twisted by 90°.[27] This ion can serve as a model for the protonated Schiff base of retinal present in rhodopsin. In contrast to nonpolar polyenes, in highly polar double-bond systems no electronic reason exists for a hula-twist pathway, although steric reasons for it persist.

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[25] In work other than ref. [23] (for example in ref. [26]) it is observed that in the 100-fs range a "hot" primary product initially forms which then assumes a more stable conformation and simultaneously cools down in the ps range. According to experience with hexatriene[12] the internal rotation in the hot primary product cannot be suppressed by cold solvent. We propose denoting only the (freezable) conformationally relaxed product as bathorhodopsin; only this product has been shown to have an all-*trans* configuration.[21]

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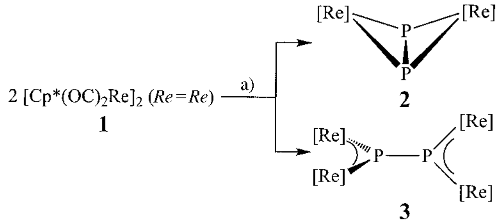
Activation of P_4 and P_2 by Transition Metal Complexes at Room Temperature[**]

Otto J. Scherer,* Markus Ehses, and
Gotthelf Wolmershäuser

*Dedicated to Professor Achim Müller
on the occasion of his 60th birthday*

The most important source of phosphorus for the preparation of complexes with P_n ligands[1] is white phosphorus P_4. The activation and cleavage of its P–P bonds[2] can be achieved in the presence of transition metal complex fragments both thermally at 60–190 °C as well as photochemically.[1]

The dropwise addition of a solution of white phosphorus in toluene to the dirhenium complex **1**[3] (Scheme 1) at room temperature gave, in addition to traces of complex **2**,[4] the tetranuclear complex **3** with a diphosphinidene ligand in approximately 40% yield.



Scheme 1. P_4 activation at room temperature. a) P_4 (0.5 equiv), toluene, room temperature. [Re] = Cp*(CO)$_2$Re.

The structures of **2** and **3** can be generally formulated as **C** (P_2 formally as a four-electron donor) and **D** (P_2 formally as an eight-electron donor), respectively. The structure type **C** with a P_2M_2 butterfly framework is relatively rare; it is observed for ML_n transition metal complex fragments with 14 and 16 valence electrons (VE).[1,4] With 15-VE-ML_n complex fragments, polyhedra with P_2M_2 tetrahedrane frameworks are formed, which have been studied in detail.[1] In both cases the P_2 ligand is coordinated side-on as a π-electron donor

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[+] X-ray crystal structure analyses.

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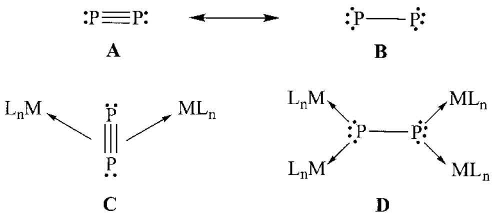
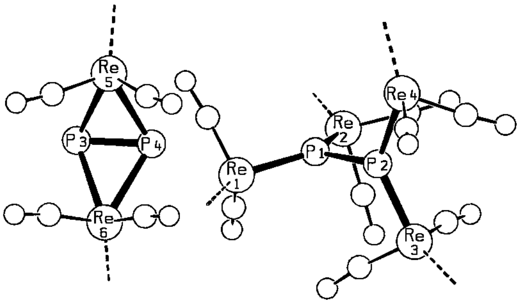


(limiting structure **A**).[5] The diphosphinidene complex **3** contains a complex-stabilized form of the unusual mesomeric structure **B** of the P_2 molecule.

Complex **3** forms red crystals that can be manipulated for short periods in air. They are insoluble in hexane, soluble in toluene, and very soluble in dichloromethane. The compound is photolabile and decomposes slowly in solution above 40 °C. The ^{31}P NMR spectrum shows a singlet at $\delta = 690$.[6] Single crystals suitable for X-ray structure analyses have so far only been obtained in the form of cocrystals of complexes **2** and **3**. The results of the structure analysis[7] reveal that the bond lengths and angles of **2** (in the cocrystal) (Figure 1) differ only slightly from those of the "pure" complex **2**[4] (Table 1). Therefore we presume that the structure parameters of **3** in the cocrystal do not differ significantly from those of the "pure" complex.

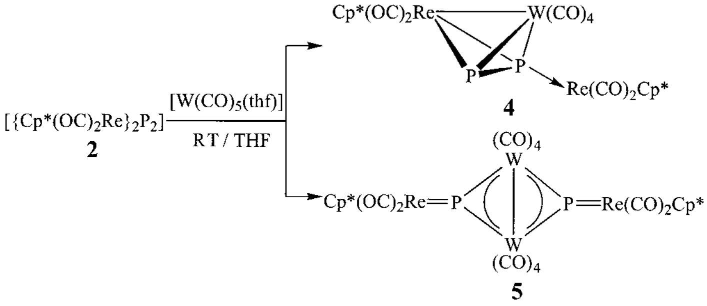


2 **3**

Figure 1. Structures of **2** and **3** in the cocrystal. Important bond lengths and angles are summarized in Table 1.

The P–P distance increases considerably on the transition from **2** (side-on-coordinated P_2; **C**) to the diphosphinidene complex **3** (P_2 formally as an 8σ-electron donor; **D**) whose P–P distance of 2.226(3) Å corresponds with that of a P–P single bond (in P_4: 2.21 Å) (Table 1). The Re1P1Re2/Re3P2Re4 planes are approximately orthogonal (91.1°); in the comparable diarsinidene complex [{Cp(OC)$_2$Mn}$_4$As$_2$] (**6**)[8] the angle between the Mn$_2$As planes is 75.9°.[8b] The sum of angles at P1 and P2 of **3** equals 359.2° in each case. The Re–P bond in **3** (av 2.33 Å) is significantly shorter than the comparable bonds in **2** (2.56/2.54 Å (cocrystal/crystal)) and thus shows multiple-bond character.

Treatment of **2** with excess [W(CO)$_5$(thf)] leads to two remarkable products (Scheme 2): compound **4** is to our knowledge the first structurally characterized example for the transformation of a M_2P_2 butterfly framework into a M_2P_2 tetrahedrane framework (42 → 40 VE, number of VE according to the Wade–Mingos rules;[9] see also reference [10]). At the same time the P_2 ligand of **2** (**C**) (which according to Table 1 shows multiple-bond character) is split into two P atoms at room temperature under formation of the tetranuclear complex **5**.



Scheme 2. P_2 activation at room temperature.

Complex **4** forms orange-red crystals, complex **5** dark red ones, which can be manipulated for short periods in air. They are insoluble in hexane, scarcely soluble in toluene, and well soluble in dichloromethane. Complex **5** decomposes gradually in solution. The ^{31}P NMR spectrum[6] of **4** with a chiral

Table 1. Selected bond lengths [Å] and angles [°] of complexes **2** (crystal[4] and cocrystal) and **3** (cocrystal only).[a]

3 in cocrystal		**2** in cocrystal		Crystals of **2**[4]	
P1–P2	2.226(3)	P3–P4	2.042(3)	P1–P1′	2.032(8)
Re1–P1	2.329(2)	Re5–P3	2.566(2)	Re1–P1	2.531(3)
Re2–P1	2.335(2)	Re6–P3	2.548(2)	Re1′–P1′	2.531(3)
Re3–P2	2.332(2)	Re5–P4	2.561(2)	Re1–P1′	2.555(3)
Re4–P2	2.326(2)	Re6–P4	2.565(2)	Re1′–P1	2.555(3)
Re–Cp*[b]	1.99/1.99	Re5–Cp*	1.95	Re–Cp*	1.95
	1.99/1.98	Re6–Cp*	1.95		
Re1-P1-Re2	131.53(8)	P3-Re5-P4	46.94(8)	P1-Re1(1′)-P1′	47.1(2)
P2-P1-Re1	114.74(9)	P3-Re6-P4	47.06(8)		
P2-P1-Re2	112.97(9)	Re5-P3-Re6	105.71(8)	Re1-P1(1′)-Re1′	105.55(12)
Re3-P2-Re4	130.94(8)	Re5-P4-Re6	105.36(8)		
P1-P2-Re3	114.02(9)	P3-P4-Re5	66.65(9)	Re1-P1-P1′	67.1(2)
P1-P2-Re4	114.27(9)	P3-P4-Re6	66.03(9)	Re1′-P1′-P1	67.1(2)
		P4-P3-Re5	66.41(9)	Re1-P1′-P1	65.8(2)
		P4-P3-Re6	66.90(9)	Re1′-P1-P1′	65.8(2)

[a] Cp* denotes the center of the cyclopentadienyl ring. The torsion angle Cp*ReReCp* is 3.6° (in cocrystal) and 37.4° (in crystals of **2**). [b] In this case Re represents the center of Re1–Re4.

ReWPP′-tetrahedrane framework[11] contains two doublets ($\delta = -87.7/-188.7$, four-coordinate P atom; ^1J(P,P) = 545.3 Hz) with tungsten satellites (^1J(W,P) = 35/22 Hz; cf. references [1, 4]). The crystal structure analysis[7] reveals a P–P distance of 2.067(2) Å for the $ReWP_2$ framework of **4** (Figure 2), a value that lies in the range observed for other complexes with M_2P_2 tetrahedrane frameworks.[1] The Re2–P1 bond length of 2.3255(11) Å corresponds to the average value of 2.33 Å in **3** (see Table 1). The mean value for Re–P bonds (2.52 Å) in the cluster differs only slightly from those in the Re_2P_2 butterfly framework of **2** (2.56/2.54 Å (cocrystal/crystal)).

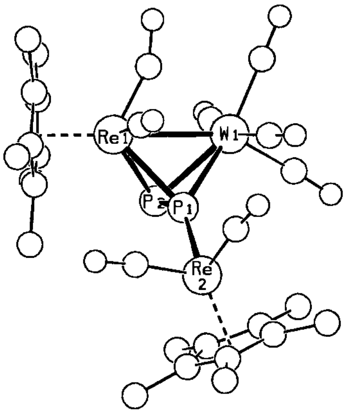


Figure 2. Crystal structure of **4**. P1–P2 2.067(2), Re1–P1 2.5151(11), Re1–P2 2.5205(12), Re2–P1 2.3255(11), Re1–W1 3.0667(3), W1–P1 2.5713(12), W1–P2 2.5388(13); P2-P1-Re2 137.83(6), Re2-P1-Re1 138.34(5), Re2-P1-W1 141.34(5), Re1-P1-W1 74.15(3).

The downfield shift of the ^{31}P NMR signal[6] of **5** ($\delta = 885$) is characteristic for planar-coordinated P atoms, which are surrounded by three metal complex fragments (in this case with metals of the 5d series; phosphinidene complexes). For instance, a value of $\delta = 977$ is found for $[\{Cp(OC)_2Mn\}_2(\mu_3\text{-}P)_2\{Fe_2(CO)_6\}](\mathit{Fe}\text{–}\mathit{Fe})$ (**7**) with three complex fragments containing metals of the 3d series.[12]

The most interesting aspect of the structure of **5**[7] is the planar six-atom framework $Re_2P_2W_2$ (Figure 3). In contrast, the comparable compounds **7**[12] and $[\{^{Me}Cp(OC)_2Mn\}_2(\mu_3\text{-}As)_2\{Mn_2(CO)_2(^{Me}Cp)_2\}]$ (**8**),[13] which were prepared from a P_1 complex or photochemically from the ^{Me}Cp derivative of **6**,[8b] respectively, and which were characterized by X-ray structure analyses, contain a M_2E_2 butterfly framework (M = Mn,Fe; E = As,P).[12, 13] The distance to the terminal Re group (P=Re) in **5** (2.245(2) Å) is particularly short. The sum of the angles at P1 and P1′ is 359.9°; the W–W bond length of 3.0523(7) Å lies in the range of a single bond, as observed for other ditungsten complexes.[14]

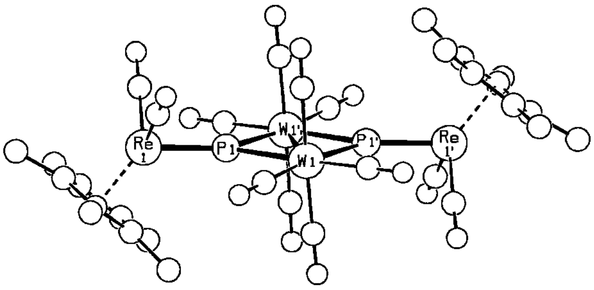


Figure. 3. Crystal structure of **5**. W1–W1′ 3.0523(7), W1(1′)–P1(1′) 2.439(2), W1(1′)–P1′(1) 2.440(2), Re1(1′)–P1(1′) 2.245(2), P1···P1′ 3.81; Re1(1′)-P1(1′)-W1(1′) 141.41(7), Re1(1′)-P1(1′)-W1′(1) 141.00(7), W1(1′)-P1(1′)-W1′(1) 77.45(5).

Experimental Section

2/3: **1** (435 mg, 0.58 mmol)[3, 4] was dissolved in toluene (40 mL) in a 50-mL-three-necked flask under exclusion of light. A solution of P_4 (ca. 20 mg, ca. 0.16 mmol) in toluene (ca. 5 mL) was added dropwise at room temperature, and the mixture was stirred at this temperature for a further 2 h. After removal of the solvent under vacuum, the residue was taken up in a small amount of toluene (ca. 5 ml) and transferred to a column (20 × 1.5 cm) packed with Al_2O_3 and petroleum ether. Several mg of a yellow-orange fraction containing **2/3** was initially eluted with petroleum ether/toluene (5/3), from which cocrystals of **2/3** were obtained by recrystallization from CH_2Cl_2/hexane (ca. 1/2) at −20 °C. Further chromatography gave an intense red fraction **3** (171 mg, 38%); however, to date only very thin platelets have been obtained from crystallization.

4/5: **2** (98 mg, 0.12 mmol)[4] in THF (15 mL) was treated at room temperature with a solution of $[W(CO)_5(thf)]$ (ca. 0.70 mmol) in THF (45 mL), prepared by photolysis (10 min) of $[W(CO)_6]$ (261 mg). After 2.5 h (IR control) the reaction was complete and the solution was orange red. After removal of the solvent in vacuum, the residue was extracted with THF (4 × ca. 5 mL), silica gel was then added to the collected extracts, and the mixture was evaporated to dryness and transferred to a column (20 × 1.0 cm) packed with silica gel (activity grade II) and petroleum ether. An orange-red fraction was eluted with petroleum ether/toluene (1/1 to 1/2), from which **5** (10 mg) was isolated. Elution with the 1/2 solvent mixture subsequently gave **4** (39 mg, 29%) as a red zone; red **5** (48 mg; overall yield 34%) was obtained as the last fraction with toluene/diethyl ether (20/1 to 1/1).

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[6] Spectroscopic data of compounds **3**–**5**: $\delta(^{31}P)$ (81.01 MHz, $CDCl_3$, 85% H_3PO_4 external): **3**: 690 (s, 2P); **4**: −87.7 („d“, 1P, ^1J(P,P) = 545.3 Hz, ^1J(W,P) = 35 Hz), −188.7 („d“, 1P, ^1J(P,P) = 545.3 Hz, ^1J(W,P) = 22 Hz); **5**: 885 („s“, 2P, ^1J(W,P) = 85.4 Hz); $\delta(^1H)$ (200.13 MHz, $CDCl_3$, $CHCl_3$ internal ($\delta = 7.25$); $T = 295$ K): **3**: 2.10 (s, 30H), 2.06 (s, 30H); **4**: 2.04 (s, 15H), 2.02 (s, 15H); **5**: 2.30 (s, 30H); IR (CH_2Cl_2): $\tilde{\nu}$(CO) [cm^{-1}]: **3**: 1968(s), 1935(s), 1922(sh), 1914(vs), 1890(s), 1871(m), 1862(m); **4**: 2040(vs), 1982(vs), 1950(s), 1913(m), 1894(m), 1857(m); **5**: 2017(s), 1974(vs, br.); 1943(m, sh), 1907(m).

[7] Crystal structure data of complexes **2/3** (in the cocrystal) and complexes **4** and **5** [in square brackets]: $C_{73}H_{92}Cl_2O_{12}P_4Re_6$ [$C_{28}H_{30}O_8P_2Re_2W$; $C_{32}H_{30}O_{12}P_2Re_2W_2$], $M_r = 2473.45$ [1112.71; 1408.60], monoclinic [monoclinic; triclinic], space group $P2_1/n$ [$P2_1/n$; $P\bar{1}$], $a = 14.485(2)$ [10.4887(6); 8.934(2)], $b = 15.8971(13)$ [17.9268(9);

9.801(2)], $c = 34.797(4)$ [17.1896(10); 12.071(3)] Å, $\alpha = 90$ [90; 82.20(2)], $\beta = 95.085(10)$ [94.768(6); 79.19(2)], $\gamma = 90$ [90; 67.21(2)]°, $V = 7981(2)$ [3221.0(3); 954.8(3)] Å^3, $Z = 4$ [4; 1], $\rho_{calcd} = 2.059$ [2.295; 2.450] g cm^{-3}, $T = 293(2)$ K, θ-range: 1.74–24.12 [2.20–25.93; 2.74–28.00]°, measured reflections: 46406 [45294; 16443], independent reflections: 12255 [5991; 4217] ($R_{int} = 0.0636$ [0.0694; 0.0620]), R values: final R values ($I > 2\sigma(I)$): $R1 = 0.0308$ [0.0247; 0.0353], $wR2 = 0.0685$ [0.0568; 0.0935], all data: $R1 = 0.0415$ [0.0303; 0.0420], $wR2 = 0.0738$ [0.0585; 0.0984]. Diffractometer: Stoe IPDS. Structure solution: direct methods [direct methods; Patterson]. Program used for solving the structure: SIR92 (Giacovazzo et al., 1993) [SHELXTL; SHELXS 86 (Sheldrick, 1990)]. Structure refinement: full-matrix least-squares methods against F^2. Program used for refining the structure: Siemens SHELXTL [SHELXTL; Siemens SHELXL 93 (Sheldrick, 1993)]. Data/parameters: 12248/904 [5991/381; 4217/232]. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100785. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Functionalized Cross-Linked Copolymers: A "C_2-Symmetric" Solid-Phase Catalyst for Enantioselective Reactions[**]

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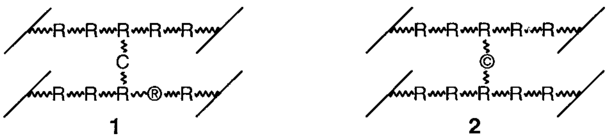
Building on the pioneering work of Merrifield,[1] solid-phase synthesis,[2] polymer-supported reagents,[3] and polymer-bound catalysts[4] have revolutionized many aspects of synthetic chemistry. Most of these exploits were accomplished with styrene/divinylbenzene (PS/DVB) copolymers,[5] but there are notable exceptions.[6] Polymer-bound catalysts are typically prepared by covalent attachment of the catalytic moiety to the PS/DVB copolymer through the chloromethylated functionality (Merrifield's resin). While excellent enantioselectivities have been achieved with these heterogeneous catalysts,[7] this route to supported catalysts has been limited to placing the catalyst at a position pendant to the polymer backbone (**1**, Figure 1). What has been largely overlooked[8] is a supported-catalyst strategy in which the catalytic moiety is located at the resin cross-link (**2**, Figure 1). We report here the rapid and convenient synthesis of this type of cross-link-functionalized resin by suspension copolymerization to yield a solid-phase "C_2-symmetric" catalyst (although the two polymer chains are not identical, the local environment is C_2-symmetric) for application in enantioselective transformations. We believe this unique cross-link functionalization provides the least disturbance to the symmetry of the catalytic center, because the two cross-linked polymer chains can be considered as symmetrically equivalent. Possible applications therefore benefit from a decrease in the number of competing diastereomeric transition states inherent in C_2-symmetric systems.[9] In most pendant catalysts, one arm of the auxiliary is attached to the polymer backbone while the other terminates with a small organic fragment, causing inherent dissymmetry between the auxiliaries. We believe cross-link-functionalized chiral resins may afford important processing advantages over pendant versions. For example, cross-link functionalization should minimize interactions between active sites which may positively influence reaction parameters such as catalytic turnover. In addition, resin-supported catalytic reagents can ease product purification as well as catalyst recovery and reuse.



1 **2**

Figure 1. Functionalized resins. R: chain monomer; C: cross-linked monomer; ®: pendant functionalization; ©: cross-link functionalization.

To obtain a cross-linked functionality, it was necessary to synthesize a monomeric chiral auxiliary (X) containing two polymerizeable units (i.e., $CH_2{=}CH{-}X{-}CH{=}CH_2$), which could then undergo suspension copolymerization with styrene. We reasoned that the resulting cross-link-functionalized polystyrene beads might provide an ideal opportunity for asymmetric catalysis, and selected enantioselective reductive alkylation of aldehydes as our target transformation.

Ohno and co-workers[10] reported that the chiral ligand **3** (1 mol%) together with titanium(IV) isopropoxide catalyzes the reductive alkylation of aldehydes (Scheme 1). We envisioned replacing the trifluoromethyl groups of **3** with styrenesulfonyl groups to give a cross-linking monomer (**4**) which, after copolymerization with styrene (**4**→**5**), could be evaluated for efficacy in the reaction of aromatic aldehydes and diethylzinc to form (S)-1-aryl-1-propanol. This auxiliary-mediated alkylation reaction was selected for our preliminary evaluation of cross-link efficacy in an enantioselective transformation because it competes with ligand-unassisted con-

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