DOI: 10.1002/ejic.200801034

vic-Dichlorodiphosphapropenes – Synthesis and Coordination Ability

Raluca Septelean,[a,b] Gabriela Nemes,[a] Jean Escudié,*[b] Ioan Silaghi-Dumitrescu,[a] Henri Ranaivonjatovo,[b] Petronela Petrar,[a] Heinz Gornitzka,[b] Luminita Silaghi-Dumitrescu,*[a] and Nathalie Saffon[c]

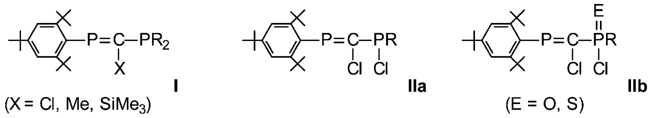
Keywords: Phosphorus / Tungsten / Palladium / Structure elucidation

New substituted 2,3-dichloro-1-$\lambda^3\sigma^2$-P,3-$\lambda^3\sigma^3$-P-diphosphapropenes Mes*P=C(Cl)-P(Cl)*t*Bu (**1**) (Mes* = 2,4,6-tri-*tert*-butylphenyl) and the oxidation compounds Mes*P=C(Cl)–P(=E)(Cl)R [R = *t*Bu, E = S (**2**), O (**3**); R = Mes, E = O (**4**)] are reported. From the reaction of **2** with $W(CO)_5$(thf) the chelate compound $W(CO)_4$[Mes*P=C(Cl)–P(S)(Cl)*t*Bu] (**5**) was obtained. Reaction of **1** or **2** with $PdCl_2$(cod) led to $PdCl_2$[*cy*Mes*PC(H)(Cl)–P(Cl)*t*Bu] (*cy*Mes*P = 5,7-di-*tert*-butyl-3,3-dimethyl-1-phosphaindane) (**6**) or $PdCl_2$[*cy*Mes*PC(H)(Cl)–P(S)(Cl)*t*Bu] (**7**), in which the coordination to the Pd atoms is accompanied by intramolecular addition of CH(*t*Bu) of Mes* to the P=C bond of the dichlorodiphosphapropene.
(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2009)

Introduction

The development of the chemistry of low-coordinate phosphorus compounds is possible owing to stabilization by kinetic protection (brought by bulky substituents) or to coordination to transition metals of such species.[1] To date, diphosphapropenes Mes*P=C(X)–PR_2 (Mes* = supermesityl = 2,4,6-tri-*tert*-butylphenyl) (**I**)[2–6] and their oxidation products with sulfur,[5–9] and in a few cases with oxygen,[10] have been reported. Monocoordinate complexes with $W(CO)_5$ and chelates with $W(CO)_4$ of **I** were obtained and characterized for the systems with R^1R^2 = Ph_2 and X = Cl,[2] Me,[3] $SiMe_3$.[6] Pt^{II} and Pd^{II} complexes with ligands bearing Me[3] or $SiMe_3$[6] at the carbon atom of **I** were prepared, and tests on the catalytic activity in Sonogashira and Suzuki reactions showed some encouraging results.[3,6] It is interesting to note that no platinum or palladium complexes of Mes*P=C(Cl)–PPh_2 could be isolated so far.[4,5]

The choice of substituents on phosphorus is important in terms of steric and electronic effects, as both influence the stability and reactivity of diphosphapropenes. We have been interested in diphosphapropenes with two different substituents on the $\lambda^3\sigma^3$ (**IIa**) or the corresponding $\lambda^5\sigma^4$ (**IIb**) phosphorus atom. The first approach was to introduce a good leaving group (such as a chlorine atom) next to the organic substituent (Scheme 1).



Scheme 1.

Furthermore, it would be interesting to retain the chlorine atom on the central sp^2 carbon atom, as in the case of the Yoshifuji ligand Mes*P=C(Cl)–PPh_2 because both chlorine atoms are easily substituted and should give access to a large family of diphosphapropene-type ligands. Such ligands with different substituents on the phosphorus atoms and two chlorine atoms in vicinal positions (one on the phosphorus atom and another on the central sp^2 carbon atom) provide supplementary reaction centers and thus modify the properties and probably might also tune the catalytic activity of such systems. We report here the synthesis of such a new diphosphapropene, 3-*tert*-butyl-2,3-dichloro-1-(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphapropene (**1**), its oxidation products, 3-thioxo- (**2**), 3-oxo- (**3**), and another new 3-oxodiphosphapropene Mes*P=C(Cl)–P(O)(Cl)Mes (**4**). The reactions of **2** with $W(CO)_5$(thf) and that of **1** and **2** with $PdCl_2$(cod) are also discussed.

Results and Discussion

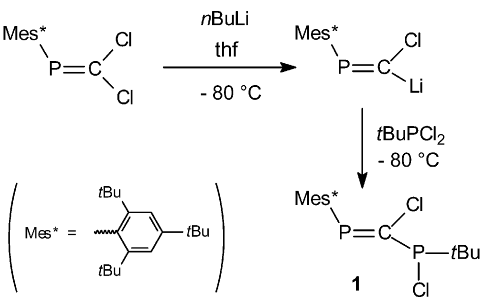
Synthesis and Characterization of the New Type of 1,3-Diphosphapropenes

Diphosphapropene **1** was obtained in good yield as a slightly air-sensitive product by the reaction of Mes*P=C(Cl)Li with *t*$BuPCl_2$ at low temperature (Scheme 2).

---

[a] Universitatea Babes-Bolyai, Cluj-Napoca, Facultatea de Chimie si Inginerie Chimica,
Kogalniceanu, Nr. 1, RO-400084, Romania
[b] Université de Toulouse, UPS, LHFA, CNRS, LHFA UMR 5069,
118 route de Narbonne, 31062 Toulouse, France
[c] Structure Fédérative Toulousaine en Chimie Moléculaire, FR 2599, Université Paul Sabatier,
118 route de Narbonne, 31062 Toulouse Cedex 09, France

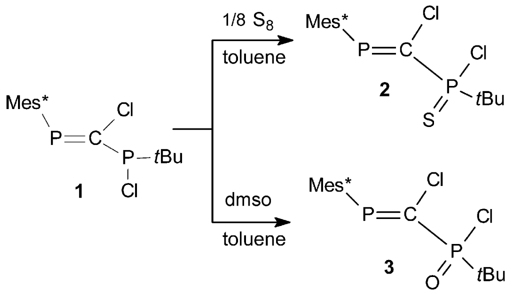
Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.



Scheme 2.

Starting from the (*Z*)-phosphacarbenoid Mes*P=C(Cl)-Li, only the *Z* isomer was formed,[11] as shown by the large $^{2}J_{\mathrm{P,P}}$ coupling constant (345.0 Hz). The ^{13}C NMR signal of the carbon atom bonded to the two phosphorus atoms was observed at $\delta = 168.4$ ppm with close $^{1}J_{\mathrm{P=C}}$ and $^{1}J_{\mathrm{P,C}}$ values (81.8 and 72.5 Hz, respectively).

By heating **1** with an excess amount of sulfur or dimethyl sulfoxide in refluxing toluene (Scheme 3), partially oxidized diphosphapropenes **2** and **3** are formed in excellent yields. Oxidation of the low-coordinate $\lambda^3\sigma^2$ phosphorus atom was not observed, even under these rather drastic conditions, as shown by their ^{31}P NMR spectra, which display low-field shifts for this atom (**2**, 341.4 ppm; **3**, 336.7 ppm). This result is in agreement with the greater basicity of the $\lambda^3\sigma^3$ sp^3 phosphorus atom than the $\lambda^3\sigma^2$ sp^2 phosphorus atom and the lower stability of the oxide or sulfide at the $\lambda^5\sigma^3$ phosphorus atom.



Scheme 3.

The (*Z*) stereochemistry was also retained on going from **1** to **2** and **3**, with $^{2}J_{\mathrm{PP}}$ coupling constants (97.2 Hz for **2**, 75.2 Hz for **3**) characteristic for such derivatives [80 Hz in (*Z*)-Mes*P=C(Cl)P(O)Ph$_2$,[10] 104 Hz in (*Z*)-Mes*P=C-(Cl)–P(S)Ph$_2$,[7] but only 53 Hz in (*E*)-Mes*P=C(Cl)-P(S)-Ph$_2$].[7] In the case of **2**, the stereochemistry was confirmed by X-ray structure analysis (Figure 1).

An alternative route to **3** was attempted, which involved reaction of Mes*P=C(Cl)Li with *t*BuP(O)Cl$_2$; however, this led only to unidentified products, whereas the same procedure applied for the synthesis of **4** (Scheme 4) was successful.

The high steric demand of the *tert*-butyl units of the supermesityl (Mes*) group hinders its free rotation; so, in all cases, the ^{13}C NMR spectra show two doublets for the Me groups of both *o*-*t*Bu groups.

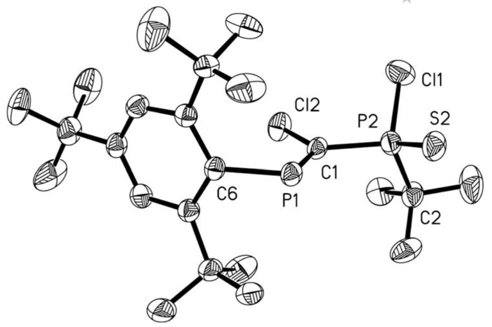
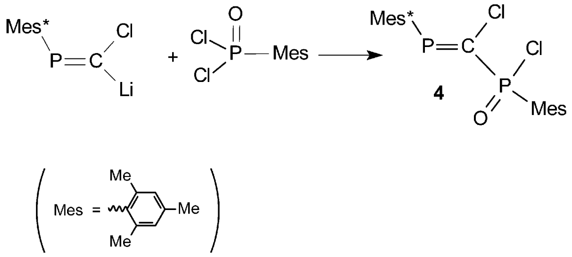


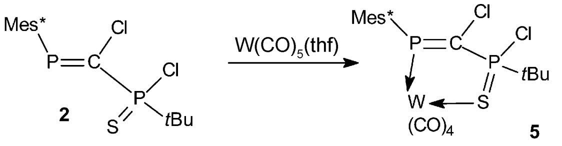
Figure 1. The molecular structure of **2** with atom labeling scheme (50% probability thermal ellipsoids; disorder and hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Cl1–P2 2.038(1), Cl2–C1 1.741(2), P1–C1 1.681(2), P1–C6 1.836(2), P2–C1 1.806(2), P2–C2 1.847(2), P2–S2 1.939(1), C1–P1–C6 100.11(8), C1–P2–C2 110.29(8), C1–P2–S2 110.83(6), C2–P2–S2 112.25(7), C1–P2–Cl1 104.61(6), C2–P2–Cl1 105.44(7), S2–P2–Cl1 113.03(3), P1–C1–Cl2 126.03(10), P1–C1–P2 117.91(9), Cl2–C1–P2 116.03(10).



Scheme 4.

Coordination Behavior of Diphosphapropenes 1 and 2

Tungsten complex **5** was obtained by addition and stirring at room temperature of diphosphapropene sulfide **2** to a solution of W(CO)$_5$(thf) (Scheme 5).



Scheme 5.

After 2 h, the ^{31}P NMR spectrum showed near-quantitative formation of complex **5** (Figure 2). Complex **5** displays ^{31}P NMR chemical shifts [δ(P=C) = 340.1 ppm and δ(P=S) = 119.8 ppm] very similar to those of starting **2** (341.4 and 110.3 ppm, respectively) with a $^{2}J_{\mathrm{P,P}}$ coupling constant of 116.0 Hz. The large $^{1}J_{\mathrm{P,W}}$ coupling constant (303.3 Hz) proves the η^1-mode of coordination on the former $\lambda^3\sigma^2$ phosphorus atom. For the CO groups four doublets of doublets (coming from coupling with the two nonequivalent phosphorus atoms) were observed in the ^{13}C NMR spectrum. The IR spectrum of **5** recorded in nujol exhibits the characteristic pattern for a $L_2W(CO)_4$ moiety with four CO stretching bands in the 1850–2050 cm^{-1} region.[12]

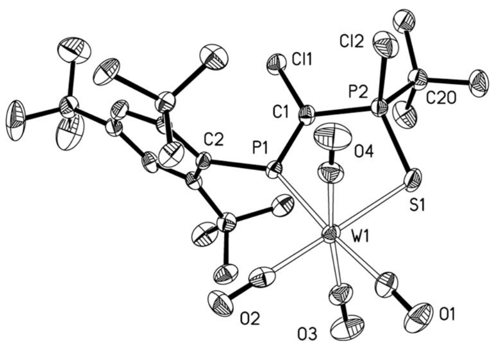


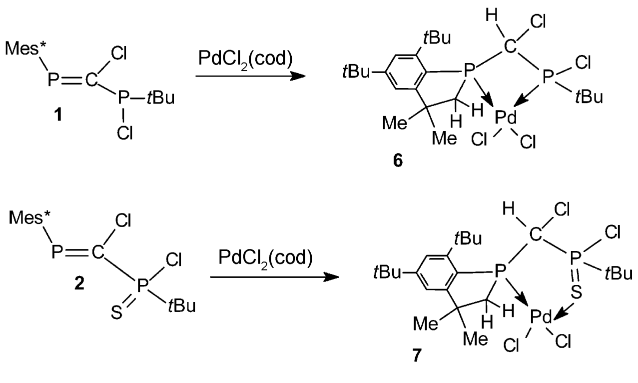
Figure 2. The molecular structure of **5** with atom labeling scheme (50% probability thermal ellipsoids; disorder and hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: W1–P1 2.434(1), W1–S1 2.576(1), P1–C1 1.678(5), P1–C2 1.838(4), C1–Cl1 1.735(4), C1–P2 1.786(4), P2–C20 1.858(5), P2–S1 1.9840(18), P2–Cl2 2.034(2), P1–W1–S1 82.39(4), C1–P1–C2 103.3(2), C1–P1–W1 116.40(16), C2–P1–W1 140.23(15), P1–C1–Cl1 125.6(3), P1–C1–P2 117.3(2), Cl1–C1–P2 116.7(3), C1–P2–C20 115.9(2), C1–P2–S1 109.75(16), C20–P2–S1 110.33(18), C1–P2–Cl2 104.05(17), C20–P2–Cl2 103.81(19), S1–P2–Cl2 112.78(9).

Monitoring the reaction by ^{31}P NMR between –20 °C and room temperature did not allow characterizing of any intermediate such as a compound with a monodentate ligand (coordinated to W either through S or P).

BP86/DZP calculations[13,14,15] predict that the bidentate derivative **5M** (where the supermesityl group has been replaced by a mesityl group) is more stable than any of the monodentate (through sulfur or phosphorus) counterpart by at least 36 $kcal\,mol^{-1}$ (see Supporting Information for details), which is in line with the experimental observation of chelate **5** only.

When **1** and **2** were allowed to react with $PdCl_2(cod)$, complexes **6** and **7** were obtained (Scheme 6), as proved by the dramatic high-field shifts observed for the coordinating phosphorus atom from 317.6 ppm (for **1**) to 8.6 ppm (for **6**) and from 341.4 ppm (for **2**) to 69.9 ppm (for **7**). The $^2J_{P,P}$ coupling constants also decrease from 345.0 to 11.9 Hz (**1** to **6**) and from 97.2 to 28.1 Hz (**2** to **7**). These changes are indicative of the transformation of the P=C double bond to a P–C single bond.[1c,d] Furthermore, the presence of two nonequivalent protons on the carbon atom bonded to phosphorus suggests the presence of a five membered-ring formed by the addition of a C–H bond from the *o*-*t*Bu of the Mes* group to the P=C bond. In general, such a type of cyclization involving a supermesityl group linked directly to double-bonded heteroatoms has been observed in various systems in the presence of a metal,[16] under irradiation or in the presence of a protic reagent.[17] When the Mes* group is bonded to a $\lambda^3\sigma^3$ phosphorus atom, such reactions occur only in the presence of Pt catalysts.[5]

Complexes **6** and **7** are the first examples of such rearrangement observed at a $\lambda^3\sigma^3$ phosphorus atom during coordination at palladium (Figures 3 and 4).



Scheme 6.

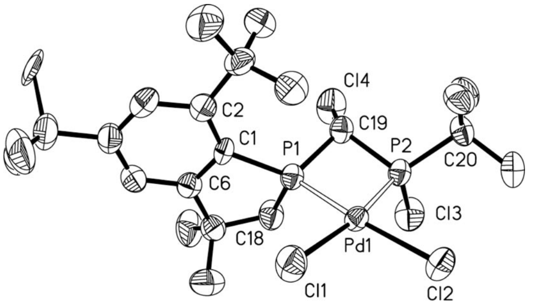


Figure 3. The molecular structure of **6** with atom labeling scheme (30% probability thermal ellipsoids; disorder, hydrogen atoms, and noncoordinated solvent molecules are omitted for clarity). Selected bond lengths [Å] and angles [°]: C1–P1 1.820(6), C18–P1 1.807(7), C19–Cl4 1.764(6), C19–P2 1.842(6), C19–P1 1.845(6), C20–P2 1.845(7), Cl3–P2 2.002(2), P1–Pd1 2.244(2), P2–Pd1 2.207(2), C6–C1–P1 105.9(4), C2–C1–P1 132.9(5), P2–C19–P1 93.0(3), C18–P1–Pd1 114.9(3), C1–P1–Pd1 129.7(2), C19–P1–Pd1 92.3(2), C19–P2–Pd1 93.5(2), C20–P2–Pd1 125.2(2), Cl3–P2–Pd1 113.83(10), P2–Pd1–P1 73.82(6).

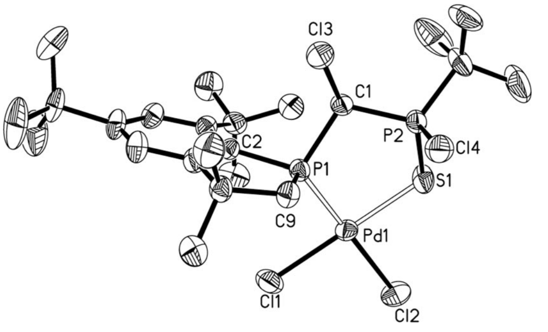


Figure 4. The molecular structure of **7** with atom labeling scheme (30% probability thermal ellipsoids; disorders, hydrogen atoms, and noncoordinated solvent molecules are omitted for clarity). Selected bond lengths [Å] and angles [°]: P1–C1 1.874(7), P1–C2 1.802(7), P1–C9 1.807(7), C1–Cl3 1.769(7), C1–P2 1.824(7), P2–Cl4 2.006(3), P2–S1 1.981(3), P1–Pd1 2.230(2), Pd1–Cl1 2.309(2), Pd1–S1 2.303(2), Pd1–Cl2 2.352(2), C2–P1–C9 96.7(3), Pd1–P1–C1 108.5(2), P1–C1–P2 109.9(3), C1–P2–S1 107.0(2), P1–Pd1–S1 94.52(7).

Crystal and Molecular Structure of Compounds 2, 5, 6, and 7

Single crystals of **2**, **5**, **6**, and **7** were subjected to X-ray diffraction analysis, and the corresponding molecular structures are shown in Figures 1–4. These data confirm the preservation of the (*Z*) configuration in all cases having a P=C bond. In **6**, the Pd atom is chelated by the two phosphorus atoms of the diphosphapropene, whereas in **5** and **7** the ligand is chelated through the $\lambda^3\sigma^3$ phosphorus atom and the sulfur atom.

A common feature in these systems is that the P=C bond length is not modified on going from the free ligand [P=C 1.681(2) Å in **2**] to the complexed ligand [P=C 1.678(1) Å in **5**], which means that coordination to the metal does not change the P=C double bond character.

The P1–W1 bond length [2.434(1) Å] is similar to those previously observed in related derivatives;[2,6] the same also applies for the S1–W1 distance [2.576(1) Å].[7] Despite the steric hindrance on the $\lambda^3\sigma^2$ phosphorus atom, a CO group is easily eliminated to give **5** with **2** acting as bidentate ligand. The W1–P1–C1–P2–S1 ring in compound **5** presents an envelope structure with the W1–P1–C1 and P2 atoms nearly in the same plane.

In **6** and **7**, the Pd atom is in a planar environment, and the P1–Pd–P2–C19 four-membered ring in **6** is nonplanar, with a P–C–P/P–Pd–P dihedral angle of 28.1°, and the S1–Pd–P1–C1 angle of the metallacycle in **7** is 7.3°.

In the crystalline structure of derivative **6**, H···Cl contacts of 2.703 and 2.823 Å (compare to 2.95 Å for the sum of the van der Waals radii)[18] are noticed between the chlorine atoms bound to Pd and the hydrogen H24 of an adjacent chloroform molecule (Figure 5). Two such units are further connected through other H···Cl interactions (2.907 Å) between H18B of the phosphole ring and one of the chlorine (Cl2) atoms on palladium (Figure 5).

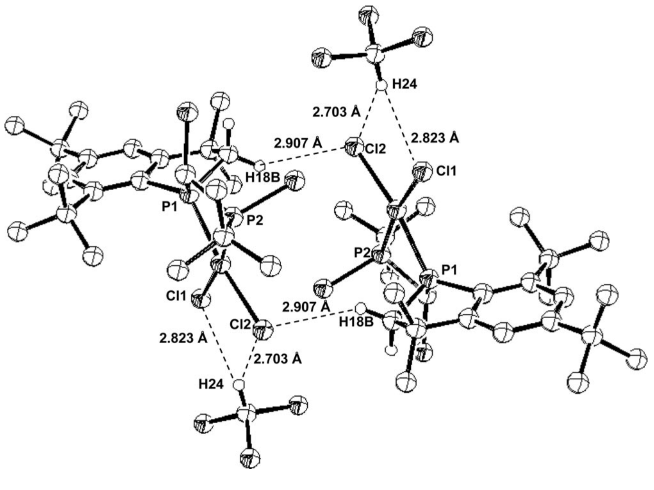


Figure 5. Short H···Cl contacts in the crystalline structure of **6** (for clarity, only selected hydrogen atoms are shown).

Perspectives

The presence in **1**–**7** of chlorine atoms in different environments (on the sp^2-hybridized carbon atom in **1**–**4** and on the sp^3-hybridized carbon atom in **5**–**7** and on the $\lambda^5\sigma^4$ phosphorus atom) is promising for synthetic purposes as a result of the possibility of functionalizing these centers and tuning this way the coordination ability of such ligands and the properties of their metal derivatives.

Experimental Section

General: All experiments were carried out in flame-dried glassware under a nitrogen or argon atmosphere by using high-vacuum-line techniques. Solvents were dried and freshly distilled by using an SPS-5MB system. NMR spectra were recorded (with $CDCl_3$ as solvent) with a Bruker Avance 300 spectrometer at the following frequencies: ^{1}H, 300.13 MHz; ^{13}C, 75.47 MHz (reference TMS); ^{31}P, 121.51 MHz (reference 85% H_3PO_4). All ^{13}C and ^{31}P NMR spectra for compounds **6** and **7** were acquired by proton decoupling. Melting points were determined with a Wild Leitz-Biomed apparatus. Mass spectra were obtained with a Hewlett–Packard 5989A spectrometer by EI at 70 eV or with a Nermag R10-10 spectrometer by CI. The molecular peaks and all the fragments correspond to ^{35}Cl. Elemental analyses were performed by the “Service de Microanalyse de l’Ecole de Chimie de Toulouse”.

Mes*P=C(Cl)–P(Cl)*t*Bu (1): A solution of *n*BuLi (1.6 M in hexane, 3.6 mL, 5.56 mmol) was added dropwise, at –80 °C, to a colorless solution of Mes*P=CCl$_2$ (2.00 g, 5.56 mmol) in thf (20 mL). The solution turned brown and was stirred at this temperature for 1 h. The lithium compound Mes*P=C(Cl)Li was then added to *tert*-butyldichlorophosphane (*t*BuPCl$_2$; 0.88 g, 5.56 mmol) in thf (20 mL) cooled to –80 °C. The reaction mixture was stirred for 20 min and warmed up to room temperature. Solvents and volatile products were removed in vacuo, and the residue was dissolved in pentane (20 mL). Lithium salts were filtered out; brown crystals were obtained after 4–5 h at –20 °C. Yield: 1.87 g (75%). M.p. 90–100 °C). ^{1}H NMR: δ = 1.14 (dd, $^3J_{P,H}$ = 14.7 Hz, $^5J_{P,H}$ = 0.6 Hz, 9 H, P-*t*Bu), 1.23 (s, 9 H, *p*-*t*Bu), 1.36 and 1.37 (2 s, 2×9 H, *o*-*t*Bu), 7.30–7.34 (m, 2 H, arom H) ppm. ^{13}C NMR: δ = 26.41 (d, $^2J_{C,P}$ = 18.6 Hz, *Me*$_3$C-P), 33.75 (*p*-C*Me*$_3$), 32.80 (d, $^4J_{C,P}$ = 6.6 Hz) and 32.93 (d, $^4J_{C,P}$ = 6.6 Hz, *o*-C*Me*$_3$), 37.57 (*p*-*C*Me$_3$), 37.70 (dd, $^1J_{C,P}$ = 34.5 Hz, $^3J_{C,P}$ = 16.7 Hz, Me$_3$*C*-P), 37.87 and 38.02 (*o*-*C*Me$_3$), 122.10 and 122.45 (*m*-CH), 134.81 (dd, $^1J_{C,P}$ = 64.1 Hz, $^3J_{C,P}$ = 32.5 Hz, *ipso*-C), 151.21 (*p*-C), 152.79 (d, $^2J_{C,P}$ = 2.3 Hz) and 152.82 (d, $^2J_{C,P}$ = 2.8 Hz, *o*-C), 168.4 (dd, $^1J_{C,P}$ = 81.8, 72.5 Hz, P=C-P) ppm. ^{31}P NMR: δ = 116.5 (d of decaplet, $^2J_{P,P}$ = 345.0 Hz, $^3J_{P,H}$ = 14.7 Hz, P-*t*Bu), 317.6 (d, $^2J_{P,P}$ = 345.0 Hz, P-Mes*) ppm. MS (CI, NH$_3$): *m*/*z* (%) = 447 (3) [M + 1], 411 (1) [M – Cl] 389 (25) [M – *t*Bu], 333 (10) [M – 2*t*Bu + 1], 57 (100) [*t*Bu]. $C_{23}H_{38}Cl_2P_2$ (447.40): calcd. C 51.75, H 8.56; found C 51.87, H 8.47.

Mes*P=C(Cl)–P(S)(Cl)*t*Bu (2): To a solution of **1** (2.71 g, 6.05 mmol) in toluene (50 mL) was added sulfur (3.00 g, 11.7 mmol) at room temperature. The reaction mixture was heated at reflux for 4 h in toluene to give the Mes*P=C(Cl)–P(S)(Cl)*t*Bu compound with 100% conversion according to ^{31}P NMR spectroscopy. After removal of the excess amount of sulfur by filtration, toluene was evaporated in vacuo, and the residue was dissolved in pentane; diphosphapropene **2** crystallized at room temperature. Yield: 2.49 g (86%). M.p. 153 °C. ^{1}H NMR: δ = 1.34 (s, 9 H, *p*-*t*Bu), 1.48 and 1.49 (2 s, 2×9 H, *o*-*t*Bu), 1.45 (d, $^3J_{P,H}$ = 21.0 Hz, 9 H, P-*t*Bu), 7.45 and 7.47 (2 t, $^4J_{H,H}$ = $^4J_{P,H}$ = 1.5 Hz, 2×1 H, arom H) ppm. ^{13}C NMR: δ = 25.91 (d, $^2J_{C,P}$ = 2.2 Hz, *Me*$_3$CP=S), 31.25 (*p*-*Me*$_3$C), 33.02 (d, $^4J_{C,P}$ = 6.7 Hz) and 33.41 (d, $^4J_{C,P}$ = 6.9 Hz, *o*-*Me*$_3$C), 35.04 (*p*-Me$_3$*C*), 37.73 and 37.96 (*o*-Me$_3$*C*), 44.77 (dd, $^1J_{C,P}$ = 53.0 Hz, $^3J_{C,P}$ = 1.5 Hz, Me$_3$*C*P=S), 122.45 and 122.96 (*m*-C), 134.20 (dd, $^1J_{C,P}$ = 63.5 Hz, $^3J_{C,P}$ = 12.5 Hz, *ipso*-C), 151.60 (*p*-C), 153.24 (d, $^2J_{C,P}$ = 2.9 Hz) and 153.52 (d, $^2J_{C,P}$ = 3.5 Hz, *o*-

C), 156.37 (dd, $^{1}J_{C,P}$ = 84.3, 50.9 Hz, P=C-P) ppm. ^{31}P NMR: δ = 110.3 (d of decaplet, $^{2}J_{P,P}$ = 97.2 Hz, $^{3}J_{P,H}$ = 21.0 Hz, *t*Bu-P=S), 341.4 (d, $^{2}J_{P,P}$ = 97.2 Hz, Mes*-P=C) ppm. MS (EI, 70 eV): *m*/*z* (%) = 478 (3) [M], 421 (10) [M – *t*Bu], 389 (1) [M – *t*Bu – S], 355 (1) [M – S – *t*Bu – Cl + 1], 329 (1) [M – 2*t*Bu – Cl], 57 (100) [*t*Bu]. $C_{23}H_{38}Cl_{2}P_{2}S$ (479.47): calcd. C 57.62, H 7.99; found C 57.59, H 8.17.

Mes*P=C(Cl)–P(O)(Cl)*t*Bu (3): To a solution of **1** (1.80 g, 4.02 mmol) in toluene (50 mL) was added dimethyl sulfoxide (0.62 g, 8.00 mmol) at room temperature. The reaction mixture was heated at reflux for 2 h in toluene to give the Mes*P=C(Cl)–PO-(Cl)*t*Bu compound. After removal of the excess amount of dmso and the solvent, diphosphapropene **3** was separated as a yellow oil from starting **1**. Recrystallization from pentane (20 mL) afforded pure **3**. Yield: 1.21 g (65%). M.p. 145–147 °C. ^{1}H NMR: δ = 1.34 (s, 9 H, *p*-*t*Bu), 1.39 (d, $^{3}J_{P,H}$ = 19.5 Hz, 9 H, P-*t*Bu), 1.48 (s, 18 H, *o*-*t*Bu), 7.45 and 7.46 (2 t, $^{4}J_{H,H}$ = $^{4}J_{P,H}$ = 1.5 Hz, 2 × 1 H, arom H) ppm. ^{13}C NMR: δ = 25.22 (*Me*$_3$CP=O), 31.22 (*p*-*Me*$_3$C), 32.93 (d, $^{4}J_{C,P}$ = 7.2 Hz) and 33.0 (d, $^{4}J_{C,P}$ = 6.9 Hz, *o*-*Me*$_3$C), 31.56 (*p*-Me$_3$*C*), 37.70 and 37.93 (*o*-Me$_3$*C*), 40.74 (d, $^{1}J_{C,P}$ = 77.7 Hz, Me$_3$*C*P=O), 122.46 and 122.88 (*m*-C), 132.50 (dd, $^{1}J_{C,P}$ = 61.3 Hz, $^{3}J_{P,C}$ = 10.9 Hz, *ipso*-C), 151.77 (*p*-C), 153.56 (d, $^{2}J_{C,P}$ = 2.7 Hz) and 153.68 (d, $^{2}J_{C,P}$ = 3.1 Hz, *o*-C) ppm. ^{31}P NMR: δ = 65.5 [d of decaplet, $^{2}J_{P,P}$ = 75.2 Hz, $^{3}J_{P,H}$ = 19.5 Hz, *t*BuP(S)], 336.7 (d, $^{2}J_{P,P}$ = 75.2 Hz, Mes*-P=C) ppm. MS (EI, 70 eV): *m*/*z* (%) = 463 (1) [M + 1], 447 (3) [M – O], 405 (1) [M – *t*Bu], 371 (1) [M – *t*Bu – Cl + 1], 57 (100) [*t*Bu]. $C_{23}H_{38}Cl_{2}OP_{2}$ (463.41): calcd. C 59.61, H 8.27; found C 59.84, H 7.89.

Mes*P=C(Cl)-P(O)(Cl)Mes (4): A solution of *n*BuLi (1.6 M in hexane, 3.6 mL, 5.56 mmol) was added dropwise, at –80 °C, to a solution of Mes*P=CCl$_2$ (2.00 g, 5.56 mmol) in thf (20 mL). The solution turned brown and was stirred at this temperature for 1 h. The lithium compound Mes*P=C(Cl)Li was then added to MesP(O)Cl$_2$ (1.30 g, 5.56 mmol) in thf (20 mL) cooled to –80 °C. The reaction mixture was stirred for 4 h and warmed up to room temperature. Solvents and volatile products were removed in vacuo, and the residue was dissolved into pentane (20 mL). Lithium salts were filtered out; compound **4** crystallized as an orange solid after 4–5 h at –4 °C. Yield: 1.78 g (61%). M.p. 104 °C. ^{1}H NMR: δ = 1.32 (s, 9 H, *p*-*t*Bu), 1.43 (d, $^{3}J_{P,H}$ = 2.1 Hz, 18 H, *o*-*t*Bu), 2.32 (s, 3 H, *p*-Me), 2.72 (s, 6 H, *o*-Me), 6.96 (d, $^{4}J_{P,H}$ = 5.4 Hz, 2 H, arom H of Mes), 7.45 (d, $^{4}J_{P,H}$ = 1.2 Hz, 2 H, arom H of Mes*) ppm. ^{13}C NMR: δ = 21.13 (d, $^{5}J_{C,P}$ = 1.6 Hz, *p*-Me of Mes), 24.36 (d, $^{3}J_{C,P}$ = 2.6 Hz, *o*-Me of Mes), 31.14 (*p*-*t*Bu), 32.58 (d, $^{4}J_{C,P}$ = 7.0 Hz, *o*-C*Me*$_3$) and 32.82 (d, $^{4}J_{C,P}$ = 7.2 Hz, *o*-C*Me*$_3$), 34.98 (*p*-*C*Me$_3$), 37.72 and 37.81 (*o*-*C*Me$_3$), 122.47 and 122.67 (*m*-CH of Mes*), 123.85 (d, $^{1}J_{C,P}$ = 121.3 Hz, *ipso*-*C* of Mes), 131.35 (d, $^{3}J_{C,P}$ = 15.6 Hz, *m*-CH of Mes), 131.36 (dd, $^{1}J_{C,P}$ = 60.6 Hz, $^{3}J_{C,P}$ = 13.5 Hz, *ipso*-C of Mes*), 143.48 (d, $^{4}J_{C,P}$ = 3.2 Hz, *p*-C of Mes), 144.00 (dd, $^{2}J_{C,P}$ = 12.9 Hz, $^{4}J_{C,P}$ = 1.6 Hz, *o*-C of *Me*s), 151.73 (*p*-C of Mes*), 153.50 (d, $^{2}J_{C,P}$ = 2.9 Hz, *o*-C of Mes*), 153.55 (d, $^{2}J_{C,P}$ = 3.4 Hz, *o*-C of Mes*), 159.42 (dd, $^{1}J_{C,P}$ = 96.1, 83.4 Hz P=C–P) ppm. ^{31}P NMR: δ = 38.01 (d, $^{2}J_{P,P}$ = 128.3 Hz, P=O), 305.5 (d, $^{2}J_{P,P}$ = 128.3 Hz, P-Mes*) ppm. MS (CI, NH$_3$): *m*/*z* (%) = 525 (3) [M + 1], 509 (1) [M – Me] 489 (25) [M – Cl], 475 (10) [M – Cl – Me + 1], 57 (100) [*t*Bu]. $C_{28}H_{40}Cl_{2}OP_{2}$ (525.47): calcd. C 64.00, H 7.67; found C 64.89, H 7.88.

W(CO)$_4$[Mes*P=C(Cl)–P(S)(Cl)*t*Bu] (5): To a solution of W(CO)$_5$-thf freshly prepared by irradiation of W(CO)$_6$ (1.50 g, 4.20 mmol) in thf (60 mL) was added a solution of **2** (0.45, 0.9 mmol) in thf (20 mL) at room temperature; the reaction mixture was stirred for 1 h. Solvents were removed in vacuo and pentane (20 mL) was added to the residue; W(CO)$_6$ was removed by filtration. Recrystallization from pentane afforded complex **5** as red crystals. Yield: 0.47 g (65%). M.p. 84 °C. ^{1}H NMR: δ = 1.36 (s, 9 H, *p*-*t*Bu), 1.45 [d, $^{3}J_{P,H}$ = 21.9 Hz, 9 H, P(*S*)-*t*Bu], 1.64 and 1.66 (2 s, 2 × 9 H, *o*-*t*Bu), 7.50–7.65 (m, 2 H, arom H) ppm. ^{13}C NMR: δ = 25.43 (d, $^{2}J_{C,P}$ = 1.0 Hz, *Me*$_3$C-P), 31.13 (*p*-*Me*$_3$C), 33.16 and 33.80 (2 s, *o*-*Me*$_3$C), 35.32 (*p*-Me$_3$*C*), 38.67 (d, $^{3}J_{C,P}$ = 1.0 Hz) and 38.92 (*o*-Me$_3$*C*), 44.63 (dd, $^{3}J_{C,P}$ = 3.2 Hz, $^{1}J_{P,C}$ = 51.5 Hz, P*C*Me$_3$), 123.05 and 123.37 (2 d, $^{3}J_{C,P}$ = 6.8 Hz, *m*-CH), 139.01 (dd, $^{3}J_{C,P}$ = 12.6 Hz, $^{1}J_{C,P}$ = 77.9 Hz, *ipso*-C), 153.54 (d, $^{4}J_{C,P}$ = 1.6 Hz, *p*-C), 154.97 (d, $^{2}J_{C,P}$ = 2.9 Hz) and 155.25 (d, $^{2}J_{C,P}$ = 1.7 Hz, *o*-C), 199.81 (dd, $^{3}J_{C,P}$ = 2.2 Hz, $^{2}J_{C,P}$ = 8.8 Hz, CO), 200.96 (dd, $^{3}J_{C,P}$ = 4.7 Hz, $^{2}J_{C,P}$ = 8.9 Hz, CO), 203.77 (dd, $^{3}J_{C,P}$ = 2.2 Hz, $^{2}J_{C,P}$ = 6.2 Hz, CO), 207.81 (dd, $^{3}J_{C,P}$ = 5.4 Hz, $^{2}J_{C,P}$ = 45.1 Hz, CO) ppm. ^{31}P NMR: δ = 119.8 [d, $^{2}J_{P,P}$ = 116.0 Hz P(S)*t*Bu], 340.1 (d, $^{2}J_{P,P}$ = 116.0 Hz, $^{1}J_{P,W}$ = 302.3 Hz, P-Mes*) ppm. MS (CI, NH$_3$): *m*/*z* (%) = 775 (9) [M – 1], 275 (100) [Mes*P – 1]. IR: $\tilde{\nu}$ = 1888, 1933, 1974, 2030 (CO) cm^{-1}. $C_{27}H_{38}Cl_{2}O_{4}P_{2}SW$ (775.35): calcd. C 41.83, H 4.94; found C 41.87, H 4.69.

PdCl$_2$[*cy*Mes*P–C(H)(Cl)–P(Cl)*t*Bu] (6): To a solution of PdCl$_2$(cod) (0.64 g, 2.24 mmol) in thf (20 mL) [freshly prepared from PdCl$_2$ (2.1 g, 11.8 mmol), conc. HCl (5 mL) and 1,5-cyclooctadiene (1.5 mL, 2.26 g, 6.69 mmol)[18]] was added a solution of **1** (1.00 g, 2.23 mmol) in CH$_2$Cl$_2$ (20 mL) at room temperature. The reaction mixture was stirred for an additional 2 h. Solvents and the volatile compounds were removed in vacuo, and pentane (20 mL) was added to the red solid residue. Recrystallization from pentane afforded complex **6** as yellow crystals. Yield: 1.37 g (98%). M.p. 183–185 °C. ^{1}H NMR: δ = 1.42 (s, 9 H, *p*-*t*Bu), 1.66 and 1.68 (2 s, 2 × 3 H, C*Me*$_2$-cycle), 1.69 (d, $^{3}J_{P,H}$ = 22.2 Hz, 9 H, P-*t*Bu), 1.81 (s, 9 H, *o*-*t*Bu), 2.78 (t, $^{2}J_{H,H}$ = $^{2}J_{H,P}$ = 15.0 Hz, 1 H, HCP), 2.97 (d, $^{2}J_{H,H}$ = 15.0 Hz, 1 H, H′CP), 6.01 (d, $^{2}J_{P,H}$ = 9.6 Hz, 1 H, P-CH-P), 7.31 (t, $^{4}J_{H,H}$ = $^{4}J_{P,H}$ = 1.8 Hz, 1 H, arom H), 7.69 (dd, $^{4}J_{H,H}$ = 1.8 Hz, $^{4}J_{P,H}$ = 6.6 Hz, 1 H, arom H) ppm. ^{13}C NMR: δ = 25.42 (d, $^{2}J_{C,P}$ = 6.1 Hz, *Me*$_3$C-P), 30.96 (*p*-*Me*$_3$C), 31.05 and 31.13 (2 s, C*Me*$_2$ cycle), 33.72 (*o*-*Me*$_3$C), 34.46 (d, $^{1}J_{C,P}$ = 32.8 Hz, Me$_3$*C*-P), 35.46 (d, $^{1}J_{C,P}$ = 1.1 Hz, CH$_2$), 38.12 (*o*-Me$_3$*C*), 43.83 (t, $^{2}J_{C,P}$ = $^{4}J_{C,P}$ = 3.6 Hz, *C*Me$_2$ cycle), 43.94 (*p*-Me$_3$*C*), 59.75 (d, $^{1}J_{C,P}$ = 7.2 Hz, P-C-P), 119.74 (d, $^{3}J_{C,P}$ = 12.3 Hz) and 125.47 (d, $^{3}J_{C,P}$ = 11.0 Hz, *m*-C), 128.41 (d, $^{1}J_{C,P}$ = 23.5 Hz, *ipso*-C), 155.08 (d, $^{2}J_{C,P}$ = 9.2 Hz) and 162.16 (d, $^{2}J_{C,P}$ = 23.7 Hz, *o*-C), 158.60 (d, $^{4}J_{C,P}$ = 3.1 Hz, *p*-C) ppm. ^{31}P NMR: δ = 8.53 (d, $^{2}J_{P,P}$ = 11.9 Hz, P-CH$_2$), 84.14 (d, $^{2}J_{P,P}$ = 11.9 Hz, P-*t*Bu) ppm. $C_{23}H_{38}Cl_{4}P_{2}Pd$ (624.73): calcd. C 44.22, H 6.13; found C 43.98, H 6.38.

PdCl$_2$[*cy*Mes*P–C(H)(Cl)–P(S)(Cl)*t*Bu] (7): To a solution of PdCl$_2$(cod) (0.30 g, 1.07 mmol) in CH$_2$Cl$_2$ (10 mL)[19] was added a solution of **1** (0.50 g, 1.065 mmol) in CH$_2$Cl$_2$ (5 mL) whilst stirring. The reaction mixture was stirred for 24 h at room temperature. Solvents and the volatile compounds were removed in vacuo, and pentane (20 mL) was added to the red solid residue. Recrystallization from pentane afforded complex **7** as red crystals. Yield: 0.43 g (62%). M.p. 210 °C. ^{1}H NMR: δ = 1.33 (s, 9 H, *p*-*t*Bu), 1.54 (d, $^{3}J_{P,H}$ = 22.5 Hz, 9 H, P-*t*Bu), 1.54 and 1.61 (2 s, 2 × 3 H, C*Me*$_2$-cycle), 1.77 (s, 9 H, *o*-*t*Bu), 2.69 (dd, $^{2}J_{H,H}$ = 15.9 Hz, $^{2}J_{H,P}$ = 11.4 Hz, 1 H, HCMe$_2$), 3.10 (d, $^{2}J_{H,H}$ = 15.9 Hz, 1 H, H′CMe$_2$), 5.46 [dd, $^{2}J_{P,H}$ = 1.2 Hz, $^{2}J_{P(S)H}$ = 7.8 Hz, 1 H, P-CH-P], 7.15 (br. s, 1 H, arom H), 7.61 (dd, $^{4}J_{P,H}$ = 7.0 Hz, $^{4}J_{H,H}$ = 1.8 Hz, 1 H, arom H) ppm. ^{13}C NMR: δ = 25.18 (d, $^{2}J_{P,C}$ = 1.0 Hz, *Me*$_3$C-P), 30.59 and 34.97 (2 d, $^{4}J_{P,C}$ = 4.8 Hz, C*Me*$_2$ cycle) 31.03 (*p*-*Me*$_3$C), 31.05 (*C*H$_2$), 34.16 (s, *o*-*Me*$_3$C), 38.52 (s, *o*-Me$_3$*C*), 42.78 (dd, $^{2}J_{P,C}$ = 35.7 Hz, $^{4}J_{P,C}$ = 4.8 Hz, *C*Me$_2$ cycle), 45.03 (d, $^{4}J_{P,C}$ = 2.3 Hz, *p*-Me$_3$*C*), 58.29 (dd, $^{1}J_{P,C}$ = 37.8, 6.3 Hz, P-*C*-P), 119.26 (d, $^{3}J_{P,C}$ = 12.1 Hz) and 126.30 (d, $^{3}J_{P,C}$ = 10.6 Hz, *m*-C), 128.63 (d, $^{1}J_{P,C}$ =

Table 1. Crystal data for compounds **2**, **5**, **6**, and **7**.

	2	**5**	**6**	**7**
Empirical formula	$C_{23}H_{38}Cl_2P_2S$	$C_{27}H_{38}Cl_2O_4P_2SW$	$C_{23}H_{38}Cl_4P_2Pd*2CHCl_3$	$C_{25}H_{42}Cl_8P_2PdS$
Formula weight	479.43	775.32	863.40	826.59
Temperature [K]	173(2)	173(2)	297(2)	193(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$C2/c$
a [Å]	13.7029(8)	13.7459(3)	11.297(3)	35.9682(10)
b [Å]	8.9466(5)	15.7079(3)	13.295(4)	10.7323(3)
c [Å]	21.7961(13)	14.6872(3)	14.647(4)	20.1577(5)
α [°]	–	–	65.584(4)	–
β [°]	92.778(10)	93.820(1)	85.517(5)	108.248(2)
γ [°]	–	–	71.068(5)	–
Volume [Å^3]	2668.9(3)	3164.20(11)	1890.8(10)	7390.0(3)
Z	4	4	2	8
Absorption coefficient [mm^{-1}]	0.449	4.016	1.298	1.239
Reflections collected	15185	29076	18286	39842
Independent reflections	5453 [R(int) = 0.0228]	6418 [R(int) = 0.0704]	6631 [R(int) = 0.0497]	6240 [R(int) = 0.0912]
Absorption correction	Multiscans	Multiscans	Multiscans	Multiscans
Min./max. transmission	1.0000/0.821127	0.6895/0.2386	0.9646/0.6666	0.9406/0.7074
Restraints/parameters	84/315	159/398	0/411	212/469
Goodness-of-fit on F^2	1.011	1.011	1.135	1.031
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0341 wR_2 = 0.0843	R_1 = 0.0326 wR_2 = 0.0658	R_1 = 0.0730 wR_2 = 0.1486	R_1 = 0.0616 wR_2 = 0.1468
R indices (all data)	R_1 = 0.0483 wR_2 = 0.0934	R_1 = 0.0595 wR_2 = 0.0755	R_1 = 0.0938 wR_2 = 0.1569	R_1 = 0.1054 wR_2 = 0.1736
Largest diff. peak and hole [eÅ^{-3}]	0.380 and –0.203	0.909 and –1.516	0.962 and –0.983	1.309 and –0.650

60.2 Hz, *ipso*-C), 152.97 (d, $^2J_{C,P}$ = 11.3 Hz) and 160.92 (d, $^2J_{C,P}$ = 20.4 Hz, *o*-C), 157.76 (d, $^4J_{P,C}$ = 3.0 Hz, *p*-C) ppm. ^{31}P NMR: δ = 69.9 (d, $^2J_{P,P}$ = 28.1 Hz P-CH$_2$), 128.6 [d, $^2J_{P,P}$ = 28.1 Hz, P(*S*)-*t*Bu] ppm. MS (EI, 70 eV): *m*/*z* (%) = 656 (1) [M], 477 (15) [M – PdCl$_2$ – 1], 445 (10) [M – PdCl$_2$ – S – 1], 421 (12) [M – PdCl$_2$ – *t*Bu], 275 (100) [Mes*P – 1]. $C_{23}H_{38}Cl_4P_2PdS$ (656.79): calcd. C 42.06, H 5.83; found C 42.22, H 5.48.

X-ray Structure Determinations: Data for structures **2**, **5**, and **7** were collected at low temperatures by using an oil-coated shock-cooled crystal with a Bruker-AXS APEX II with Mo-K_α radiation (λ = 0.71073 Å). Compound **6** was measured at room temperature with a Bruker-SMART APEX system. The structures were solved by direct methods[19] and all non hydrogen atoms were refined anisotropically by using the least-squares method on F^2 (Table 1).[20] CCDC-696780 (for **2**), -696781 (for **5**), -696782 (for **6**), and -704605 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Results on the BP86/DZP calculations on models of **5**.

Acknowledgments

We thank the French Ministry of Foreign Affairs (ECO-NET program no. 18824SD) and the Romanian Ministry of Education, Research and Youth (PNII TD-418, ET 49 and RIOSIN, CEEX Projects) for financial support.

---

[1] a) M. Regitz, O. J. Scherer (Eds.), *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, Thieme, Stuttgart, **1990** and references cited therein; b) K. B. Dillon, F. Mathey, J. F. Nixon, *Phosphorus: The Carbon Copy*, John Wiley & Sons, Chichester, **1998**, pp. 147–154; c) J. Escudié, H. Ranaivonjatovo, L. Rigon, *Chem. Rev.* **2000**, *100*, 3639–3696; d) J. Escudié, H. Ranaivonjatovo, *Organometallics* **2007**, *26*, 1542–1559.

[2] S. Ito, M. Yoshifuji, *Chem. Commun.* **2001**, 1208–1209.

[3] H. Liang, K. Nishide, S. Ito, M. Yoshifuji, *Tetrahedron Lett.* **2003**, *44*, 8297–8300.

[4] H. Liang, S. Ito, M. Yoshifuji, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1177–1180.

[5] H. Liang, S. Ito, M. Yoshifuji, *Org. Biomol. Chem.* **2003**, *1*, 3054–3058.

[6] S. Ito, K. Nishide, M. Yoshifuji, *Organometallics* **2006**, *25*, 1424–1430.

[7] S. Ito, H. Liang, M. Yoshifuji, *Chem. Commun.* **2003**, 398–399.

[8] H. Liang, S. Ito, M. Yoshifuji, *Org. Lett.* **2004**, *6*, 425–427.

[9] S. Ito, H. Liang, M. Yoshifuji, *J. Organomet. Chem.* **2005**, *690*, 2531–2535.

[10] K. Nishide, H. Liang, S. Ito, M. Yoshifuji, *J. Organomet. Chem.* **2005**, *690*, 4809–4815.

[11] a) S. J. Goede, F. Bickelhaupt, *Chem. Ber.* **1991**, *124*, 2677–2684; b) E. Niecke, M. Nieger, O. Schmidt, D. Goudat, W.-W. Schoeller, *J. Am. Chem. Soc.* **1999**, *121*, 519–522; c) M. Yoshifuji, S. Ito, *Top. Curr. Chem.* **2003**, *223*, 67–89.

[12] B. Hutchinson, K. Nakamoto, *Inorg. Chim. Acta* **1969**, *3*, 591–595.

[13] D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100.

[14] J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822–8824.

[15] ADF2008.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.

[16] a) M.-A. David, J. B. Alexander, D. S. Glueck, G. P. A. Yap, L. M. Liable-Sands, A. L. Rheingold, *Organometallics* **1997**, *16*, 378–383; b) M.-A. David, S. N. Paisner, D. S. Glueck, *Organometallics* **1995**, *14*, 17–19; c) C. A. Akpan, P. B. Hitchock, J. F. Nixon, M. Yoshifuji, T. Niitsu, N. Inamoto, *J. Organomet. Chem.* **1988**, *338*, C35–C37; d) M. Freytag, P. J. Dyson, L. Ernst, P. G. Jones, R. Schmutzler, *Inorg. Chem. Commun.* **2002**, *5*, 808–810; e) C.-H. Tsang, C. A. Rohrick, T. S. Saini, B. O. Patrick, D. P. Gates, *Organometallics* **2002**, *21*, 1008–1010; f) A. J. Termaten, T. Nijbacker, M. Schakel, M. Lutz, A. L. Spek, K. Lammertsma, *Chem. Eur. J.* **2003**, *9*, 2200–2208.

[17] a) M. Yoshifuji, T. Sato, N. Inamoto, *Chem. Lett.* **1988**, 1735–1738; b) M. E. García, V. Riera, M. A. Ruiz, D. Sáez, J. Vaissemann, J. C. Jeffery, *J. Am. Chem. Soc.* **2002**, *124*, 14304–14305; c) S. Shah, M. C. Simpson, R. C. Smith, J. D. Protasiewicz, *J. Am. Chem. Soc.* **2001**, *123*, 6925–6926; d) K. Tsuji, S. Sasaki, M. Yoshifuji, *Heteroat. Chem.* **1998**, *9*, 607–613.
[18] M. Winter, *WebElements, The Periodic Table on the Web*, http://www.webelements.com.
[19] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.
[20] G. M. Sheldrick, *SHELXL-97 Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, **1997**.

Received: October 21, 2008