), W1−P3 2.5700(8), W1−C44 1.967(2), W1−C45 1.975(3), W1−C46 1.970(2), P1−C2 1.741(3), C2−C3 1.408(3), C3−C4 1.398(4), C4−C5 1.389(4), C5−C6 1.403(3), C6−P1 1.747(3), C2−Si1 1.903(3), Si1−C1 1.871(3), C1−Si2 1.878(2), C1−Si3 1.881(3), C1−H1 0.979; P1−W1−P2 98.18(2), P2−W1−P3 98.63(3), P3−W1−P1, 99.15(3), P1−W1−C44 97.22(7), P1−W1−C46 80.46(8), P1−W1−C45 165.57(7), C6−P1−C2 106.7(1), P1−C2−Si1 119.1(1), Si1−C1−Si3 116.7(1), Si3−C1−Si2 114.9(1), Si1−C1−Si2 118.2(1)

Therefore the particularities of the structure are just a consequence of the coordination. The value of the dihedral angles $C_{ring}-C_{ring}-P-W$ (for example $C_3-C_2-P_1-W$ = 154.2°) should be 180° and they are found between 145 and 160° in the structure. As it appears in the ORTEP plot, the three phosphinine rings do not experience this strain and are not significantly distorted (if one excepts small deviations from planarity). This phenomenon is obvious from the ORTEP plot and this confirms the strain in the complex.

In conclusion, we have developed a simple access to the first phosphinine-based tripodal ligands using a "one pot sequence" from 1,3,2-diazaphosphinines. This simple synthetic scheme seems to be flexible enough to allow the introduction of various functional groups on phosphinines and should provide an access to more sophisticated cavities incorporating, for example, other heteroatom-based ligands which can serve as a hemilabile moiety. These developments as well as those concerning the coordinating behavior of ligands such as **8** and **13** and are currently under investigation and will be reported in due course.

Experimental Section

General: All reactions were routinely performed under nitrogen using Schlenk techniques and dry, oxygen-free solvents. Dry toluene and hexane were obtained by distillation from sodium/benzophenone and dry CH_2Cl_2 was obtained by distillation from P_2O_5. Dry celite was used for filtration. − NMR: Bruker AC-200 SY operating at 200.12 MHz for ^1H, 50.32 MHz for ^{13}C, and 81.01 MHz for ^{31}P; chemical shifts (ppm) are relative to TMS (^1H and ^{13}C) or 85% H_3PO_4 (^{31}P). List of abbreviations used: s, singlet, d, doublet, t, triplet, q, quadruplet, p, pseudo, m, multiplet. − Elemental analyses: "Service d'analyse du CNRS", Gif-sur-Yvette, France. Phosphinine **1** was prepared according to a published method.[11]

Synthesis of Ligand 4: A solution of diazaphosphinine **1** (0.63 g, 3.0 mmol) and tris(phenylethynyl)phenylsilane (0.29 g, 0.7 mmol) in toluene (25 mL) was heated at 125 °C for 44 hours. After this period, ^{31}P NMR analysis showed the presence of intermediates **2** and **3**. Trimethylsilylacetylene (0.78 g, 7.9 mmol) was then added and the resulting reaction mixture was heated at 90 °C for 2 hours. After cooling the flask to room temperature, celite (0.5 g) was added and the volatiles were evaporated. The resulting brown powder was then poured onto the top of a silica-gel column for chromatography. A first fraction, eluted with hexane, yielded the 2,6-bis(trimethylsilyl)phosphinine which is formed as a by-product. A second fraction, eluted with a mixture of toluene/hexane (70:30), yielded ligand **4**. The tripodal ligand **5** was recovered (mixture with **4**) in an additional fraction with a mixture of toluene/hexane (65:35). After evaporation of solvents, **4** was recovered as a yellow oil (0.19 g, 40% based on silane). − ^1H NMR ($CDCl_3$): δ = 0.30 (s, 18 H, $SiMe_3$), 6.90−7.50 (m, 20 H, C_6H_5), 7.73−8.20 (dd, 4 H, H-5 and H-4). − ^{13}C NMR ($CDCl_3$): δ = 0.7 (s, $SiMe_3$), 92.8 (s, C*C*−Si), 110.8 (s, C*C*−Ph), 125.0−135.0 (m, C_6H_5), 137.4 (s, C-5), 138.6 (d, ^3J = 5.0 Hz, C-4), 145.6 (s, Cq of C_6H_5), 154.7 (d, ^2J = 8.6 Hz, C-3), 162.2 (dd, ^1J = 91.5 Hz, ^3J = 7.8 Hz, C-2), 167.1 (d, ^1J = 84.5 Hz, C-6). − ^{31}P NMR ($CDCl_3$): δ = 269.6 (s). − MS ; *m/z* (%): 692 (100) [M]. − $C_{42}H_{42}P_2Si_3$ (693.0): calcd. C 72.79, H 6.11; found C 72.95, H 6.20.

Synthesis of Ligand 7: A solution of diazaphosphinine **1** (0.63 g, 3.0 mmol) and tris(propynyl)phenylsilane (0.16 g, 0.7 mmol) in toluene (25 mL) was heated at 100 °C for 20 hours. After this period a ^{31}P NMR control indicated the complete formation of intermediate **6**. Trimethylsilyacetylene (0.78 g, 7.9 mmol) was then added and the resulting reaction mixture was heated at 90 °C for 3.5 hours. After cooling the flask to room temperature, celite (0.5 g) was added and volatiles were evaporated. The resulting brown powder was then poured on to the top of a silica-gel column for chromatography. A first fraction, eluted with hexane, yielded the 2,6-bis(trimethylsilyl)phosphinine formed as a by-product. A second fraction, eluted with a mixture of toluene/hexane (70:30), yielded ligand **7**. After evaporation of solvents, **7** was recovered as a yellow oil (0.32 g, 70% based on the silane). − ^1H NMR ($CDCl_3$): δ = 0.20 (s, 27 H, $SiMe_3$), 2.16 (s, 9 H, Me of phosphinine), 7.07−7.27 (m, 5 H, C_6H_5), 7.53 (d, ^3J = 6.5 Hz, 3 H, H-4), 7.84−7.93 (m, 3 H, H-5). − ^{13}C NMR ($CDCl_3$): δ = 0.7 (d, ^3J = 4.0 Hz, $SiMe_3$), 29.9 (s, Me of phosphinine), 126.0−129.7 (C_6H_5), 131.1 (d, ^3J = 25.0 Hz, C-4), 138.4 (s, Cq of C_6H_5), 139.3 (d, ^2J = 10.0 Hz, C-5), 151.9 (d, ^2J = 10.5 Hz, C-3), 163.6 (td, ^1J = 87.50 Hz, ^3J = 5.5 Hz, C-2), 166.7 (d, ^1J = 83.0 Hz, C-6). − ^{31}P NMR ($CDCl_3$): δ = 272.5 (s). − MS ; *m/z* (%): 648 [M] (100), 575 (31) [M − $SiMe_3$]. − $C_{33}H_{47}P_3Si_4$ (649.0): calcd. C 61.07, H 7.30; found C 61.25, H 7.28.

Synthesis of Ligand 8: A solution of intermediate **6** in toluene (20 mL), prepared as described above from diazaphosphinine **1** (0.50 g, 2.40 mmol) and tris(propynyl)phenylsilane (0.12 g, 0.56 mmol), was heated with 4-octyne (1.10 g, 10 mmol) at 120 °C for one week. Celite (0.5 g) was then added and toluene and the excess of alkyne were evaporated yielding a brown solid, which was purified by chromatography. A fraction eluted with a mixture of hexane/toluene (50:50) yielded **8** which was isolated as a brown oil after evaporation of solvents (0.29 g, 76% based on the silane). − ^1H NMR ($CDCl_3$): δ = 0.92−1.03 (m, 18 H, 6 C*H*$_3$−CH$_2$), 1.52−1.71 (m, 12 H, 6 CH$_3$−C*H*$_2$), 2.17 (s, 9 H, Me of phosphinine), 2.61−2.68 (m, 6 H, CH$_2$−C-5), 2.79−2.91 (m, 6 H, CH$_2$−C-6), 7.16−7.32 (m, 5 H, C_6H_5), 7.62 (d, ^3J = 8.0 Hz, 3 H, H-4). − ^{13}C NMR ($CDCl_3$): δ = 15.0 and 15.1 (2s, 2 Me of *n*-propyl groups), 25.3 (s, Me of phosphinine), 27.7 (d, ^3J = 8.0 Hz, *C*H$_2$−CH$_2$−C-6), 29.1 (s, *C*H$_2$−CH$_2$−C-5), 36.9 (s, *C*H$_2$−C-5), 37.6 (d, ^2J = 36.5 Hz, *C*H$_2$−C-6), 126.0−129.7 (C_6H_5), 135.2 (d, ^3J = 19.0 Hz, C-4), 138.4 (s, Cq of C_6H_5), 147.3 (d, ^2J = 10.0 Hz, C-5), 149.5 (d, ^2J = 12.5 Hz, C-3), 161.3 (dt, ^1J = 76.0 Hz, ^3J = 5.5 Hz, C-2), 167.8 (d, ^1J = 60.0 Hz, C-6). − ^{31}P NMR ($CDCl_3$): δ = 247.0 (s). − MS ; *m/z* (%): 685 (92) [M + 1], 491 (100) [M − $C_{12}H_{18}P$], 299 (37) [M − 2 $C_{12}H_{18}P$]. − $C_{42}H_{59}P_3Si$ (684.9): calcd. C 73.65, H 8.68; found C 73.80, H 8.82.

Synthesis of Complex 9: A solution of ligand **8** (0.27 g, 0.39 mmol) in toluene (5 mL) was added to a solution of [W(CO)$_5$(THF)] (0.31 g, 0.78 mmol) in toluene (10mL). The resulting mixture was then heated at 110 °C for 20 hours. After cooling to room temperature, celite (0.5 g) was added and the mixture was evaporated to dryness yielding a brown powder which was purified by chromatography over silica gel. A first fraction, eluted with hexane, yielded traces of $W(CO)_6$. A second fraction, eluted with a mixture of hexane/toluene (80:20), yielded complex **9** as a red oil after evaporation of solvents (0.20 g, 56% based on the ligand). Microcrystals suitable for an X-ray analysis study were obtained by slow diffusion of methanol in a toluene solution of the complex. − ^1H NMR ($CDCl_3$): δ = 0.77−1.18 (m, 18 H, 6 C*H*$_3$−CH$_2$), 1.71−1.84 (m, 12 H, 6 CH$_3$−C*H*$_2$), 2.08 (s, 9 H, Me−C-3), 2.47 (t, ^3J = 7.9 Hz, 6 H, C*H*$_2$−C-5), 2.80−2.99 (m, 6 H, CH$_2$−C-6), 7.17−7.31 (m, 5

H, C_6H_5), 7.80−7.84 (m, 3 H, H_4). − ^{13}C NMR ($CDCl_3$): δ = 15.1 (s, 2 CH_3CH_2), 25.5 (s, *Me*−C-3), 27.4 (d, ^3J = 6.0 Hz, CH_2−CH_2−C-5), 29.9 (d, ^4J = 7.5 Hz, CH_2−CH_2−C6), 25.3 (d, ^2J = 23.5 Hz, CH_2−C-6), 37.3 (d, ^2J = 3.0 Hz, CH_2−C-5), 128.6−129.7 (C_6H_5), 131.0 (d, ^3J = 27.0 Hz, C-4), 136.7 (s, Cq of C_6H_5), 148.4 (d, ^2J = 9.0 Hz, C-5), 149.7 (d, ^2J = 15.0 Hz, C-3), 149.7 (signal of C-2 which is partially masked), 157.3 (s, C-6), 210.4 (dt, ^2J = 29.0 Hz, ^2J = 7.0 Hz, CO). − ^{31}P NMR ($CDCl_3$): δ = 213.1 (s). − IR (KBr): ν (CO) = 1950, 1875 cm^{-1}. − $C_{45}H_{59}0_3P_3SiW$ (952.8): calcd. C 56.73, H 6.24; found C 56.70, H 6.20.

Synthesis of Triyne 10: Tris(bromodimethylsilyl)methane was synthesized following a reported procedure.[15] This compound (4.55g, 10.6 mmol) was added to three equivalents of MeCCLi (1.47g, 32.0 mmol) suspended in THF (60 mL) cooled to −78 °C. The mixture was stirred at −78 °C for 30 minutes and at room temperature for an additional two hours. After evaporation of the volatiles, the mixture was purified by column chromatography on silica gel with hexanes as eluent. The title compound was obtained as a viscous oil in 55% yield (nonoptimized). − ^{1}H NMR ($CDCl_3$): δ = −0.50 (s, 1 H, CH), 0.34 (s, 18 H, 3 $SiMe_2$), 1.87 (s, 9 H, Me). − ^{13}C NMR ($CDCl_3$): δ = 3.1 (s, $SiMe_2$), 3.2 (s, CH), 5.6 (s, C−Me), 86.4 (s, C−Si), 104.3 (s, *C*−Me). − MS (CI, NH_3); *m*/*z* (%): 306 (10) [M + 1], 291 (15) [M − CH_3+1].

Synthesis of Ligand 12: A solution of diazaphosphinine **1** (0.53 g, 2.5 mmol) and ligand **10** (0.17 g, 0.56 mmol) in toluene (20 mL) was heated at 100 °C for 30 hours. After this period a ^{31}P NMR control indicated the complete formation of intermediate **11**. Trimethylsilylacetylene (0.99 g, 10 mmol) was then added and the resulting reaction mixture was heated at 90 °C for 5 hours. After cooling the flask to room temperature, celite (0.5 g) was added and the volatiles were evaporated. The resulting brown powder was then purified by column chromatography on silica gel. A first fraction, eluted with hexane, yielded the 2,5-bis(trimethylsilyl)phosphinine as by-product. A second fraction, eluted with a mixture of hexane/CH_2Cl_2 (90:10), yielded ligand **12**. After evaporation of solvents, **12** was recovered as a white solid (0.32 g, 75% based on the silane). − ^{1}H NMR ($CDCl_3$): δ = 0.06 (br. s, 1 H, CH), 0.30 (s, 18 H, $SiMe_2$), 0.50 (d, ^4J = 2.0 Hz, 27 H, $SiMe_3$), 2.36 (s, 9 H, Me of phosphinine), 6.93 (d, ^3J = 8.1 Hz, 3 H, H-4), 7.78 (dd, ^3J = 8.1 Hz, 3 H, H-5). − ^{13}C NMR ($CDCl_3$): δ = 0.8 (d, ^3J = 5.5 Hz, $SiMe_3$), 3.0 (br. s, CH), 5.0 (d, ^3J = 16.5 Hz, $SiMe_2$), 27.1 (s, Me of phosphinine), 130.2 (d, ^3J = 25.0 Hz, C-4), 138.7 (d, ^2J = 11.5 Hz, C-5), 149.3 (d, ^2J = 12.5 Hz, C-3), 166.0 (d, ^1J = 83.5 Hz, C-2), 168.9 (d, ^1J = 89.0 Hz, C-6). − ^{31}P NMR ($CDCl_3$): δ = 263.0 (s). − MS ; *m*/*z* (%): 731 (8) [M], 549 (100) [M − phosphinine]. − $C_{34}H_{61}P_3Si_6$ (731.3): calcd. C 55.84, H 8.41; found C 55.69, H 8.38.

Synthesis of Ligand 13: A solution of diazaphosphinine **1** (0.69 g, 3.25 mmol) and ligand **10** (0.22 g, 0.72 mmol) in toluene (20 mL) was heated at 100 °C for 30 hours. After this period a ^{31}P NMR control indicated the complete formation of intermediate **11**. 4-Octyne (1.20 g, 11 mmol) was then added and the resulting reaction mixture was heated at 120 °C for 13 days. After cooling the flask to room temperature, celite (0.5 g) was added and the volatiles were evaporated. The resulting brown powder was then purified by column chromatography on silica gel. A first fraction, eluted with hexane, yielded the 2,3,4,5-tetrapropylphosphinine as by-product. A second fraction, eluted with a mixture of hexane/toluene (50:50), yielded ligand **13**. After evaporation of solvents, **13** was recovered as a viscous oil (0.18 g, 35% based on the silane). − ^{1}H NMR ($CDCl_3$): δ = 0.08 (br. s, 1 H, CH), 0.45 (d, ^4J = 2.0 Hz, 18 H, $SiMe_2$), 0.95−1.05 (m, 18 H, 6 CH_3−CH_2), 1.56−1.65 (m, 12 H, 6 CH_3−CH_2), 2.35 (s, 9 H, Me of phosphinine), 2.52−2.58 (m, 6 H, CH_2−C-5), 2.72−2.90 (m, 6 H, CH_2−C-6), 6.77 (d, ^4J = 1.3 Hz, 3 H, H-4). − ^{13}C NMR ($CDCl_3$): δ = 3.0 (br. s, CH), 4.7 (d, ^3J = 15.3 Hz, $SiMe_2$), 15.0 (s, Me), 25.3 (s, C-5−CH_2−CH_2−CH_3), 26.5 (s, Me of phosphinine), 27.6 (d, ^3J = 10.0 Hz, C-6−CH_2−CH_2−CH_3), 36.8 (s, CH_2−C-5), 37.6 (d, ^2J = 34.5 Hz, CH_2−C-6), 134.4 (d, ^3J = 20.0 Hz, C-4), 146.5 (d, ^2J = 11.5 Hz, C-5 or C-3), 147.2 (d, ^2J = 14.5 Hz, C-3 or C-5), 166.4 (d, ^1J = 78.0 Hz, C-2 or C-6), 166.8 (d, ^1J = 58.3 Hz, C-6 or C-2). − ^{31}P NMR ($CDCl_3$): δ = 242.6 (s). − MS ; *m*/*z* (%): 767 (8) [M], 573 (100) [M − phosphinine]. − $C_{43}H_{73}P_3Si_3$ (767.2): calcd. C 67.32, H 9.59; found C 67.45, H 9.70.

Synthesis of Complex 14: A solution of ligand **13** (0.15 g, 0.20 mmol) in toluene (5 mL) was added to a solution of [$W(CO)_5$(THF)] (0.16 g, 0.40 mmol) in toluene (10mL). The resulting mixture was then heated at 110 °C for 20 hours. After completion, celite (0.5 g) was added and the mixture was evaporated to dryness,yielding a red-brown powder, which was purified by chromatography over silica gel. A first fraction, eluted with hexane, yielded traces of $W(CO)_6$. A second fraction, eluted with a mixture of hexane/toluene (80:20), yielded complex **14** as a red oil after evaporation of solvents (0.11 g, 56% based on **13**). This oil turned into a red solid after trituration in methanol. − ^{1}H NMR ($CDCl_3$): δ = 0.00 (s, 9 H, CH_3 of $SiMe_2$), 0.50 (s, 9 H, CH_3 of $SiMe_2$), 0.86 (t, ^3J = 7.3 Hz, 9 H, 3 CH_3−CH_2), 0.97 (t, ^3J = 7.3 Hz, 9 H, 3 CH_3−CH_2), 1.40 (m, 6 H, 3 CH_3−CH_2−CH_2), 1.63 (m, 6 H, 3

Table 1. Crystal data of **9** and **14**

Compound	**9**	**14**
Molecular formula	$C_{45}H_{59}O_3P_3SiW$	$C_{46}H_{73}O_3P_3Si_3W$
Molecular weight	952.77	1035.07
Crystal habit	red cube	red cube
Crystal dimensions(mm)	0.22×0.22×0.22	0.18×0.18×0.18
Crystal system	Tetragonal	Monoclinic
Space group	P-42_1c	$P2_1/n$
a (Å)	18.2250(2)	13.389(5)
b (Å)	18.2250(2)	25.355(5)
c (Å)	26.4180(4)	14.643(5)
β (°)		91.190(5)
V (Å^3)	8774.75(19)	4970(3)
Z	8	4
d (g.cm^{-3})	1.442	1.383
F000	3888	2136
μ (cm^{-1})	2.807	2.530
T (K)	148.0(1)	150.0(1)
Maximum θ	26.36	30.03
hkl ranges	0 22; 0 16; 0 32	−14 18; −35 34; −20 17
Reflections measured	4882	32691
Independent reflections	4882	13911
R_{int}	0.0000	0.0791
Reflections used	4487	11094
Criterion	>2sigma(I)	>2sigma(I)
Refinement type	Fsqd	Fsqd
Hydrogen atoms	mixed	mixed
Parameters refined	487	524
Reflections / parameter	9	21
$wR2$	0.1026	0.0776
$R1$	0.0379	0.0295
Flack′s parameter	0.422(10)	not applicable
Weighs a, b[a]	0.0633; 17.81	0.0339; 0.1547
GoF	1.054	1.022
difference peak/hole (eÅ^{-3})	1.302(0.122)/ −0.718(0.122)	0.945(0.147)/ −1.531(0.147)

[a] $w = 1/[\sigma^2(F_o^2)+(aP)^2+ bP]$, where $P = (F_o^2+2F_c^2)/3$; $R1$ is the conventional R factor as defined in SHELXL-97.[16]

$CH_3-CH_2-CH_2$), 2.41 (s, 9 H, Me of phosphinine), 2.46−3.40 (m, 12 H, 6 $CH_3-CH_2-CH_2$), 6.87 (br. s, 3 H, H-4), 6.03 (q, ^4J = 8.5 Hz, 1 H, CH). − ^{13}C NMR ($CDCl_3$): δ = 1.4 (q, ^3J = 15.6 Hz, *C*H), 4.7 (s, $SiMe_2$), 5.0 (s, $SiMe_2$), 14.1 (s, CH_3), 14.9 (s, CH_3), 25.5 (s, C-5−$CH_2-CH_2-CH_3$), 27.2 (s, Me of phosphinine), 27.6 (s, C-6−$CH_2-CH_2-CH_3$), 35.3 (AXY_2, Σ *J* = 16.0 Hz, CH_2−C-6), 38.1 (s, *C*H_2−C-5), 132.5 (AXY_2, Σ *J* = 28.7 Hz, C-4), 149.2 (AXY_2, Σ *J* = 19.3 Hz, C-5 or C-3), 149.7 (AXY_2, Σ *J* = 10.3 Hz, C-3 or C-5), 160.0 (AXY_2, Σ *J* = 30.8 Hz, C-6), 162.0 (s, C-2), 213.7 (dt, ^2J = 21.2 Hz, ^2J = 9.2 Hz, CO). − ^{31}P NMR ($CDCl_3$): δ = 211.6 (^1J = 227.7 Hz). − IR (KBr): ν (CO) = 1950, 1875 cm^{-1}. − MS; *m*/*z* (%): 1007 (8) [M − CO], 979 (90) [M − 2 CO], 951 (25) [M − 3 CO], 767 (20) [M − $W(CO)_3$]. − $C_{46}H_{73}O_3P_3Si_3W$ (1035.1): calcd. C 53.38, H 7.11; found C 53.42, H 7.18.

X-Ray Structural Analysis: For compounds **9** and **14**, data were collected on a KappaCCD diffractometer. Mo-K_α (λ = 0.71073 Å) radiation and a graphite monochromator were used in all cases. The crystal structures were solved and refined using SIR-97[16a] and refined with SHELXL-97.[16b] Other experimental details are given in Table 1. The ORTEP drawings reported in this article were generated using the winGX program created by Professor L. J. Farrugia (ORTEP III for Windows, available on the internet as a freeware at louis@chem.gla.ac.uk, Department of Chemistry at the University of Glasgow).

Crystallographic Data (excluding structure factors) for the structures reported have been deposited with the Cambridge Data Centre as supplementary publication nos. CCDC-142208 (**9**) and CCDC-142209 (**14**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

The authors thank the *CNRS* and the *Ecole Polytechnique* for support of this work.

[1] [1a] D. W. Meek, in *Homogeneous Catalysis with Metal Phosphine Complexes* (Ed.: L. H. Pignolet), Plenum Press, New York, **1983**. − [1b] C. Bianchini, C. Mealli, A. Meli, M. Sabat, in *Stereochemistry of Organometallic and Inorganic Compounds* (Ed.: I. Bernal), Elsevier, Amsterdam, **1986**; *Vol. 1*, p 146. − [1c] C. Bianchini, *Comments Inorg. Chem.* **1988**, *8*, 27−43.

[2] Leading references in these different areas are quoted in the following reference: C. Bianchini, A. Meli, M. Peruzzini, F. Vizza, *Organometallics* **1990**, *9*, 226−240.

[3] C. Bianchini, P. Barbaro, A. Meli, M. Peruzzini, A. Vacca, F. Vizza, *Organometallics* **1993**, *12*, 2505−2514.

[4] [4a] C. Bianchini, D. Fabbri, S. Gladiali, A. Meli, W. Pohl, F. Vizza, *Organometallics* **1996**, *15*, 4604−4611. − [4b] C. Bianchini, A. Meli, *Acc. Chem. Res.* **1998**, *31*, 109−116.

[5] F. A. Cotton, B. Hong, in *Progress in Inorganic Chemistry* (Ed.: S. J. Lippard), John Wiley and Sons, Inc., **1992**; *Vol. 40*, p 180.

[6] [6a] C. Elschenbroich, M. Nowotny, A. Behrendt, W. Massa, S. Wocadlo, *Angew. Chem. Int. Ed. Engl.* **1992**, *104*, 1343−1345. − [6b] N. Mézailles, N. Avarvari, L. Ricard, F. Mathey, P. Le Floch, *Inorg. Chem.* **1998**, *37*, 5313−5316. − [6c] P. Rosa, L. Ricard, P. Le Floch, F. Mathey, G. Sini, O. Eisenstein, *Inorg. Chem.* **1998**, *37*, 3154−3158.

[7] F. Mathey, P. Le Floch, *Chem. Ber.* **1996**, *129*, 263−268.

[8] N. Mézailles, N. Avarvari, N. Maigrot, L. Ricard, F. Mathey, P. Le Floch, L. Cataldo, T. Berclaz, M. Geoffroy, *Angew. Chem. Int. Ed.* **1999**, *38*, 3194−3197.

[9] [9a] A. Jouaiti, M. Geoffroy, G. Bernardinelli, *Tetrahedron Lett.* **1992**, *33*, 5071−5074. − [9b] A. Jouaiti, M. Geoffroy, G. Terron, G. Bernardinelli, *J. Am. Chem. Soc.* **1995**, *117*, 2251−2258. − [9c] M. van de Sluis, V. Beverwijk, A. Termaten, E. Gavrilova, F. Bickelhaupt, H. Kooijman, N. Veldman, *Organometallics* **1997**, *16*, 1144−152.

[10] [10a] N. Avarvari, P. Le Floch, L. Ricard, F. Mathey, *Organometallics* **1997**, *16*, 4089−4098. − [10b] N. Avarvari, P. Rosa, F. Mathey, P. Le Floch, *J. Organomet. Chem.* **1998**, *567*, 151−155.

[11] N. Avarvari, P. Le Floch, F. Mathey, *J. Am. Chem. Soc.* **1996**, *118*, 11978−11979.

[12] [12a] N. Avarvari, N. Mézailles, L. Ricard, P. le Floch, F. Mathey, *Science* **1998**, *280*, 1587−1589. − [12b] N. Avarvari, N. Maigrot, L. Ricard, F. Mathey, P. Le Floch, *Chem. Eur. J.* **1999**, *5*, 2109−2118.

[13] [13a] F. A. Cotton, C. S. Kraihanzel, *J. Am. Chem. Soc.* **1962**, *84*, 4432. − [13b] J. Chatt, H. R. Watson, *J. Chem. Soc.* **1961**, 4980.

[14] P. Le Floch, L. Ricard, F. Mathey, *Polyhedron* **1990**, *9*, 991.

[15] L. H. Gade, C. Becker, *Inorg. Chem.* **1993**, *32*, 2308.

[16] [16a] SIR97, an integrated package of computer programs for the solution and refinement of crystal structures using single crystal data: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. − [16b] G. M. Sheldrick, *SHELXL-97*, Universität Göttingen, Germany, **1997**.

Received April 3, 2000
[I00127]