(η^8-Cyclooctatetraene)(η^4-1,2- and -1,3-diphosphacyclobutadiene)titanium: Preparation, Structure, and Reactivity

Paul Binger*, Gerald Glaser, Stefan Albus, and Carl Krüger

Max-Planck-Institut für Kohlenforschung,
Kaiser-Wilhelm-Platz 1, D-45470 Mülheim a. d. Ruhr, Germany

Received August 1, 1995

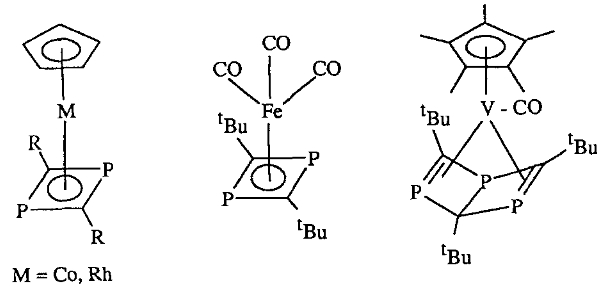
Key Words: (Cyclooctatetraene)titanium complexes / Diphosphacyclobutadiene / Cyclodimerization / Phosphaalkyne

The synthesis of the (η^8-cyclooctatetraene)(η^4-1,3- and -1,2-diphosphacyclobutadiene)titanium complexes **3a–c** and **4a, b** by cyclodimerization of the phosphaalkynes **2a–c** [**a**: R = *t*Bu, **b**: R = adamantyl (ad), and **c**: R = (*i*Pr)(Me_3Si)N] in the coordination sphere of the (η^8-cyclooctatetraene)titanium complex **1** is described. The molecular structures of **3a–c** and **4a, b** were determined by spectroscopic methods (^{31}P, ^{1}H, and ^{13}C NMR). In the case of **3a** and **4a**, X-ray analyses were carried out. The increased reactivity of **4a** compared to **3a** was utilized to separate **3a** from **4a**. Displacement of the 1,2-diphosphete (isolated as its cyclodimer **5**) from **3b** was achieved by reaction with hexachlorethane.

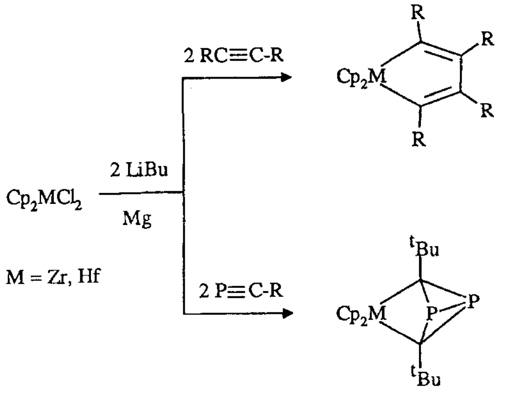
Recently, we reported on a high-yield synthesis of an (η^8-cyclooctatetraene)(η^4-1,3,5,7-tetraphosphabarrelene)zirconium derivative by cyclotetramerization of the phosphaalkyne **2a** in the coordination sphere of bis(cyclooctatetraene)zirconium[1]. Since this behavior of **2a** differs considerably from that found in the reaction of zirconocene derivatives with **2a**, which leads to the formation of (1,3-diphosphabicyclo[1.1.0]butanediyl)zirconocene[2], we studied the reactivity of phosphaalkynes toward other bis(cyclooctatetraene) complexes of the group-4 metals. The results obtained by the use of bis(cyclooctatetraene)titanium (**1**) are presented in this paper.

It is well documented that the reactivity of phosphaalkynes **2** toward transition metal complexes is similar to that of alkynes. This indicates that reactions of both types of compounds are characterized by a side-on coordination to the metal[3]. Differences exist in the products, since in cycloaddition reactions of alkynes at a late transition metal center benzene derivatives or cyclooctatetraenes are formed catalytically[4], whereas with phosphaalkynes η^4-1,3-diphosphacyclobutadiene complexes are the most typical products obtained by a stoichiometric [2 + 2] cycloaddition[5–7], a cyclotrimerization representing an exception[8,9]. Some representative examples are shown in Scheme 1.

Scheme 1. Representative examples of transition metal complexes with cyclooligomers of **2a**



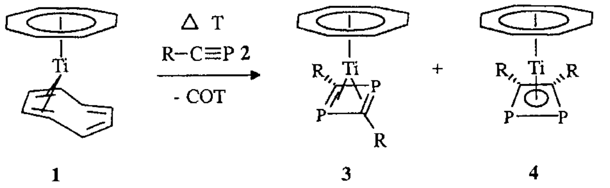
Interestingly, both alkynes[11] and phosphaalkynes[2] dimerize stoichiometrically with metallocenes of Zr or Hf to give metallacyclopentadienes and the above-mentioned tricyclic metal compounds, respectively.



(1)

The reaction of bis(cyclooctatetraene)titanium (**1**) with the phosphaalkynes **2a–c** proceeds slowly. After heating for few days at 80–85 °C replacement of the η^4-bonded cyclooctatetraene of **1** by two equivalents of **2a** or **2b** was complete. In contrast to the zirconium analog of **1**, which reacts with **2a** by cyclotetramerization[1], the reaction of **1** with **2a** or **2b** affords in a clean [2 + 2] cycloaddition η^4-bonded diphosphacyclobutadiene (diphosphete) in more than 60% yield. However, these cycloadditions are not regioselective as observed with appropriate late metal complexes[3,5], since (η^8-cyclooctatetraene)titanium complexes of 1,3-diphosphete (**3a, b**) and 1,2-diphosphete (**4a, b**) were obtained in nearly equal amounts. This is the first time that a 1,2-diphosphete formation was observed by a [2 + 2] cycloaddition of two molecules of a phosphaalkyne in the coordination sphere of a transition metal complex.

The phosphaalkyne **2c** is much less reactive than **2a** and **b**. The titanium complex **3c** was formed regioselectively as the only product in 64% yield by heating of a toluene solution of **1** and **2c** in an autoclave for two weeks at 140 °C.



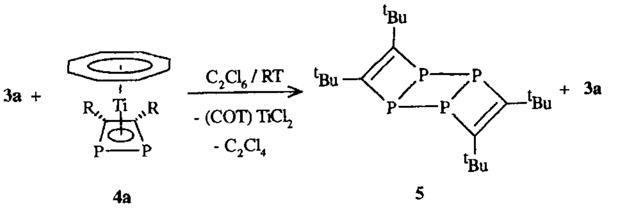
(2)

2, 3, 4		yield	3 : 4
a	^{t}Bu	62%	11 : 9
b	Ad.	60%	3 : 2
c	(TMS)(iPr)N	64%	100 : 0

The new complexes were isolated as dark green air-sensitive crystals (**3a**, **4a**) or as green (**3b**, **4b**) and violet (**3c**) powders. Whereas **3a**, and **4a** are soluble in most organic solvents, **3b**, **4b**, and **3c** are only slightly soluble in these solvents, so that their ^{13}C-NMR spectra could not be recorded.

For an unambiguous structure determination of **3** and **4** it was necessary to separate **3a**, **b** from **4a**, **b**. After all attempts had failed to isolate pure isomers by fractional crystallization or by chromatographic methods, we achieved a purification of **3a** from the 11:9 mixture of **3a**/**4a** by a chemical method.

In a mixture of **3a**/**4a**, only **4a** reacts with hexachloroethane at room temperature in a redox process yielding (cot)TiCl$_2$, tetrachloroethene, and the free 1,2-diphosphete ligand which was isolated as its [4 + 2] cycloadduct **5** (eq. 3). After stirring for five days the resulting mixture of **3a**, **5**, tetrachloroethene, and (cot)TiCl$_2$ could be separated by fractional crystallization. It is reasonable to assume that 3,4-di-*tert*-butyl-1,2-diphosphete is an intermediate in the formation of **5**, which immediately dimerizes in a [4 + 2] cycloaddition reaction. Compound **5** was prepared recently by reaction of 1,2-dihydro-1,2-diiodo-1,2-diphosphete with (ethene)bis(triphenylphosphane)platinum and by transformation of bis(η^5-cyclopentadienyl)(1,3-diphosphabicyclo[1.1.0]butanediyl)zirconium into **5** by transmetalation with bis(triphenylphosphane)nickel dichloride[12]. In both cases a 1,2-diphosphete intermediate was postulated.



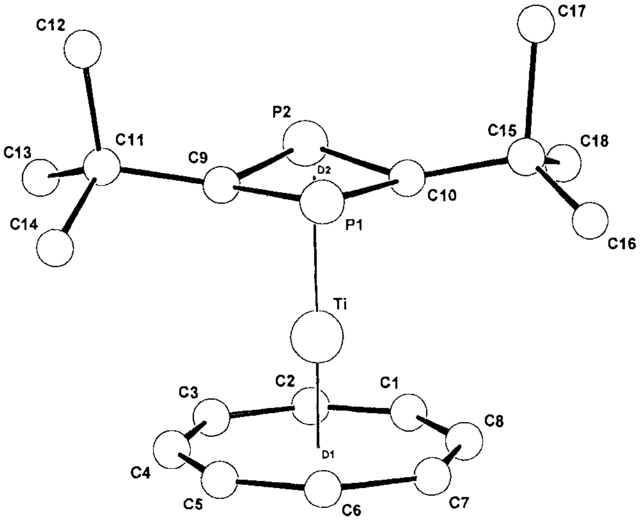
(3)

With the help of pure **3a** and **3c** the complexes **3a**−**c** and **4a**, **b** were characterized by their ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra and by elemental analysis, but the structure of each of the isomers of **3** and **4** could be determined unambiguously only by means of an X-ray analysis.

For this purpose suitable, dark green crystals of **3a** were obtained after reaction of **4a** with hexachloroethane and crystallization from pentane at −78 °C, whereas a suitable crystal of **4a** was selected from a crystalline mixture of **3a** and **4a**.

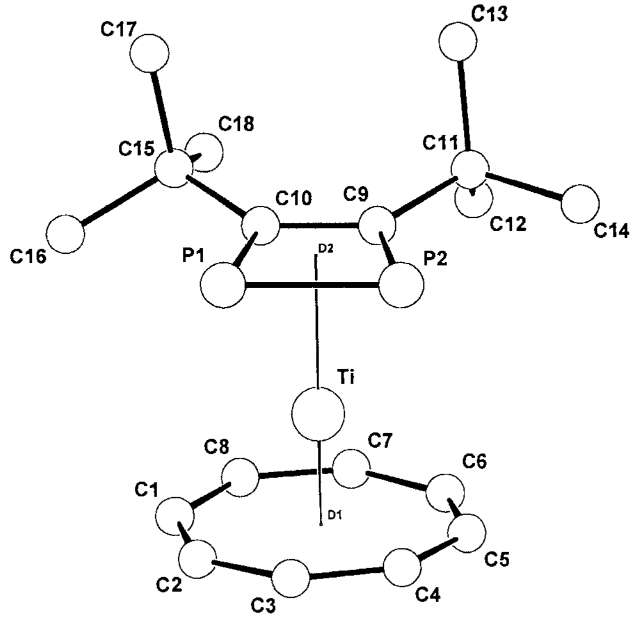
As shown in Figures 1 and 2 both complexes consist of a planar diphosphete and a planar cyclooctatetraene symmetrically bound to titanium. The most striking feature of the η^4-bonded 1,3-diphosphete in complex **3a** are alternating P−C distances within the four-membered ring. The distances P2−C9 [1.820(9) Å] and P1−C10 [1.836(9) Å] are distinctly longer than the P2−C10 [1.748(9) Å] and P1−C9 [1.747(8) Å] distances. This indicates an increased double bond character of the P1−C9 and P2−C10 bonds. In contrast, in η^4-1,3-diphosphete complexes of CpCo or (η^5-indenyl)cobalt almost equal P−C distances (on average 1.797 Å) are found indicating a delocalized π system[6a−c]. In the 1,2-disphosphete complex **4a** the C9−C10 distance [1.429(3) Å] lies nearly exactly in the middle between a single and double bond length whereas the P1−P2 distance [2.175(1) Å] is only slightly shorter than the P−P distances in 3,4-di-*tert*-butyl-1,2-dihydro-1,2-diiododiphosphete [2.192(4) Å][13], but perceptibly longer than P=P bonds (2.019−2.045 Å)[14]. The two P−C distances P1−C10 and P2−C9 [1.815(5) and 1.806(2) Å] are found in a region close to the P−C distances in the above mentioned (1,3-diphosphete)cobalt complexes, but also close to the P−C single-bond length [1.827(6) Å] in 1,2-dihydro-1,2-diiododiphosphete[13], much shorter than in normal P−C single-bond lengths[15]. It should also be mentioned that the first structurally characterized (1,2-diphosphete)metal complex **4a** shows P−P−C and P−C−C angles as calculated by Schoeller[16] whereas the observed P−P, P−C, and C−C bond lengths are longer than calculated or expected for an η^4-π complex. (For further selected bond distances and angles see Figures 1 and 2.)

Figure 1. Molecular structure of **3a**. − Selected bond lengths [Å] and angles [°]: Ti−P1 2.527(3), Ti−P2 2.508(3), Ti−C9 2.348(7), Ti−C10 2.317(8), P1−C9 1.747(8), P1−C10 1.836(9), P2−C9 1.820(9), P2−C10 1.748(9), C9−C11 1.52(1); C9−P1−C10 81.6(4), C9−P2−C10 82.0(4), P1−C9−P2 98.1(4), P1−C10−P2 97.5(4), P1−C10−C15 118.4(9), P2−C10−C15 139.6(9)



The ^{31}P- and ^{13}C-NMR data of **3a**−**c** differ considerably from those of η^4-1,3-diphosphete complexes of e.g. cobalt

Figure 2. Molecular structure of **4a**. – Selected bond lengths [Å] and angles [°]: Ti–P1 2.487(1), Ti–P2 2.494(1), Ti–C9 2.392(2), Ti–C10 2.381(2), C1–C2 1.390(5), P1–C10 1.815(2), P2–C9 1.806(2), P1–P2 2.175(1), C9–C11 1.535(3); P1–P2–C9 78.4(1), P2–P1–C10 77.8(1), P1–C9–C10 102.0(1), C10–C9–P2 101.8(1), C10–C9–C11 135.1(2), C11–C9–P2 121.7(1)



and rhodium[6]. The phosphorus signals in the ^{31}P-NMR spectra of **3a** and **3b** appear at δ = 214.5 and 213.4, near a region characteristic of phosphorus incorporated in a P=C bond. Comparable phosphorus values of η^4-1,3-diphosphete complexes of cobalt and rhodium lie in the region of δ = 28–46[6]. The (isopropyltrimethylsilyl)amino substituent in Cp(η^4-1,3-diphosphete)cobalt complexes of **2c** induces an upfield shift of the phosphorus resonance to δ = −0.54 (Cp = η^5-cyclopentadienyl) and −5.81 (Cp = indenyl)[10]. A comparable upfield shift is observed for the phosphorus signal of the 1,3-diphosphete complex **3c**, which appears at δ = 117.0. The same tendency is found in the ^{13}C-NMR spectra of **3a**. Compared with the signal of the ring carbon atom in (η^5-cyclopentadiene)(2,4-di-*tert*-butyl-1,3-diphosphete)cobalt that of the ring carbon atom in **3a** is shifted by 47.4 ppm to lower field (δ = 107.5 → 154.9). It now lies in a region typical for sp^2 carbon atoms, but in between the regions found for η^2-P=C metal bonds (δ = 76.7) and a free P=C double bond (δ = 219.8) of an (η^8-cyclooctatetraene)(1,3,5,7-tetraphosphabarrelene)zirconium complex[1]. Comparable values were found for the η^2-carbon atoms in a (1,3,5-triphospha-Dewar-benzene)vanadium complex (δ = 135.7)[8].

Interestingly, the signals of the two phosphorus atoms of the 1,2-diphosphete complexes **4a** and **4b** are found at considerably larger values (**4a**: δ = 133.6, **4b**: 139.7) compared to those of the corresponding 1,3-diphosphete complexes **3a** and **3b**. Since, on the other hand, the corresponding diphosphete ring carbon atoms of the complexes **3a** and **4a** exhibit nearly the same ^{13}C-chemical shifts [**3a**: δ = 154.9 ($J_{C,P}$ = 54.2 Hz); **4a**: δ = 153.9 ($J_{C,P}$ = 49.5 Hz)] it is impossible to distinguish between the structures of **3a**, **4a** by means of NMR-spectroscopic methods.

In summary, we have shown in this paper that phosphaalkynes **2a–c** are cyclodimerized in the coordination sphere of the 12-valence electron fragment "cotTi" to give new (1,3- and -1,2-diphosphete)titanium complexes, e.g. **3a–c** and **4a, b**. This behavior of **2** differs strongly from that in the presence of the 14-valence electron fragments "Cp_2Ti" and "Cp_2Zr", since with these metal fragments 1,3-diphosphabicyclo[1.1.0]butanediyl complexes are formed by cyclodimerization of **2**[2].

This work was supported by the *Deutsche Forschungsgemeinschaft* (Graduiertenkolleg "Phosphor als Bindeglied verschiedener chemischer Disziplinen").

Experimental

All experiments were carried out under argon in anhydrous solvents. – MS[17]: Varian CH-5 at 70 eV. – ^{1}H and ^{13}C NMR[18]: Bruker AMX 300 and AMX 400; chemical shifts relative to solvent signals, calculated to TMS. – ^{31}P NMR[18]: Bruker AMX 300 and AMX 400, external standard H_3PO_4. – Elemental analyses: Dornis and Kolbe, Mülheim an der Ruhr.

Bis(cyclooctatetraene)titanium (**1**)[19], Phosphaalkynes **1a**, **1b**[20], and **1c**[21] were prepared by known procedures.

(η^8-Cyclooctatetraene)(η^4-2,4-di-tert-butyl-1,3-diphosphete)titanium (**3a**) *and (η^8-Cyclooctatetraene)(η^4-3,4-di-tert-butyl-1,2-diphosphete)titanium* (**4a**): A solution of bis(cyclooctatetraene)titanium (**1**) (2.3 g, 9 mmol) and 2-*tert*-butyl-1-phosphaacetylene (**2a**) (2 g, 20 mmol) in toluene (40 ml) was heated at 85 °C for 2 d after which time the reaction was complete (^{31}P-NMR monitoring). The solvent was removed in vacuo (10^{-3} mbar), and the solid residue was dissolved in pentane (20 ml). After removal of some insoluble particles by filtration the green solution was cooled to −78 °C. After 6 d dark green crystals (1.96 g, 62%) had formed which were separated by filtration and dried in vacuo (10^{-3} mbar). These crystals (dec. 154 °C) consisted of a mixture of the complexes **3a** and **4a** in a ratio of 11:9 (^{31}P-NMR analysis).

Separation of **3a** *and* **4a**: To a solution of the complexes **3a** and **4a** in a ratio of 11:9 (0.3 g, 0.9 mmol) in pentane (40 ml) was added hexachloroethane (0.7 g, 3 mmol). After stirring of the mixture at 20 °C for 5 d some insoluble particles were separated by filtration and the mother liquid was cooled to −78 °C. The first two crops of crystals were pure **3a** (122 mg, 92% as dark green plates), the third fraction contained mainly compound **5**.

3a: ^{1}H NMR ([D$_8$]toluene, 32 °C, 300 MHz): δ = 1.24 (s, *t*Bu), 6.51 (s, cot). – ^{13}C NMR ([D$_8$]toluene, 32 °C, 75 MHz): δ = 154.9 (t, $J_{C,P}$ = 54.2 Hz, ring-C), 38.9 (t, $J_{C,P}$ = 9.0 Hz, *t*Bu), 33.4 ($^1J_{C,H}$ = 125, $J_{C,P}$ = 4.8 Hz, *t*Bu), 94.3 ($^1J_{C,H}$ = 169 Hz, cot). – ^{31}P NMR ([D$_8$]toluene, 32 °C, 121.5 MHz): δ = 214.5 (s). – X-ray data: Table 1.

4a (determined as a 9:11 mixture with **3a**): ^{1}H NMR ([D$_8$]toluene, 32 °C, 300 MHz): δ = 1.26 (s, *t*Bu), 6.45 (s, cot). – ^{13}C NMR ([D$_8$]toluene, 32 °C, 75 MHz): δ = 153.9 (pseudo t, $J_{C,P} + J_{C,P'}$ = 49.5 Hz, ring-C), 39.0 (pseudo t, $J_{C,P} + J_{C,P'}$ = 6.1 Hz, *t*Bu), 33.4 (q, $^1J_{C,H}$ = 126, pseudo t, $J_{C,P} + J_{C,P'}$ = 9.3 Hz, *t*Bu), 94.6 (d, $^1J_{C,H}$ = 168 Hz, cot). – ^{31}P NMR ([D$_8$]toluene, 32 °C, 121.5 MHz): δ = 133.6 (s). – $C_{18}H_{26}P_2Ti$ (351.9) (mixture of **3a** and **4a**): calcd. C 61.36, H 7.39, P. 17.61; found C 60.94, H 7.67, P 17.31. – MS, *m/z* (%) (mixture of **3a** and **4a**): 352 [M$^+$] (38), 337 [M$^+$ – Me] (30), 214 [M – C_2tBu$_2$]$^+$ (15), 152 [Ticot]$^+$ (100). – X-ray data: Table 1.

5: NMR data identical with those reported in ref.[12].

(η^8-Cyclooctatetraene)(η^4-2,4-diadamantyl-1,3-diphosphete)-titanium (**3b**) *and (η^8-Cyclooctatetraene)(η^4-3,4-diadamantyl-1,2-diphosphete)titanium* (**4b**): A mixture of complex **1** (0.60 g, 2.3 mmol) and 3.25 ml of a 40-% solution of **2b** (1.1 g, 6 mmol) in hexamethyldisiloxane diluted with toluene (30 ml) was heated at 80 °C for 3 d. All volatile components were removed in vacuo (10^{-3} mbar), the solid residue was dissolved in pentane (60 ml), insoluble particles were removed by filtration, and the clear, dark green solution was cooled to −78 °C. After two weeks a 3:2 mixture of **3b** and **4b** (^{31}P-NMR analysis) was obtained by filtration and drying at 10^{-3} mbar as a green powder; 0.70 g (60%), dec. 276 °C. – MS, *m/z* (%): 508 [M$^+$] (88), 294 [C$_2$ad$_2$]$^+$ (33), 214 [M$^+$ – C$_2$ad$_2$] (20), 152 [Ticot]$^+$ (100). – ^{1}H NMR ([D$_8$]toluene, 32 °C, 200 MHz): δ = 1.63 (m, 6H, ad), 1.78 (m, 3H, ad), 1.96 (m, 6H, ad), 6.49 (s, cot of **4b**), 6.58 (s, cot of **3b**). – ^{31}P NMR ([D$_8$]toluene, 32 °C, 81 MHz): δ = 213.4 (s, P of **3b**), 139.7 (s, P of **4b**). – C$_{30}$H$_{38}$P$_2$Ti (507.9). calcd. C 70.87, H 7.56; found C 70.73, H 7.56.

(η^8-Cyclooctatetraene){[2,4-diisopropyl(trimethylsilyl)amino]-1,3-diphosphete}titanium (**3c**): A solution of **1** (0.41 g, 1.6 mmol) and **2c** (0.69 g, 3 mmol) in toluene (30 ml) was heated at 140 °C for 14 d in a pressure vessel. The solvent was removed in vacuo (10^{-3} mbar) and the residue dissolved in pentane (70 ml). After removal of insoluble particles by filtration the clear, violet solution was cooled to −78 °C from which **3c** was isolated as a dark violet powder after one week; 0.50 g (64%) **3c**; dec. 156 °C. – MS, *m/z* (%): 498 [M$^+$] (47), 356 [M$^+$ – (*i*Pr)(TMS)NC] (100), 282 (83), 252 [(cot)(*i*PrNCP)Ti]$^+$ (32), 152 [Ticot]$^+$ (93), 73 [TMS$^+$] (87). – ^{1}H NMR ([D$_8$]toluene, 32 °C, 200 MHz): δ = 0.25 (s, 18H, TMS), 1.15 (d, $J_{H,H}$ = 7.0 Hz, 12H, *i*Pr), 3.51 (m, 2H, *i*Pr), 6.64 (s, 8H, cot). – ^{31}P NMR ([D$_8$]toluene, 32 °C, 81 MHz): δ = 117.0 (s). – C$_{22}$H$_{40}$N$_2$P$_2$Si$_2$Ti (498.1): calcd. C 53.01, H 8.03; found C 52.88, H 8.14.

Table 1. Data of the crystal structure determinations for **3a** and **4a**[a]

	4a	**3a**
Formula	$C_{18}H_{26}P_2Ti$	$C_{18}H_{26}P_2Ti$
M_r [g·mol^{-1}]	352.3	352.3
Crystal color	black	black
Crystal size [mm]	0.35×0.42×0.21	0.35×0.35×0.39
T [K]	293	293
a [Å]	8.825(2)	16.469(3)
b [Å]	14.235(1)	16.469(3)
c [Å]	14.444(1)	11.846(2)
α [°]	90.0	90.0
β [°]	90.47(1)	90.0
γ [°]	90.0	120.0
V [Å^3]	1814.3(4)	2782.6(7)
d_{cal} [g·cm^{-3}]	1.29	1.26
μ [cm^{-1}]	6.32	6.18
F(000) [e]	744	1116
Z	4	6
Crystal system	monoclinic	hexagonal
Space group	$P2_1/c$ [No.14]	$P6_3$ [No. 173]
Diffractometer	Enraf Nonius CAD-4	
Radiation	Mo-K_α	Mo-K_α
λ [Å]	0.71069	0.71069
Scan mode	ω–2θ	ω–2θ
2θ$_{max}$	54.9	54.9
Measured reflections	4480 (±*h*,+*k*,+*l*)	13130 (+*h*,±*k*,±*l*)
Independent reflections	4141	4242
Observed reflections [$I > 2\sigma(I)$]	3314	3696
Refined parameters	294	294
R	0.035	0.027
R_w	0.040	0.086
Δρ$_{max}$ [e Å^{-3}]	0.30	0.23

[a] H-atom positions were found and refined isotropically. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, FRG, on quoting the depository number CSD-59075, the names of the authors, and the journal citation.

---

[1] P. Binger, G. Glaser, B. Gabor, R. Mynott, *Angew. Chem.* **1995**, *107*, 114–116; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 81–83.

[2] [2a] P. Binger, B. Biedenbach, C. Krüger, M. Regitz, *Angew. Chem.* **1987**, *99*, 789–799; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 764–765. – [2b] T. Wettling, B. Geißler, R. Schneider, S. Barth, P. Binger, M. Regitz, *Angew. Chem.* **1992**, *104*, 761–762; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 758–759.

[3] Reviews: [3a] J. F. Nixon, *Chem. Rev.* **1988**, *88*, 1327–1362. – [3b] M. Regitz, P. Binger, *Angew. Chem.* **1988**, *100*, 1541–1565; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1484–1508. – [3c] P. Binger in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme Verlag, **1990**, p. 90–107.

[4] [4a] N. E. Schore, *Chem. Rev.* **1988**, *88*, 1081–1119. – [4b] D. Walther, D. Braun, W. Schulz, U. Rosenthal, *Z. Anorg. Allg. Chem.* **1989**, *577*, 270–282.

[5] Ni: T. Wettling, G. Wolmershäuser, P. Binger, M. Regitz, *J. Chem. Soc., Chem. Commun.* **1990**, 1541–1543.

[6] Co, Rh: [6a] P. B. Hitchcock, M. J. Maar, J. F. Nixon, *J. Chem. Soc., Chem. Commun.* **1986**, 737–738. – [6b] P. Binger, R. Milczarek, R. Mynott, M. Regitz, W. Rösch, *Angew. Chem.* **1986**, *98*, 645–646; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 644–645. – [6c] P. Binger, R. Milczarek, R. Mynott, C. Krüger, Y.-H. Tsay, E. Raabe, M. Regitz, *Chem. Ber.* **1988**, *121*, 637–645. – [6d] P. Binger, B. Biedenbach, R. Mynott, C. Krüger, P. Betz, M. Regitz, *Angew. Chem.* **1988**, *100*, 1219–1221; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1158–1160. – [6e] P. Binger, B. Biedenbach, R. Mynott, R. Benn, A. Rufinska, P. Betz, C. Krüger, *J. Chem. Soc., Dalton Trans.* **1990**, 1771–1777. – [6f] H. F. Dare, J. A. K. Howard, M. V. Pilotti, F. G. A. Stone, J. Szameitat, *J. Chem. Soc., Dalton Trans.* **1990**, 2263–2269.

[7] Fe: [7a] M. Driess, D. Hu, H. Pritzkow, H. Schäufele, U. Zenneck, M. Regitz, W. Rösch, *J. Organomet. Chem.* **1987**, *334* C35–C38. – [7b] P. Binger, B. Biedenbach, R. Schneider, M. Regitz, *Synthesis* **1989**, 960–961. – Mo: [7c] G. Brauers, M. Green, C. Jones, J. F. Nixon, *J. Chem. Soc., Chem. Commun.* **1995**, 1125–1126.

[8] R. Milczarek, W. Rüsseler, P. Binger, K. Jonas, K. Angermund, C. Krüger, M. Regitz, *Angew. Chem.* **1987**, *99*, 957–958; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 908.

[9] A report on the synthesis of a molybdenum(0) complex of 1,3,5-triphosphabenzene is for some reason doubtful[10]; A. R. Barron, A. H. Cowley, *Angew. Chem.* **1987**, *99*, 956; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 907–908.

[10] J. Haas, Dissertation, Universität Kaiserslautern, **1990**.

[11] [11a] E. Negishi, *Acc. Chem. Res.* **1987**, *20*, 65–72. – [11b] E. Negishi, T. Takahashi, *Synthesis* **1988**, 1–19.

[12] B. Geißler, S. Barth, U. Bergsträßer, M. Slany, J. Durkin, P. B. Hitchcock, M. Hofmann, P. Binger, J. F. Nixon, P. von Ragué Schleyer, M. Regitz, *Angew. Chem.* **1995**, *107*, 485–488; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 484–487.

[13] R. Schneider, Dissertation, Universität Kaiserlautern, **1991**.

[14] M. Yoshifuji in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme Verlag, **1990**, p. 321–337.

[15] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, **1987**, 1.

[16] W. W. Schoeller, T. Busch, *Angew. Chem.* **1993**, *105*, 635–637; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 617–618.

[17] D. Henneberg, H. Damen, W. Joppek, W. Schmöller, Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr.

[18] R. Mynott, B. Gabor, C. Wirtz, Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr.

[19] H. J. Kablitz, G. Wilke, *J. Organomet. Chem.* **1973**, *51*, 241–271.

[20] [20a] G. Becker, G. Gresser, W. Uhl, *Z. Naturforsch., Part B*, **1981**, *36*, 16–19. – [20b] Optimized procedure: W. Rösch, V. Hees, M. Regitz, *Chem. Ber.* **1987**, *120*, 1645–1652.

[21] R. Appel, M. Poppe, *Angew. Chem.* **1989**, *101*, 70–71; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 53–54.

[95116]