656 *Organometallics* **2010,** *29,* 656–661
DOI: 10.1021/om9009334

ORGANOMETALLICS
Article

Partial Ring-Opening and Rearrangement Reactions of P,C-Cages to Yield Unusual Phosphinous Acids Stabilized by Pentacarbonyltungsten

Maren Bode,[†] Gregor Schnakenburg,[†] Jörg Daniels,[†] Angela Marinetti,[‡] and Rainer Streubel*,[†]

[†]*Institut für Anorganische Chemie, Gerhard-Domagk-Strasse 1, 53121 Bonn, Germany and* [‡]*Institut de Chimie des Substances Naturelles, 1 Avenue de la Terrasse, 91198 Gif-sûr-Yvette Cedex, France*

Received October 23, 2009

First reactions of polycyclic phosphirane complexes **3a**−**c** are reported that include lithium hydroxide induced partial ring-opening and rearrangement reactions to give new tricyclic phosphinous acid complexes **4**−**7** as final products. Besides multinuclear NMR and IR spectroscopy and mass spectrometry, the molecular structures of complexes **4**−**6** were established by single-crystal X-ray crystallography.

Introduction

Although phosphiranes have been known since 1963,[1] studies on their reactivity were comparatively rare until the early 1990s. Since then several synthetic applications were developed such as cationic ring-opening polymerization, providing access to new polymers containing trivalent phosphorus.[2] Furthermore, theoretical studies also revealed possible applicability in radical ring-opening polymerization.[3] Anionic ring-opening polymerization presents a more complicated overall picture,[4] as attack at the carbon center of the phosphirane unit appears to be feasible, although nucleophilic attack at phosphorus may effectively compete as indicated by the polarization of $P^{\delta+}-C^{\delta-}$ bonds.

The preferential nucleophilic attack at phosphorus has been demonstrated experimentally in reactions of phosphirane tungsten complexes **I** with nucleophiles, although divergent outcomes had been observed for these reactions.[5] Here, nucleophilic attack usually followed one of the two following reaction pathways, assuming that transient species **II** with a five-coordinated phosphorus center were involved: (1) loss of an alkene derivative and formation of phosphanide complexes **III** or (2) ring-opening of **II** to give carbanionic complexes **IV** (Scheme 1). In the latter case, the carbanionic center in **IV** then subsequently reacted with either a proton source or a CO group of the pentacarbonyltungsten fragment.[5]

All studies hitherto described were conducted using monocyclic phosphiranes, so that the quest is still open on how P,C-cage compounds having a phosphirane subunit would behave. Another special point of interest to study polycyclic phosphirane derivatives derives from their rigid geometry, chirality that might especially suit their uses as chiral auxiliaries, and small Tolman angles[6] of such ligands; in some cases a surprising chemical inertness of the phosphorus center, i.e., toward hydrolysis and oxidation, was observed.[7] Unfortunately, the synthesis of polycyclic phosphiranes usually requires complicated multistep reaction sequences, and therefore P,C-cage structures and substitution patterns are very much restricted. In consequence, and with some exceptions,[8,9] the knowledge about the chemistry of P,C-cage derivatives is comparatively scarce. Here, we present the synthesis of sterically encumbered tetracyclic P,C-cage ligands using an optimized protocol and first results of reactions of the phosphirane subunit with lithium hydroxide.

Experimental Results

Tetracyclic P,C-cage tungsten complexes **3a**−**c** were obtained via thermolysis of *P*-C_5Me_5-substituted 2*H*-azaphosphirene tungsten complex **1**[10] in toluene in the presence of alkynyl esters. ^{31}P NMR spectroscopic reaction monitoring revealed that the formation of the polycyclic phosphirane derivatives **3a**,[11]**b**,**c**[12] proceeded via intramolecular [4+2] cycloaddition reactions of transient 1*H*-phosphirene tungsten complexes **2a**−**c** (Scheme 2).

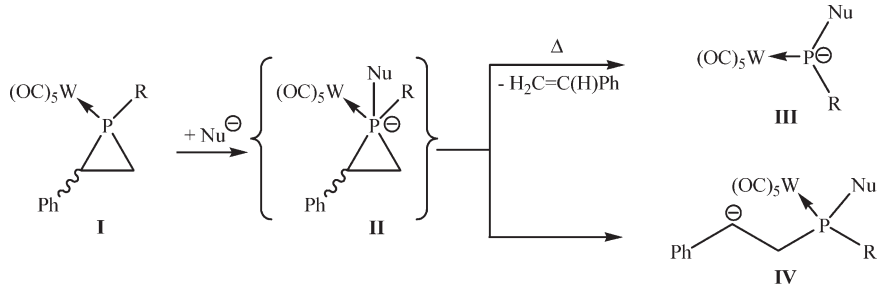
$^{31}P\{^1H\}$ NMR chemical shifts of the "*closed*" P,C-cage complexes **3a**−**c** are between −70 and −90 ppm and show a notable influence of the substituents at the α-carbon atoms. A typical feature of these complexes are the $^1J(W,P)$ coupling constant

*Corresponding author. E-mail: r.streubel@uni-bonn.de.

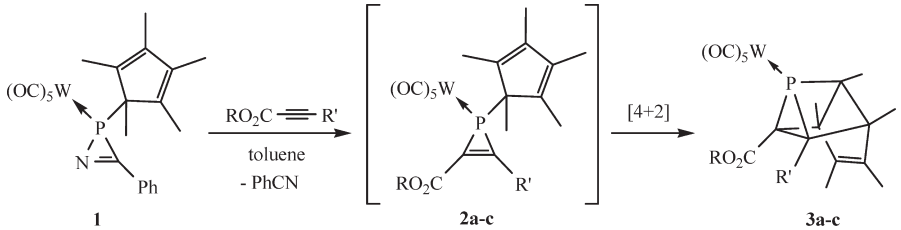
(1) Wagner, R. I. U.S. patents 3 086 053 and 3 086 056, **1963**. Wagner, R. I.; Freeman, L. D.; Goldwhite, H.; Rowsell, D. G. *J. Am. Chem. Soc.* **1967**, *89*, 1102.
(2) Kobayashi, S.; Kadokawa, J.-I. *Macromol. Rapid Commun.* **1994**, *15*, 567.
(3) Coote, M. L.; Hodgson, J. L. *Macromolecules* **2005**, *38*, 8902.
(4) Coote, M. L.; Hodgson, J. L.; Krenske, E. H.; Wild, S. B. *Heteroat. Chem.* **2007**, *18*, 118. Coote, M. L.; Krenske, E. H.; Maulana, I.; Steinbach, J.; Wild, S. B. *Heteroat. Chem.* **2008**, *19*, 178.
(5) Marinetti, A.; Mathey, F. *Tetrahedron* **1989**, *45*, 3061.
(6) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(7) Liedtke, J.; Loss, S.; Alcaraz, G.; Gramlich, V.; Grützmacher, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 1623.
(8) Hofmann, M.; Höhn, C.; Heinemann, F. W.; Zenneck, U. *Chem.—Eur. J.* **2009**, *15*, 5998.
(9) Panhans, J.; Heinemann, F. W.; Zenneck, U. *J. Organomet. Chem.* **2009**, *694*, 1223.
(10) Streubel, R.; Rhode, U.; Jeske, J.; Ruthe, F.; Jones, P. G. *Eur. J. Inorg. Chem.* **1998**, 2005.
(11) Streubel, R.; Bode, M.; Frantzius, G. v.; Hrib, C.; Jones, P. G.; Monsees, A. *Organometallics* **2007**, *26*, 1371.
(12) Rhode, U.; Ruthe, F.; Jones, P. G.; Streubel, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 215.

 Published on Web 01/07/2010

Scheme 1. Reactions of Phosphirane Complexes I with Nucleophiles[5]

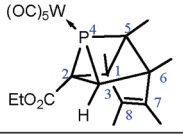
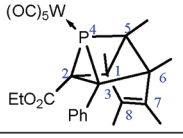
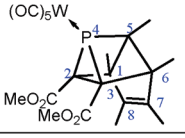


Scheme 2. Synthesis of P,C-Cage Complexes 3a,[11]**b,c**[12]



2,3a: R = Et, R' = H; **2,3b**: R = Et, R' = Ph; **2,3c**: R =Me, R' =CO_2Me

Table 1. Selected NMR Spectroscopic Data of P,C-Cage Complexes 3a,[11]**b,c**[12]

R/R'	Et / H	Et / Ph	Me / CO_2Me
	3a	**3b**	**3c**
			
δ ^{31}P{^{1}H} (|^1*J*(W,P)|)	-88.6 (231)	-76.9 (233)	-69.1 (241)
δ ^{1}H (|*J*(P,H)|)			
PC^3-H	2.82 (4.8)	---	---
PC^5-CH_3	0.21 (19.2)	0.64 (19.3)	0.56 (18.9)
δ ^{13}C{^{1}H} (|*J*(P,C)|)			
PC^3-R'	49.8 (9.6)	65.6 (8.4)	70.0 (5.7)
PC^5-CH_3	68.9 (33.0)	63.7(34.3)	66.1 (32.3)
δ in [ppm]; *J* in [Hz]; solvent: **3a**: toluene-d8; **3b,c**: $CDCl_3$			

magnitudes of about 230−241 Hz as well as comparatively large $|^1J(P,C)|$ values for C^5 centers (cf. Table 1).

X-ray crystallography (Figures 1, 2 and ref 12) revealed that the cage structure is not significantly influenced by the different substituents on the phosphirane ring, so that bond lengths and angles observed in the cage are identical within the margins of error; although some bonds in the more congested derivative **3b** appear to be marginally longer (**3b**: e.g., P−W: 2.464(1) Å; P−C4: 1.844(3) Å) than in **3a** (P−W: 2.455(2) Å; P−C4: 1.839(7) Å) or **3c** (P−W: 2.457(8) Å; P−C4: 1.836(3) Å). Typical structural features of these cage structures are small bond angle sums at phosphorus ($\sum\angle$ P(PR_3)) of 195° (**3a** and **3c**) or 196° (**3b**), thus yielding a strained, rigid cage that possesses a long P−C1 bond of 1.908(7) Å (**3a**), 1.916(3) Å (**3b**), or 1.924(3) (**3c**[12]); for comparison, typical P(III)−C^{sp3} bond lengths are around 1.855 Å.[13]

Reaction of the polycyclic phosphirane tungsten complex **3a**, bearing a proton and a *C*-ester group at the phosphirane ring-carbons, with lithium hydroxide and subsequent protonation gave the partially cage-opened complex **4** (Scheme 3, Figure 4). Reactions of complexes **3b,c** followed a more complicated course, selectively yielding **5** in the case of **3b** or a mixture of **6** and a not fully identified compound **7** (ratio: 1.3:1) in the case of **3c**; formation of **5** and **6** evidently involved rearrangement reactions. Complexes **5** and **6** were structurally confirmed by single-crystal X-ray structures (Figure 5 and 6), both revealing the P−OH function. On the basis of the NMR spectroscopic and mass spectrometric data we concluded that complex **7** is most probably an isomer of complex **6** possessing also a P−OH function (δ ^{1}H = 4.25 ($|J(P,H)|$ = 1.9 Hz)).

The formation of products **4**−**7** is remarkable, as only very few examples of cyclic diorganyl-phosphinous acid complexes can be found in the literature (Figure 3).[14−19] They are usually obtained by substitution at phosphorus[14,15] or hydrolysis of a

(13) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

(14) Borst, M. L. G.; Bulo, R. E.; Gibney, D. J.; Alem, Y.; de Kanter, F. J. J.; Ehlers, A. W.; Schakel, M.; Lutz, M.; Spek, A. L.; Lammertsma, K. *J. Am. Chem. Soc.* **2005**, *127*, 16985.

(15) Holand, S.; Mathey, F. *Organometallics* **1988**, *7*, 1796.

(16) Sierra, M. L.; Maigrot, N.; Charrier, C.; Ricard, L.; Mathey, F. *Organometallics* **1991**, *10*, 2835.

Scheme 3. Reactions of P,C-Cage Complexes 3a−c with Lithium Hydroxide

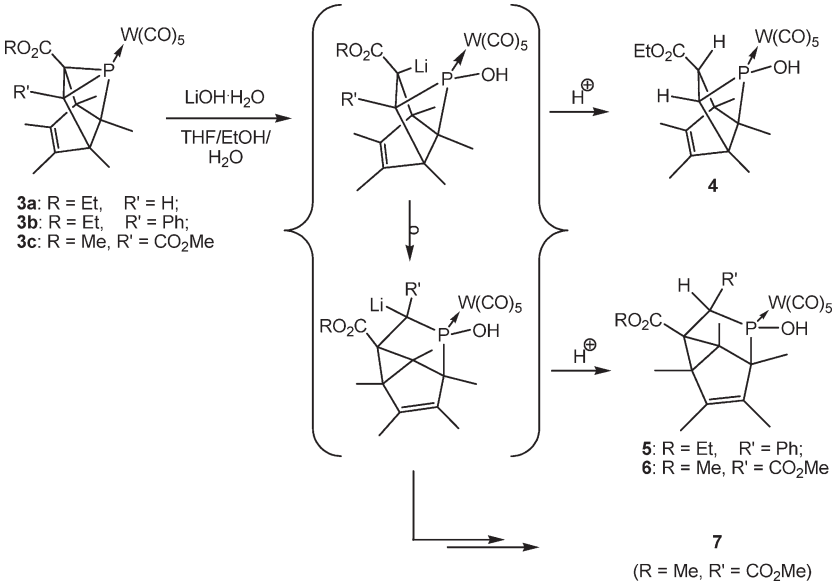
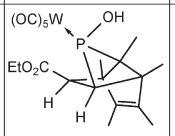
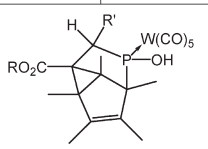


Table 2. Selected NMR Spectroscopic Data of P,C-Cage Complexes 4−6

R/R'	Et / H	Et / Ph	Me / CO_2Me
	4	**5**	**6**
			
δ $^{31}P\{^1H\}$ ($\|^1J(W,P)\|$)	140.2 (253)	182.1 (257)	174.6 (263)
δ ^1H ($\|J(P,H)\|$)			
PC-H	2.97 (4)	3.33 (16.3)	3.22 (15.0)
PC-CH_3	0.95 (13.4)	1.52 (18.5)	1.48 (20.0)
δ $^{13}C\{^1H\}$ ($\|J(P,C)\|$)			
PCH	52.1 (24.9)*	50.7 (32.2)	50.3 (23.9)
PC-CH_3	56.8 (17.8)	61.4 (19.2)	62.2 (23.6)
C-CO_2R	53.1 (12.3)†	37.8 (18.9)	36.3 (14.2)

δ in [ppm]; *J* in [Hz]; solvent: $CDCl_3$; *: R=H; †: C(H)CO_2Et

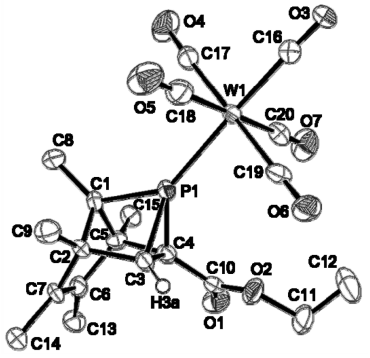


Figure 1. Molecular structure of one independent molecule of **3a**[11] in the crystal (thermal ellipsoids at 50% probability level; H atoms (except H3a) are omitted for clarity). As the values for the second independent molecule of the unit cell do not deviate significantly from the one displayed here, it is neither displayed nor discussed (see Supporting Information). Selected bond length [Å] and angles [deg]: P1−W1 2.455(2), P−C3 1.829(7), P−C4 1.839(7), P−C1 1.908(7), C3−C4 1.549(10), C3−P−C4 50.0 (3), $\sum\angle P(PR_3)$ 195 (±2)°.

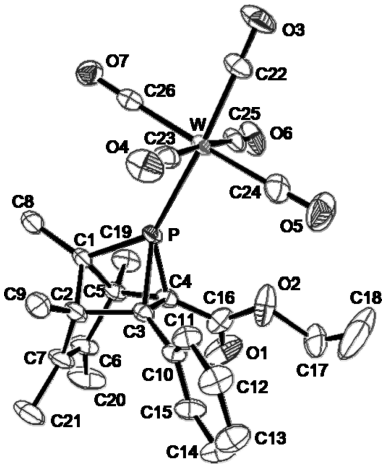


Figure 2. Molecular structure of **3b** in the crystal (thermal ellipsoids at 50% probability level; H atoms are omitted for clarity). Selected bond length [Å] and angles [deg]: P−W 2.464(8), P−C3 1.827(3), P−C4 1.844(3), P−C1 1.916(3), C3−C4 1.560(4), C3−P−C4 50.3 (1), $\sum\angle P(PR_3)$ 196 (±2)°.

double bond[16,17] often during column chromatography. Only in the case of phosphorine complex **13** did the P−OH function result from a planned nucleophilic attack of the hydroxide at phosphorus in the corresponding phosphinine complex. As non-ligated diorganylphosphinous acids (R_2POH) usually rearrange to the corresponding pentavalent secondary phosphine-oxides ($R_2P(O)H$),[20,21] most known diorganylphosphinous acids are stabilized by transition metal complexation, as first reported by Chatt in 1968.[22] It is noteworthy that due to the air- and moisture-

(17) Le Floch, P.; Carmichael, D.; Mathey, F. *Organometallics* **1991**, *10*, 2432.
(18) Le Floch, P.; Ricard, L.; Mathey, F. *Polyhedron* **1990**, *9*, 991.
(19) Alonso, M.; Alvarez, M. A.; Garcia, M. E.; Ruiz, M. A.; Hamidov, H.; Jeffery, J. C. *J. Am. Chem. Soc.* **2005**, *127*, 15012.
(20) Hoge, B.; Bader, J.; Beckers, H.; Kim, Y. S.; Eujen, R.; Willner, H.; Ignatiev, N. *Chem.—Eur. J.* **2009**, *15*, 3567.
(21) Some stabilization can be achieved by introduction of strongly electron-withdrawing groups such as CF_3; B. Hoge et al.[20] showed that in some cases $R^F{}_2POH$ are more stable than $R^F{}_2P(H)O$.
(22) Chatt, J.; Heaton, B. T. *J. Chem. Soc. A* **1968**, 2745.

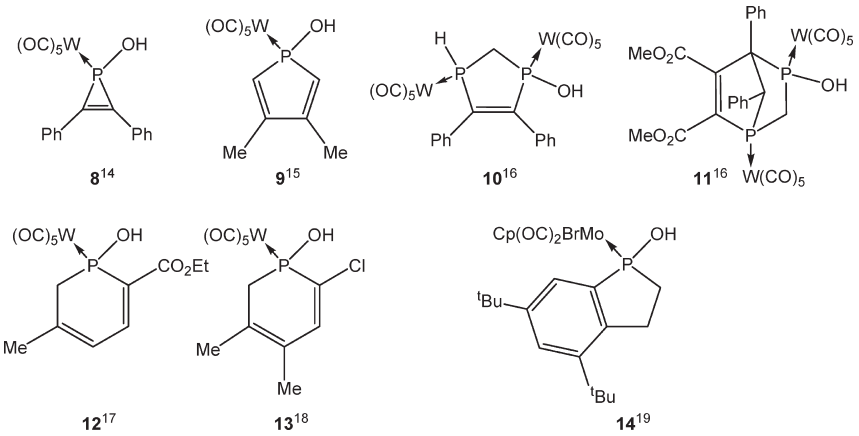


Figure 3. Examples of cyclic diorganylphosphinous acid complexes.[14−19]

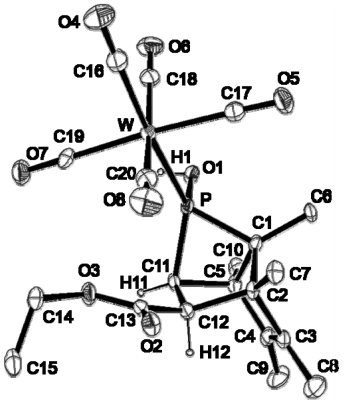


Figure 4. Molecular structure of **4** in the crystal (thermal ellipsoids at 50% probability level; H atoms (except H1, H11, and H12) are omitted for clarity). Selected bond length [Å] and angles [deg]: P−W 2.540 (1), P−O1 1.610 (4), P−C1 1.846 (5), P−C11 1.880 (5), C11−C12 1.530 (7), C1−P−C11 71.9 (2), $\sum\angle P(PR_3)$ 280(±2)°.

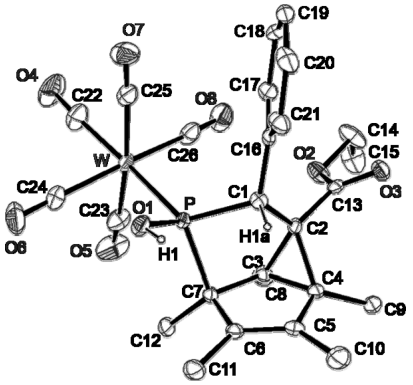


Figure 5. Molecular structure of **5** in the crystal (thermal ellipsoids at 50% probability level; H atoms (except H1 and H1a) are omitted for clarity). Selected bond length [Å] and angles [deg]: P−W 2.532 (1), P−O1 1.597 (2), P−C1 1.870 (3), P−C7 1.885 (3), C1−C2 1.533(4), C1−P−C7 90.0 (1), $\sum\angle P(PR_3)$ 306(±2)°.

stability of the preligands, phosphinous acid complexes have found applications in transition-metal-catalyzed transformations,[23] hinting also at potentially interesting uses of ligands **4**−**7**.

(23) Ackermann, L. *Synthesis* **2006**, *10*, 1557.

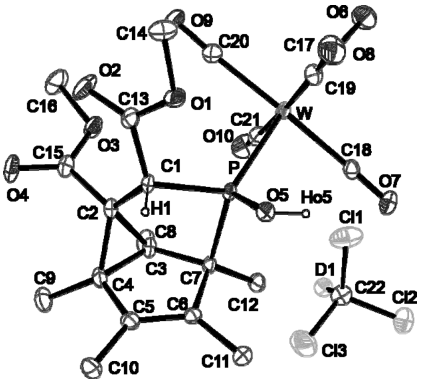


Figure 6. Molecular structure of **6**·$CDCl_3$ in the crystal (thermal ellipsoids at 50% probability level; H atoms (except H1 and Ho5) are omitted for clarity). Selected bond length [Å] and angles [deg]: P−W 2.497 (1), P−O5 1.616 (2), P−C1 1.854 (2), P−C7 1.873 (2), C1−C2 1.524(3), C1−P−C7 90.4 (1), $\sum\angle P(PR_3)$ 296(±2)°.

The products **4**−**7** display considerably downfield shifted $^{31}P\{^1H\}$ resonances, thus reflecting the conversion of a three- into a four- (**4**) or five-membered phosphorus heterocycle (**5**, **6**) and the presence of a P−OH group. This is accompanied by an increase of the $^1J(W,P)$ coupling constant magnitude (253−273 Hz) and a decrease of $|^1J(P,C)|$ values, as in complex **4**, which displays a $^1J(P,C^5) = 17.8$, vs 33 Hz in **3a**.

As expected the *partially opened* and rearranged polycyclic ligands in **4**−**6** (Figures 4−6) have notably larger $\sum\angle P(PR_3)$ values, especially the *C*-phenyl-substituted derivative **5** (306° compared to 196° in the *closed cage* complex **3b**). Striking is that significantly longer W−P bonds were observed (2.532(1) Å in **5** vs 2.464(8) Å in **3b**), although bonding of phosphorus to the OH group usually shortens all and every other bond (to phosphorus). Compared to the only other structurally characterized cyclic diorganylphosphinous acid, **14**[19] (Figure 3), complexes **4**−**6** exhibit comparable P−O bond lengths around 1.61 Å and slightly longer P−C bond lengths (1.84 Å (**14**) and 1.85−1.89 Å in **4**−**6**) most probably due to the different ring systems and substitution patterns involved.

Conclusions

First investigations on the reactivity of various polycyclic phosphirane complexes toward lithium hydroxide showed partial ring-opening and formation of new cyclic phosphinous acid complexes. Here a significant

dependence of the reaction pathway on the substitution pattern was observed, as either cleavage of the P−C bond or isomerization leading to complexes with semibullvalene-type structures **5** (reaction of **3b**) and **6** (reaction of **3c**) was observed. Nucleophilic attack of the hydroxide at the phosphorus atom can be assumed as the first step followed by the cleavage of one of the phosphirane P−C bonds. The quest for nucleophilic bond cleavage of nonligated polycyclic phosphiranes remains open for future investigations.

Experimental Section

General Procedures. All operations were performed in an atmosphere of purified and dried argon. Solvents were distilled from sodium. NMR data were recorded on a Bruker Avance 300 spectrometer at 30 °C using $CDCl_3$ as solvent and internal standard; shifts are given relative to tetramethylsilane (^{1}H: 300.1 MHz; ^{13}C: 75.5 MHz) and 85% H_3PO_4 (^{31}P: 121.5 MHz) in ppm. Mass spectra were recorded on a Kratos MS 50 spectrometer (EI, 70 eV); only *m*/*z* values are given. Elemental analyses were performed using an Elementa (Vario EL) analytical gas chromatograph. Infrared spectra were collected on a Nicolet 380 FT-IR. Melting points were obtained on a Büchi 535 capillary apparatus. X-ray crystallographic analysis of **3a**,**b**, **4**−**6**: Data were collected on a Nonius KappaCCD diffractometer at 123 K using Mo Kα radiation (λ = 0.71073 Å). The structure was refined by full-matrix least-squares on F^2 (SHELXL-97[24]). All non-hydrogens were refined anisotropically. The hydrogen atoms were included in calculated positions using a riding model.

X-ray Crystallographic Analysis of 3a. Suitable pale yellow single crystals were obtained from concentrated *n*-pentane solutions upon cooling to 4 °C; $C_{20}H_{21}O_7PW$; crystal size 0.32 × 0.32 × 0.16 mm^3, triclinic, $P\bar{1}$, a = 10.7147(5) Å, b = 13.2996(5) Å, c = 16.8471(5) Å, α = 75.655(2)°, β = 83.494(2)°, γ = 70.934(2)°, V = 2196.92(15) Å^3, Z = 4, $2\theta_{max}$ = 56°, collected (independent) reflections = 27 583 (10 518), R_{int} = 0.1322, μ = 5.368 mm^{-1}, 536 refined parameters, R_1 (for $I > 2\sigma(I)$) = 0.0528, wR_2 (for all data) = 0.1282, max./min. residual electron density = 2.707/−3.634 e Å^3.

Synthesis of {Pentacarbonyl[1,5,6,7,8-pentamethyl-2-(ethoxycarbonyl)-3-phenyl-4-phosphatetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct-7-en-κ*P*]tungsten(0)} (3b). A 0.17 mL (1.0 mmol) amount of ethyl phenylpropiolate was dissolved in 13 mL of toluene and heated to 90 °C. Then a solution of 0.50 g (0.84 mmol) of **1** in 62 mL of toluene was slowly (ca. 10−20 min) added using a dropping funnel and reflux condenser. The reaction mixture was stirred at 90 °C for another 30 min, and then the solvent was evaporated and the solid was purified by low-temperature column chromatography to deliver a yellow solid, mp 104 °C. Yield: 137 mg (25.0%). Selected data for **3b**: ^{1}H NMR: δ 0.64 (d, J(P,H) = 19.3 Hz, 3H, C^{cage}-C^5-CH$_3$), 0.67 (t, J(H,H) = 7.1 Hz, 3H, CH_2CH_3), 1.36 (s, 3H, C^{cage}-CH$_3$), 1.56 (s, 3H, C^{cage}-CH$_3$), 1.65 (s, 3H, C^{cage}-CH$_3$), 1.94 (s, 3H, C^{cage}-CH$_3$), 3.71−3.91 (m$_c$, (J(H,H) = 7.1 Hz(q)), 2H, OCH_2), 7.10−7.14 (m$_c$, 2H, Ph), 7.27−7.32 (m$_c$, 3H, Ph). ^{13}C{^{1}H} NMR: δ 4.8 (d, J(P,C) = 5.8 Hz, C^{cage}-CH$_3$), 10.9 (s, C^{cage}-CH$_3$), 11.1 (s, C^{cage}-CH$_3$), 12.0 (d, J(P,C) = 2.3 Hz, C^{cage}-CH$_3$), 12.5 (s, CH_2CH_3), 13.1 (d, J(P,C) = 3.6 Hz, C^{cage}-CH$_3$), 52.6 (d, J(P,C) = 6.8 Hz, C^{cage}), 59.0 (s, OCH_2), 63.7 (d, J(P,C) = 34.3 Hz, C^{cage}), 65.5 (d, J(P,C) = 8.4 Hz, C^{cage}), 67.6 (d, J(P,C) = 4.8 Hz, C^{cage}), 72.1 (d, J(P,C) = 5.2 Hz, C^{cage}), 126.9 (s, Ph), 127.2 (s, Ph (2x)),128.3 (d, J(P,C) = 7.1 Hz, Ph (2x)), 131.9 (s, Ph), 138.8 (d, J(P,C) = 12.6 Hz, C^{cage}), 142.0 (d, J(P,C) = 10.0 Hz, C^{cage}), 168.7 (s, CO_2), 192.9 (d$_{Sat}$, J(P,C) = 7.8 Hz, ^1J(W,C) = 125.1 Hz, *cis*-CO), 196.6 (d, J(P,C) = 33.3 Hz, *trans*-CO). ^{31}P NMR: δ −76.9 (q$_{Sat}$, ^1J(W,P) = 232.7 Hz, ^3J(P,H) = 19 Hz). MS (EI, 70 eV): *m*/*z* 664 [M$^{\bullet+}$, 73]. FTIR (KBr; ν(CO)): $\tilde{\nu}$ 2077 (m), 1998 (m), 1956 (s, shoulder), 1939 (s), 1927(s), 1920 (s, shoulder), 1712 (m) [cm^{-1}]. Anal. Calcd: C 47.01, H 3.79. Exptl: C 46.92, H 4.08. X-ray crystallographic analysis: Suitable colorless single crystals were obtained from concentrated *n*-pentane solutions upon cooling to 4 °C; $C_{26}H_{25}O_7PW$; crystal size 0.56 × 0.32 × 0.16 mm^3, monoclinic, $C2/c$, a = 32.9185(12) Å, b = 8.9633(2) Å, c = 20.9422(8) Å, α = 90°, β = 120.6280(13)°, γ = 90°, V = 5317.1(3) Å^3, Z = 8, $2\theta_{max}$ = 58°, collected (independent) reflections = 22 141 (6972), R_{int} = 0.0545, μ = 4.446 mm^{-1}, 6 restraints, 331 refined parameters, R_1 (for $I > 2\sigma(I)$) = 0.0296, wR_2 (for all data) = 0.0657, max./min. residual electron density = 1.681/−2.143 e Å^3.

Reaction of 3a−c. To a solution of 4-phosphatetracyclo-[3.3.0.0^{2,4}.0^{3,6}]oct-7-ene complex (**3a**−**c**) in THF was added absolute ethanol, and the reaction mixture was cooled to 0 °C. Then a solution of lithium hydroxide monohydrate in distilled water was added dropwise. The reaction mixture was stirred at 0 °C for 3 h and then at rt for another 12 h. Using a 1 M solution of potassium hydrogensulfate the mixture was brought to pH 3, and then THF was removed in vacuo. The reaction mixtures were extracted with ethyl acetate (2×) and dichloromethane. The joined organic phases were washed with brine and then dried using magnesium sulfate. The solvents were evaporated, and the raw products were obtained as yellow paste-like residues, which were washed with *n*-pentane (**4**, **5**) or purified by low-temperature column chromatography (**6**/**7**).

4: white solid, mp 115 °C. Yield: 132 mg (46.0%). Selected data: ^{1}H NMR: 0.95 (d, J(P,H) = 13.4 Hz, 3H, C^{cage}-C^5-CH$_3$), 1.26 (t, J(H,H) = 7.1 Hz, 3H, CH_2CH_3), 1.44 (s, 3H, C^{cage}-CH$_3$), 1.51 (s, 3H, C^{cage}-CH$_3$), 1.74 (d, J(P,H) = 1.2 Hz, 3H, C^{cage}-CH$_3$), 1.78 (m, 3H, C^{cage}-CH$_3$), 2.14 (dd, J(P,H) = 43.3 Hz, J(H,H) = 4.4 Hz, 1H, PCH), 2.41 (br s, 1H, OH), 2.97 (ps. "t"(= dd), $J \approx$ 4 Hz), J(H,H) = 4.4 Hz, 1H, PCH-C(H)CO_2Et), 4.20 (dq, J(H,H) = 11.1 Hz, J(H,H) = 7.2 Hz, 2H, OCH_2). ^{13}C{^{1}H} NMR: δ 4.8 (d, J(P,C) = 2.9 Hz, C^{cage}-CH$_3$), 8.9 (d, J(P,C) = 1.6 Hz, C^{cage}-CH$_3$), 10.7 (s, C^{cage}-CH$_3$), 11.7 (d, J(P,C) = 1.0 Hz, C^{cage}-CH$_3$), 12.9 (s, CH_2CH_3), 14.7 (d, J(P,C) = 0.6 Hz, C^{cage}-CH$_3$), 52.1 (d, J(P,C) = 24.9 Hz, C^{cage}-C^3), 53.1 (d, J(P,C) = 12.3 Hz, C^{cage}-C^2), 56.8 (d, J(P,C) = 17.8 Hz, C^{cage}-C^5), 59.9 (s, Et-CH_2), 67.4 (d, J(P,C) = 11.6 Hz, C^{cage}-C$^{1/6}$), 71.3 (d, J(P,C) = 25.5 Hz, C^{cage}-C$^{1/6}$), 133.0 (d, J(P,C) = 10.0 Hz, C^{cage}-C$^{7/8}$), 149.5 (d, J(P,C) = 6.5 Hz, C^{cage}(C$^{7/8}$), 169.3 (d, J(P,C) = 6.5 Hz, CO_2Et), 195.8 (d, J(P,C) = 7.4 Hz, *cis*-CO), 197.3 (d, J(P,C) = 28.4 Hz, *trans*-CO). ^{31}P NMR: δ −140.2 (dq$_{Sat}$, ^1J(W,P) = 253.0 Hz, ^1J(P,H) = 43.2 Hz (d), J(P,H) = 13.4 Hz (q)). MS (EI, 70 eV): *m*/*z* 606 [M$^{\bullet+}$, 29]. FTIR (KBr): $\tilde{\nu}$ 3263 (w, OH), 2974 (w, OH), 2938 (w, OH), 2070 (s, CO), 1982 (s, CO), 1964 (s, CO), 1936 (s, CO), 1918 (s, shoulder, CO), 1695 (s, CO) [cm^{-1}]. Anal. Calcd: C 39.63, H 3.82. Exptl: C 39.63, H 4.05. X-ray crystallographic analysis: Suitable pale yellow single crystals were obtained from concentrated diethyl ether solutions upon cooling to 4 °C; $C_{20}H_{23}O_8PW$; crystal size 0.20 × 0.10 × 0.08 mm^3, monoclinic, $P2_1/n$, a = 11.4434(3) Å, b = 14.0714(5) Å, c = 14.2623(5) Å, α = 90°, β = 101.036(2)°, γ = 90°, V = 2254.11(13) Å^3, Z = 4, $2\theta_{max}$ = 55°, collected (independent) reflections = 16 661 (5028), R_{int} = 0.0788, μ = 5.237 mm^{-1}, 272 refined parameters, R_1 (for $I > 2\sigma(I)$) = 0.0385, wR_2 (for all data) = 0.0960, max./min. residual electron density = 3.231/−3.120 e Å^3.

5: white solid. Yield: 34 mg (41.5%). Selected data: ^{1}H NMR: 0.96 (t, J(H,H) = 7.1 Hz, 3H, Et-CH$_3$), 1.19 (s, 3H, C^{cage}-CH$_3$), 1.43 (s, 3H, C^{cage}-CH$_3$), 1.52 (d, J(P,H) = 18.5 Hz, 3H, C^{cage}-C^5-CH$_3$), 1.82 (s, 6H, C^{cage}-CH$_3$), 2.48 (br s, 1H, OH), 3.33 (d, J(P,H) = 16.3 Hz, 1H, PC-CH), 3.77−4.08 (m$_c$, 2H, OCH_2), 7.30 (s, 5H, Ph). ^{13}C{^{1}H} NMR: 10.4 (d, J(P,C) = 1.3 Hz, C^{cage}-CH$_3$), 11.0 (d, J(P,C) = 1.9 Hz, C^{cage}-CH$_3$), 11.1 (d, J(P,C) = 7.6 Hz, C^{cage}-CH$_3$), 11.4 (d, J(P,C) = 0.6 Hz, C^{cage}-CH$_3$), 12.8 (s, Et-CH$_3$), 15.5 (d, J(P,C) = 14.5 Hz, C^{cage}-CH$_3$), 37.8 (d, J(P,C) = 18.9 Hz, C^{cage}), 43.8 (d, J(P,C) = 27.0 Hz, C^{cage}), 46.9 (d, J(P,C) = 9.2 Hz, C^{cage}), 50.7 (d, J(P,C) = 32.2 Hz, C^{cage}), 59.4

(24) Sheldrick, G. M. *SHELXL-97*; Universität Göttingen, **1997**.

Table 3. Reaction Conditions for the Synthesis of 4−7

3	R	R′	**3**: *m* [mg] (*n* [mmol])	LiOH: *m* [mg] *n* [mmol]	THF: *V* [mL]	EtOH: *V* [mL]	H_2O: *V* [mL]
a	Et	H	276 (0.47)	100 (2.40)	6	2	1.5
b	Et	Ph	78 (0.12)	25 (0.60)	1.5	0.5	0.4
c	Me	CO_2Me	594 (0.94)	200 (4.80)	12	4	3

(s, Et-CH_2), 61.4 (d, J(P,C) = 19.2 Hz, C^{cage}), 126.1 (d, J(P,C) = 3.2 Hz, Ph), 127.3 (d, J(P,C) = 2.7 Hz, Ph (2×)), 128.9 (d, J(P,C) = 5.0 Hz, Ph (2x)), 131.5 (d, J(P,C) = 5.3 Hz, Ph), 135.5 (d, J(P,C) = 1.8 Hz, C^{cage}), 136.9 (d, J(P,C) = 7.3 Hz, C^{cage}), 168.4 (s, CO_2Et), 195.1 (d, J(P,C) = 7.3 Hz, *cis*-CO), 196.8 (d, J(P, C) = 27.2 Hz, *trans*-CO). ^{31}P NMR: δ 182.1 ((pseudo) $quint_{Sat}$, ^1J(W,P) = 258 Hz, $J \approx 17$ Hz (ps. quint)). MS (EI, 70 eV): m/z 682 [$M^{\bullet+}$, 34]. FTIR (KBr): $\tilde{\nu}$ 3168 (w, OH), 2964 (w, OH), 2071 (w, CO), 1990 (w, CO), 1981 (w, CO), 1946 (s, CO), 1927 (s, CO), 1915(s, CO), 1680 (w, CO) [cm^{-1}]. Anal. calcd: C 45.77, H 3.99. Exptl: C 45.52, H 4.02. X-ray crystallographic analysis: Suitable pale yellow single crystals were obtained from concentrated diethyl ether solutions upon cooling to 4 °C; $C_{26}H_{27}O_8PW$; crystal size 0.30 × 0.30 × 0.10 mm^3, orthorhombic, $P2_12_12_1$, a = 10.2703(2) Å, b = 11.9683(2) Å, c = 21.9000(6) Å, α = 90°, β = 90°, γ = 90°, V = 2691.91(10) $Å^3$, Z = 4, $2\theta_{max}$ = 56°, collected (independent) reflections = 20 427 (6421), R_{int} = 0.0425, μ = 4.396 mm^{-1}, 332 refined parameters, R_1 (for $I > 2\sigma(I)$) = 0.0245, wR_2 (for all data) = 0.0580, max./min. residual electron density = 1.506/−1.372 e $Å^3$.

6: white solid, mp 171 °C. Yield: 181 mg (29.7%). Selected data: ^{1}H NMR: δ 1.18 (s, 3H, C^{cage}-CH_3), 1.28 (d, J(P,H) = 0.6 Hz, 3H, C^{cage}-CH_3), 1.45 (d, J(P,H) = 20.2 Hz, 3H, C^{cage}-CH_3), 1.72−1.76 (m_c, 6H, C^{cage}-CH_3), 3.20 (d, J(P,H) = 14.9 Hz, 1H, C^{cage}-H), 3.67 (s, 3H, OCH_3), 3.76 (d, J(P,H) = 0.5 Hz, 3H, OCH_3) (OH not detected). $^{13}C\{^1H\}$ NMR: δ 10.0 (d, J(P,C) = 1.3 Hz, C^{cage}-CH_3), 10.9 (d, J(P,C) = 7.1 Hz, C^{cage}-CH_3), 11.0 (d, J(P,C) = 1.9 Hz, C^{cage}-CH_3), 11.3 (s, C^{cage}-CH_3), 14.8 (d, J(P,C) = 16.5 Hz, C^{cage}-CH_3), 36.3 (d, J(P,C) = 14.2 Hz, C^{cage}), 42.9 (d, J(P,C) = 24.2 Hz, C^{cage}), 46.4 (d, J(P,C) = 7.4 Hz, C^{cage}), 50.3 (d, J(P,C) = 23.9 Hz, CH^{cage}), 50.6 (s, OCH_3), 51.5 (s, OCH_3), 62.0 (d, J(P,C) = 23.6 Hz, C^{cage}), 132.6 (d, J(P,C) = 5.8 Hz, C^{cage}), 136.6 (d, J(P,C) = 7.8 Hz, C^{cage}), 167.7 (d, J(P,C) = 1.6 Hz, CO_2), 169.3 (d, J(P,C) = 4.8 Hz, CO_2), 194.7 (d_{Sat}, J(P, C) = 7.4 Hz, ^1J(W,C) = 125.3 Hz, *cis*-CO), 196.4 (d, J(P,C) = 28.1 Hz, *trans*-CO). ^{31}P NMR: δ 174.6 ((pseudo) $quint_{Sat}$, ^1J(W,P) = 264.6 Hz, J_{PH} = 19.1 Hz (pseudo quint)). MS (EI, 70 eV): m/z 650 [$M^{\bullet+}$, 40]. FTIR (KBr): $\tilde{\nu}$ 3407 (w, OH), 2962 (w, OH), 2078 (s, CO), 1998 (m, CO), 1962 (s, shoulder, CO), 1922 (s, CO), 1712 (s, CO) [cm^{-1}]. Anal. Calcd: C 38.79, H 3.57. Exptl: C 39.15, H 3.91. X-ray crystallographic analysis: Suitable pale yellow single crystals were obtained from a concentrated chloroform-d_1 solution upon cooling to 4 °C; $C_{21}H_{23}O_{10}PW \cdot CDCl_3$; crystal size 0.62 × 0.23 × 0.17 mm^3, monoclinic, $P2_1/n$, a = 12.0292(4) Å, b = 18.2659(6) Å, c = 12.7250(3) Å, α = 90°, β = 98.664(2)°, γ = 90°, V = 2764.08(14) $Å^3$, Z = 4, $2\theta_{max}$ = 55°, collected (independent) reflections = 18 933 (5992), R_{int} = 0.0341, μ = 4.578 mm^{-1}, 425 refined parameters, R_1 (for $I > 2\sigma(I)$) = 0.0194, wR_2 (for all data) = 0.0429, max./min. residual electron density = 0.574/−0.843 e $Å^3$.

7: white solid, mp 132 °C. Yield: 35 mg (5.8%). Selected data: ^{1}H NMR: 1.42 (s, 6H, C^{cage}-CH_3), 1.47 (d, J(P,H) = 19.0 Hz, 3H, C^{cage}-C^1-CH_3), 1.55 (dq, J(P,H) = 3.5 Hz, J(H,H) = 1.1 Hz, 3H, C^{cage}-CH_3), 1.60 (dq, J(P,H) = 1.8 Hz, J(H,H) = 1.1 Hz, 3H, C^{cage}-CH_3), 3.72 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 4.25 (d, J(P,H) = 1.9 Hz, 1H, OH), 8.03 (d, J(P,H) = 12.4 Hz, 1H, C^{cage}-H). $^{13}C\{^1H\}$ NMR: δ 8.2 (s, C^{cage}-CH_3), 9.4 (d, J(P,C) = 5.5 Hz, C^{cage}-CH_3), 11.1 (s, C^{cage}-CH_3), 11.2 (d, J(P,C) = 2.3 Hz, C^{cage}-CH_3), 14.5 (d, J(P,C) = 15.8 Hz, C^{cage}-CH_3), 39.9 (d, J(P, C) = 12.0 Hz, C^{cage}), 42.2 (d, J(P,C) = 29.7 Hz, CH^{cage}), 49.1 (d, J(P,C) = 20.4 Hz, C^{cage}), 50.5 (d, J(P,C) = 4.5 Hz, C^{cage}), 51.3 (s, OCH_3), 51.7 (s, OCH_3), 63.2 (d, J(P,C) = 14.5 Hz, C^{cage}), 134.6 (d, J(P,C) = 5.8 Hz, C^{cage}), 139.1 (d, J(P,C) = 7.4 Hz, C^{cage}), 168.4 (d, J(P,C) = 2.9 Hz, CO_2Me), 176.2 (d, J(P,C) = 5.2 Hz, CO_2Me), 195.3 (d, J(P,C) = 7.8 Hz, ^1J(W,C) = 125.3 Hz, *cis*-CO), 197.2 (d, J(P,C) = 28.1 Hz, *trans*-CO). ^{31}P NMR: δ 155.7 (ps. $quint_{Sat}$, ^1J(W,P) = 273.4 Hz, J(P,H) = 15.8 Hz). MS (EI, 70 eV): m/z 650 [$M^{\bullet+}$, 36]. FTIR (KBr): $\tilde{\nu}$ 3411 (w, OH), 2962 (w, OH), 2071 (m, CO), 1979 (m, CO), 1957 (m, CO), 1942 (s, CO), 1935 (s, CO), 1914 (s, CO), 1894 (m, shoulder, CO), 1712 (s, CO) [cm^{-1}]. Anal. Calcd: C 38.79, H 3.57. Exptl: C 37.94, H 4.69.

Acknowledgment. We thank the University of Bonn, the ICSN/Institut de Chimie des Substances Naturelles (CNRS), and the COST action CM0802 "PhoSciNet" for financial support.

Supporting Information Available: CIF files giving X-ray crystallographic data for **3a**, **3b**, and **4**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data of **3a**, **3b**, and **4**−**6** have also been deposited at the Cambridge Crystallographic Data Centre under the numbers CCDC-751252 (**3a**), CCDC-751253 (**3b**), CCDC-751254 (**4**), CCDC-751255 (**5**), and CCDC-751256 (**6**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.