P−H Activation By Zirconium Amido Complexes: From New Phosphanidozirconium Complexes to the First Zr_2P_6 Cluster with the $[RP-P-PR]^{3-}$ Ligand [R = Me_2(*i*PrMe_2C)Si]

Matthias Driess,*[a] Joachim Aust,[a] and Klaus Merz[a]

Dedicated to Prof. Karl Wieghardt on the occasion of his 60th birthday

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A new, efficient and salt-free method to synthesize phosphanidozirconium complexes is reported. Treatment of $[Cp_2Zr(PHR)_2]$ **3** [R = Me_2(*i*PrMe_2C)Si] with $[Zr(NEt_2)_4]$ furnishes the first unsymmetrically substituted 1,3-dizircona-2,4-diphosphetane $[Cp_2Zr(PR)_2Zr(NEt_2)_2]$ (**1**; Cp = η^5-C_5H_5) in quantitative yield, which undergoes intermolecular ligand exchange reactions at 140 °C to form the mixed substituted derivative $[Cp_2Zr(PR)_2ZrCp(NEt_2)]$ (**2**) in 28% yield. An X-ray diffraction analysis of **2** revealed that the four-membered Zr_2P_2 ring is only slightly puckered. The Brønsted acid-base reaction of $[Cp^*Zr(NMe_2)_3]$ (**4**; Cp^* = C_5Me_5) with the P–H acidic silylphosphane RPH_2 affords the corresponding tris-(phosphanido) complex $[Cp^*Zr(PHR)_3]$ (**5**) in the form of a red-brown oil in quantitative yield. Heating of the latter at 140 °C leads to the first dinuclear zirconium phosphanide cluster $[(Cp^*Zr)_2(R_2P_3)_2]$ (**6**), which has been isolated in the form of dark green crystals in 12% yield and structurally characterized by X-ray diffraction analysis.

Introduction

During the last few years substantial progress has been achieved in the development of nucleophilic, and at the same time soft, phosphorus-transfer reagents, in which Zr−P compounds play an excellent role as versatile building blocks for the synthesis of organophosphorus compounds. Since the initial work on phosphanidozirconium compounds by Issleib and Häckert[1] it has become well established that $Cp_2Zr(+4)$ and $Cp_2Zr(+3)$complexes (Cp = η^5-C_5H_5) with bridging and/or terminal phosphanido ligands can serve as soluble, mild and selective PR_2^-, PR^{2-} and P^{3-} equivalents.[2] The latter types of complexes are superior to the respective ionogenic alkali and alkaline earth metal phosphanides since, during their synthesis, they can initiate simultaneous Zr-assisted P−P and/or P−C cross-coupling reactions between several primary organophosphorus moieties, affording new polyphosphorus ligands. This synthetic potential is impressively demonstrated by the $[Cp_2Zr]$-induced cyclooligomerisation of phosphaalkynes[3] and the formation of Zr−P complexes with unsubstituted phosphorus atoms, starting from P_4 and $[Cp_2Zr]$ complex fragments.[4] The formation of Zr−P bonds in phosphanidozirconocene compounds is usually achieved by salt metathesis reactions between lithium phosphanides and $[Cp_2ZrX_2]$ (X = halogen) or through oxidative addition of (oligo)phosphanenes, P−C multiple bonds and P_4 to $[Cp_2Zr]$ fragments as reactive intermediates.[5] The latter methods also frequently involve redox processes at the zirconium and phosphorus atoms, which make product predictions more difficult. Here we report a new method for the synthesis of Zr−P complexes through σ-metathesis reactions, starting from strong Brønsted-basic amidozirconium complexes ($[Zr]-NR_2$) and P−H-acidic silylphosphanenes. Hitherto, only the reverse process, that is, the simple protolytic fission of the Zr−P bond with NH-containing amines, has been described.[6] Furthermore, we report the preparation of the first zirconium tris(silylphosphanido)-complex **5**, which can be converted into the $(ZrP_3)_2$ cluster **6**.

[a] Lehrstuhl für Anorganische Chemie I: Molekül- und Koordinationschemie
Ruhr Universität Bochum, Fakultät für Chemie
Universitätsstrasse 150, 44801 Bochum, Germany
Fax: (internat.) + 49-234/321-4378
E-mail: matthias.driess@ruhr-uni-bochum.de

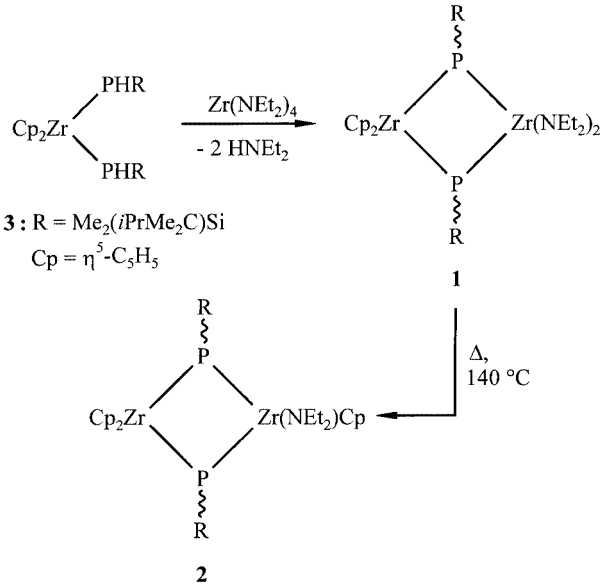
Results and Discussion

The Zr_2P_2 complex **1** is furnished in almost quantitative yield by heating the diphosphanido complex **3** with $[Zr(NEt_2)_4]$ in boiling benzene, while compound **3** is accessible upon reaction of $[Cp_2ZrCl_2]$ with RP(H)Li in 71% yield [molar ratio 1:2, toluene, 0 °C; R = Me_2(*i*PrMe_2C)Si; $\delta(^{31}P)$ = −51.0 (d, $^1J_{P,H}$ = 214 Hz)]. In contrast to the $[Cp_2Zr(PHR)_2]$ derivatives (R = *t*Bu, Aryl) hitherto known,[7] **3** is not only easily accessible and thermally resist-

ant up to 120 °C but also suitable for selective P−H bond activation.

Compound **1** was isolated in the form of a red-brown oil. Its structure can be deduced from the simple features of the ^{1}H and ^{31}P NMR spectra, while its composition is proven by the EI mass spectrum. The ^{31}P NMR spectrum of **1** shows a singlet for both μ_2-bridging P atoms at relatively low field (δ = 287.6 ppm), as expected for Zr_2P_2 complexes.[9]

Surprisingly, **1** undergoes metathesis reactions in boiling xylene at 140 °C to give the unsymmetrical **2**, which contains one $Cp(Et_2N)$- and one Cp_2-substituted Zr atom, in 28% yield (Scheme 1). The mechanism of this unprecedented Cp/NEt_2 exchange reaction at the zirconium atoms is still unknown. However, the formation of **2** probably occurs intermolecularly, as indicated by the strong concentration dependence of the reaction. The complex is formed in only 1.5% yield if **3** is reacted with $[Zr(NEt_2)_4]$ in boiling xylene. The ^{31}P NMR spectrum of **2** at 28 °C shows one singlet at δ = 273.8 ppm which is consistent with an fast inversion of configuration at phosphorus on the time scale of the experiment. This inversion process could not be frozen out at low temperature due to the moderate solubility of **2** in CH_2Cl_2, $CHCl_3$, Et_2O and aromatic solvents. Its ^{1}H NMR spectrum shows, as expected, three anisotropic sets of Cp groups and one type of ethyl protons. Additionally, the constitution of **2** has been corroborated by an single-crystal X-ray diffraction analysis. The four-membered Zr_2P_2 skeleton is slightly puckered (Zr1-Zr2-P1/Zr1-Zr2-P2 = 3.2°). The Zr1−P1 [2.552(3) Å] and Zr1−P2 [2.527(3)] bond lengths are similar to the values for Zr2−P1 [2.550(3) Å] and Zr2−P2 [2.615(3) Å] (Figure 1).



Scheme 1

The Zr−P distances are practically identical to the values observed in other Zr(+4)-phosphanide complexes but ca. 4% shorter than the single bonds in isostructural Zr_2P_2

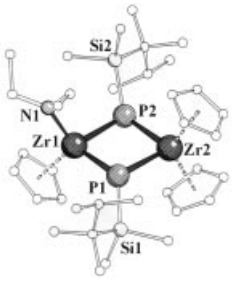
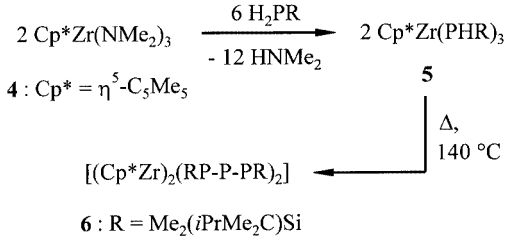


Figure 1. Molecular structure of **2**; hydrogen atoms are omitted for clarity; selected distances [Å] and angles [°]: Zr1−N1 1.958(11), Zr1−P1 2.552(3), Zr1−P2 2.527(3), Zr2−P1 2.550(3), Zr2−P2 2.615(3), P1−Si1 2.225(4), P2−Si2 2.210(4); P2−Zr1−P1 89.8(1), P1−Zr2−P2 87.90(9)

complexes with Zr(+3) centers.[1,9] The Zr−N and Si−P distances are unexceptional. The P atoms are pyramidal coordinated (ΣP1 = 344.5°, ΣP2 = 340.0°) and possess practically identical endocyclic angles at the Zr centers.

In another P−H/Zr−N σ-metathesis reaction, starting from the tris(amido) complex **4** and H_2PR in the molar ratio of 1:3 in boiling toluene, the first zirconium tris(phosphanido) complex $[Cp^*Zr(PHR)_3]$ (**5**; $Cp^* = \eta^5$-C_5Me_5) has been prepared (Scheme 2).



Scheme 2

This compound can be isolated in the form of a red-brown oil in quantitative yield and has been characterized by its ^{1}H and ^{31}P NMR spectra and mass spectrum. Its temperature-independent ^{31}P NMR spectrum shows a shielded ^{31}P nucleus at δ = −173.5 [$^1J_{P,H}$ = 182.4 Hz] with significantly different δ and $^1J_{P,H}$ values compared with $[Cp_2Zr(PHR)_2]$ complexes of type **3** [R = silyl; δ = −51 to −78 ppm, $^1J_{P,H}$ = 204 to 215 Hz].[7,9c] Prolonged heating of a solution of **5** in xylene at 140 °C (four days) furnishes a reaction mixture from which the novel cluster **6** can be isolated by fractional crystallization in 12% yield. The dark green crystals are only sparingly soluble in common organic solvents. Its temperature-invariable ^{31}P NMR spectrum shows an AA′BB′CC′ spin system of higher order which is in accordance with an identical chelating coordination mode of both [RP−P−PR] ligands toward the Zr centers. Since the appearance of the spectrum remains unchanged in polar solvents (THF, DMF) even at low temperature, there is no indication for a dissociation process in solution. However, the structure of **6** could only be established by an X-ray diffraction analysis. This revealed a Zr_2P_6 cluster core with a center of symmetry as a characteristic structural mo-

tif, which can be simply described as a dimer of two butterfly-like ZrP_3 frameworks (Figure 2).

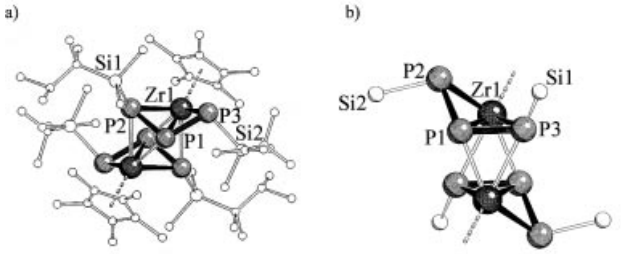
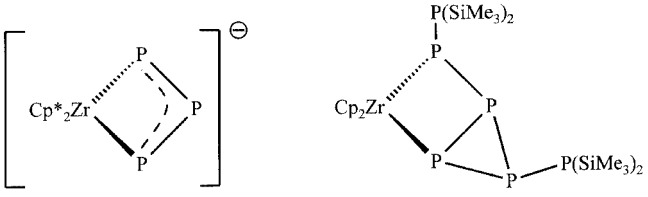


Figure 2. a) Molecular structure of **6**; hydrogen atoms are omitted for clarity; selected distances [Å] and angles [°]: Zr1−P1 2.731(3), Zr1−P2 2.665(3), Zr1−P3 2.593(3), Zr1−P1A 2.617(3), Zr1−P2A 2.796(3), P1−P3 2.175(4), P1−P2 2.184(4), P3−Si2 2.267(4), P2−Si1 2.284(4); P3−Zr1−P2 83.05(9), P3−Zr1−P1 48.14(8), P2−Zr1−P1 47.73(9), P1−P3−Zr1 69.2(1), P3−P1−Zr1 64.57(9), P2−P1−P3 106.2(1); b) view along the distorted octahedral connection between the two hypothetical ZrP_3 halves in **6**; organo groups are omitted for clarity

The hypothetical ZrP_3 halves have a distorted octahedral geometry and are connected to each other through the two Zr1−P1−P3 and Zr1A−P1A−P3A triangular faces (see Figure 2b), which leads to significantly different Zr−P distances between the ZrP_3 moieties [Zr1−P2A 2.796(3) Å, Zr1−P1A 2.617(3) Å]. However, the Zr−P distances within the butterfly-like ZrP_3 framework are also quite different: the Zr1−P1 distance of the bridgehead bond [2.731(3) Å] is, as expected, longer than the Zr1−P2 [2.665(3) and Zr1−P3 bonds [2.593(3) Å], due to ring strain. Apparently, a stabilization of the hypothetical ZrP_3 halves is achieved by the formation of Zr,P,P multiple-center bonds and the closing of vacant coordination sites at the Zr atom. While the P1 atom is substituent-free, the P2 and P3 atoms bear terminal silyl groups, which are *exo*,*endo* configured with respect to the hypothetical ZrP_3 butterfly-like framework. The almost equal P-P distances in the ZrP_3 halves [2.175(4) and 2.184(4) Å] lie between the values observed in the related complexes **A** (2.10 Å)[10] and **B** (2.24 Å) shown in



A : Cp* = η^5-C_5Me_5 **B** : Cp = η^5-C_5H_5

Scheme 3

Scheme 3,[11] and they imply, in contrast to the electronic situation in **A**, no contribution of stabilizing P-P π-interactions in the R_2P_3 ligand. The geometric features suggest that **6** is the first zirconium oligophosphanide cluster containing an $[RP-P-PR]^{3-}$ anion. The synthesis of the parent anion $[HP-P-PH]^{3-}$ by reduction of P_4 with alkali metals in liquid ammonia has recently been reported.[12]

Experimental Section

General Remarks: All manipulations were carried out under anaerobic conditions in dry argon using standard Schlenk techniques. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. NMR spectra were recorded on a Bruker Avance250 spectrometer at ambient temperature operating at 250.1 MHz (^{1}H) and 101.3 MHz (^{31}P). Chemical shifts are reported relative to TMS at 0.00 (^{1}H) and to 85% H_3PO_4 in D_2O at 0.00 (^{31}P). Mass spectra were measured on a Varian MAT CH7 spectrometer. Elemental analyses were performed by the microanalytical service of the department. The starting materials H_2PR [R = Me_2(*i*PrMe$_2$C)Si],[13] [$Zr(NEt_2)_4$] and [Cp*$Zr(NMe_2)_3$] (**4**)[14] were prepared according to literature procedures.

Preparation of 1: [$Zr(NEt_2)_4$] (0.79 g, 2.1 mmol) was added to a solution of **3** (1.21 g, 2.1 mmol) in benzene and refluxed for 8 h. Subsequently, the volatile components of the mixture were evaporated off at 80 °C (10^{-3} Torr), affording the oily red-brown product in pure form according to NMR spectroscopy and EI mass spectrometry. Yield: (1.67 g, 2.07 mmol), 99%. ^{1}H NMR (C_6D_6): δ = 0.53 (d, $^3J_{P,H}$ = 3.7 Hz, 12 H, $SiMe_2$), 1.12 (d, $^3J_{H,H}$ = 6.6 Hz, 12 H, $CHMe_2$), 1.16 (s, 12 H, $SiCMe_2$), 1.98 (t,$^3J_{H,H}$ = 7.4 Hz, 12 H, NCH_2Me), 2.15 (sept., $^3J_{H,H}$ = 6.6 Hz, 2 H, $CHMe_2$), 3.23 (q, $^3J_{H,H}$ = 7.4 Hz, 8 H, NCH_2Me), 5.89 (t, $^3J_{P,H}$ = 1.9 Hz, 10 H, Cp) ppm. ^{31}P NMR (C_6D_6): δ = 287.6 (s) ppm. MS (EI, 70 eV): *m*/*z* (%) = 805 (3) [M^+], 720 (4) [M − (*i*PrMe$_2$C)]$^+$, 65 (100) [Cp^+].

Preparation of 2: A solution of **1** (1.10 g, 1.36 mmol) in xylene was heated at 140 °C for 2 days, affording a deep-brown reaction mixture. After removal of the solvent and other volatile components at 80 °C and 10^{-3} Torr, the resulting residue was taken up in ca. 5 mL hexane. The desired product crystallized after several days at −15 °C in the form of green-brown crystals. Yield: (0.31 g, 0.38 mmol), 28%. ^{1}H NMR (C_6D_6): δ = 0.52 (d, $^3J_{P,H}$ = 3.7 Hz, 12 H, $SiMe_2$), 1.14 (d, $^3J_{H,H}$ = 6.6 Hz, 12 H, $CHMe_2$), 1.15 (s, 12 H, $SiCMe_2$), 2.04 (t,$^3J_{H,H}$ = 7.4 Hz, 6 H, NCH_2Me), 2.15 (sept., $^3J_{H,H}$ = 6.6 Hz, 2 H, $CHMe_2$), 3.31 (q, $^3J_{H,H}$ = 7.4 Hz, 4 H, NCH_2Me), 5.89 (t, $^3J_{P,H}$ = 2.0 Hz, 5 H, Cp), 5.92 (t, $^3J_{P,H}$ = 1.8 Hz, 5 H), 5.97 (t, $^3J_{P,H}$ = 1.1 Hz, 5 H, Cp) ppm. ^{31}P NMR (C_6D_6): δ = 273.8 (s) ppm. MS (EI, 70 eV): *m*/*z* (%) = 720 (4) [M − (*i*PrMe$_2$C)]$^+$, 648(8) [M − (*i*PrMe$_2$C) − NEt_2]$^+$, 65 (80) [Cp^+], 29 (100) [Et^+]. correct C, H-combustion analysis: $C_{35}H_{63}NP_2Si_2Zr_2$ (798.4): calcd. C 52.65, H 7.95; found C 51.98, H 7.90.

Preparation of 3: A solution of LiP(H)R [R = Me_2(*i*PrMe$_2$C)Si] (6.8 mmol) in 20 mL toluene, freshly prepared from H_2PR (1.20 g, 6.8 mmol) and 4.26 mL of a 1.6 M solution of BuLi in hexane (Aldrich) in 50 mL toluene at 0 °C, was added to a solution of [Cp_2ZrCl_2] (1.0 g, 3.4 mmol) in 50 mL toluene at −70 °C. The reaction mixture was allowed to warm to room temperature within 8 h and then stirred for one day. After filtration, the solvent was removed under reduced pressure affording a solid residue. The latter was redissolved in ca. 20 mL hexane from which the desired product crystallized after a few days in the form of pale red crystals. Yield: (1.38 g, 2.41 mmol), 71%. ^{1}H NMR (C_6D_6): δ = 0.54 (s, 12 H, $SiMe_2$), 1.12 (d, $^3J_{H,H}$ = 6.6 Hz, 12 H, $CHMe_2$), 1.14 (s, 12 H, $SiCMe_2$), 2.12 (sept., $^3J_{H,H}$ = 6.6 Hz, 2 H, $CHMe_2$), 2.61 (d $^1J_{P,H}$ = 214 Hz, 2 H, PH,), 5.93 (s, 10 H, Cp) ppm. ^{31}P NMR (C_6D_6): δ = −51.0 (d, $^1J_{P,H}$ = 214 Hz) ppm. MS (EI, 70 eV): *m*/*z* (%) = 394 (9) [M − PH(*i*PrMe$_2$C)$SiMe_2$]$^+$, 143 (98) [*i*PrMe$_2$C)$SiMe_2$]$^+$. Correct C, H combustion analysis: $C_{26}H_{50}P_2Si_2Zr$ (572.0): calcd. C 54.59, H 8.81; found C 54.12, H 8.80.

Preparation of 5: A solution of **4** (1.72 g, 5.24 mmol) in 50 mL toluene was treated with H_2PR [R = Me_2(*i*PrMe$_2$C)Si] (2.76 g,

15.72 mmol) and refluxed at 110 °C for 3 h, resulting in an clear dark solution. After removal of all volatile components at ca. 60 °C and 10^{-3} Torr, the oily red-brown product was isolated in practically quantitative yield. Yield: (3.94 g, 5.23 mmol), 99.8%. ^{1}H NMR (C_6D_6): δ = 0.56 (s, 18 H, $SiMe_2$), 1.14 (d, $^3J_{H,H}$ = 6.6 Hz, 18 H, $CHMe_2$), 1.15 (s, 18 H, $SiCMe_2$), 1.87 (m, $^1J_{P,H}$ = 182.4 Hz, 3 H, PH), 2.13 (sept., $^3J_{H,H}$ = 6.6 Hz, 3 H, $CHMe_2$), 2.22 (s, 15 H, C_5Me_5) ppm. ^{31}P NMR (C_6D_6): δ = −173.5 (d, $^1J_{P,H}$ = 182 Hz) ppm. MS (EI, 70 eV): *m*/*z* (%) = 752 (3) [M^+], 577 (5)[M − PH(*i*PrMe$_2$C)SiMe$_2$]$^+$, 143 (98) [*i*PrMe$_2$C)SiMe$_2$]$^+$, 73 (100) [$SiMe_3^+$].

Preparation of 6: A red-brown solution of **5** (1.36 g, 1.8 mmol) in 10 mL xylene was heated at 140 °C for three days, affording a dark green solution. After removal of all volatile components under vacuum (10^{-3} Torr) at a maximum of 100 °C (oil bath), the solid residue was redissolved in ca. 10 mL hexane, from which dark green crystals precipitated after six days. Yield: (0.26 g, 0.21 mmol), 12%. ^{1}H NMR (C_6D_6): δ = 0.52 (s, 12 H, $SiMe_2$), 0.54 (s, 12 H, $SiMe_2$), 1.11 (d, $^3J_{H,H}$ = 6.6 Hz, 12 H, $CHMe_2$), 1.13 (d, $^3J_{H,H}$ = 6.6 Hz, 12 H, $CHMe_2$), 1.16 (br. s, 24 H, $SiCMe_2$), 2.15 (br. m, 4 H, $CHMe_2$), 2.05 (s, 30 H, C_5Me_5) ppm. ^{31}P NMR (C_6D_6, assignment according to $[RP_A-P_B-P_CR]_2$ and simulations [16]): $\delta(P_A)$ = −123.0 (m, $^1J_{P_A,P_B}$ = 374, $^2J_{P_A,P_C}$ = 68 Hz), $J_{P_A,P_{A'}}$ = 23.0, $J_{P_A,P_{B'}}$ = 3.0, $J_{P_A,P_{C'}}$ = 2.5 Hz; other long-range couplings = 0), δ_{P_B} = −62.6 (m, $^1J_{P_B,P_A}$ = 374, $^1J_{P_B,P_C}$ = 269, $J_{(P_B,P_{B'}}$ = 8.6, $J_{P_B,P_{A'}}$ = 3.0 Hz; other long-range couplings = 0), δ_{P_C} = −85.4 (m, $^1J_{P_C,P_B}$ = 269, $^2J_{P_C,P_A}$ = 68, $J_{P_C,P_{C'}}$ = 4.9, $J_{P_C,P_{A'}}$ = 2.5 Hz; other long-range couplings = 0). Correct C, H combustion analysis: $C_{52}H_{106}P_6Si_4Zr_2$ (1212.0): calcd. C 51.53, H 8.81; found C 51.12, H 8.76.

X-ray Crystallographic Study

1: Triclinic, space group $P\bar{1}$, a = 10.1276(18), b = 21.453(5), c = 17.066(3) Å, α = 83.016(9)°, β = 73.063(9)°, γ = 83.157(9)°, V = 2007.2(4) Å^3, 5230 independent reflections [$I > 2\sigma(I)$], 349 parameters, $R1$ = 0.0823 (observed reflections), $wR2$ = 0.1951 (all data).

6: Monoclinic, space group $P2_1/c$, a = 11.719(8), b = 12.861(9), c = 20.817(14) Å, β = 90.643(15)° Volume = 3137(4) Å^3, 4024 independent reflections [$I > 2\sigma(I)$], 281 parameters, $R1$ = 0.0843 (observed reflections), $wR2$ = 0.2390 (all data).

The intensities were measured with a Bruker-axs-SMART diffractometer. (Mo-K_α radiation, λ = 0.71707 Å, ω-scan, The structures were solved by direct methods (SHELXS 97). Refinements were carried out with the SHELXL-97 package.[16] All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were placed in calculated positions and refined isotropically in riding mode. All refinements were made by full-matrix least-squares on F^2.

CCDC-158194 (**1**) and -158195 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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