Unexpected reaction pathway during the palladation of 2,5-diphenylphosphacymantrene

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ABSTRACT

A new reaction of *P*-alkoxypalladation was found. 2,5-Diphenylphosphacymantrene reacts with Na_2PdCl_4 and NaOAc in MeOH or EtOH to give *P*-methoxy or *P*-ethoxy derivatives with Pd_2Cl_2 dimeric core. The products **2** and **3** were characterized by ^1H, ^{31}P, ^{13}C NMR spectra and X-ray crystal structure data.

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1. Introduction

Cyclopalladation, that is a direct substitution of hydrogen atom for palladium with the formation of the five- or six-membered chelated metallocycle is thoroughly studied and reviewed [1,2]. The necessary pre-requisite for this reaction is the presence of a donor atom (N, P, S) in a suitable position. It is most popular in the arene and ferrocene series. However, no data were published about its application in the cymantrene series. It was interesting to apply it to 2,5-diphenylphosphacymantrene having a phosphorus atom (whose donor properties were confirmed by the coordination to the W(CO)$_5$ fragment [3]) in a "benzylic" position to phenyl groups which might form the five-membered palladocycle.

2. Results and discussion

We have studied the behaviour of 2,5-diphenylphosphacymantrene (**1**) under the conditions of cyclopalladation, that is, upon treatment with Na_2PdCl_4 in alcoholic solvent (MeOH or EtOH) in the presence of a weak base NaOAc (ratio of components 1:1:1). Reaction proceeds quickly at room temperature, and after 30–40 min no starting compound **1** was found but the structure of the product was unexpected.

After usual workup the products have been isolated as red-orange microcrystals (**2** from MeOH, **3** from EtOH). Probably, the first step of the reaction is coordination of the phosphorus atom of **1**

with positively charged palladium. Then several pathways seem possible as shown on the Chart below.
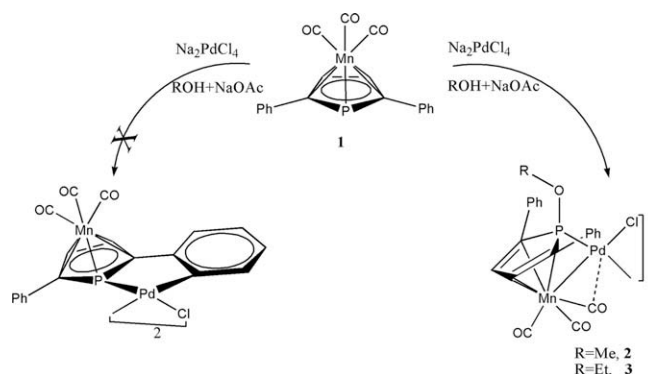
Cyclopalladation into one of phenyl rings was feasible with the formation of the stable five-membered metallocycle widely abundant in organopalladium chemistry. However, it was not compatible with ^1H NMR spectra that unequivocally evidenced that both phenyl rings in **2** and **3** are equivalent. They exhibit two groups of protons with the intensity ratio 4:6 corresponding to the proton amounts ortho: (meta + para). The chemical shifts of the phosphorus atoms in **2** and **3** underwent the large downfield shift by ~120 ppm comparing to **1**. Simultaneously, in ^1H NMR spectra in addition to the signals of started **1** (δ 6.0 ppm, 2H, d, Cp-ring; δ

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7.3 ppm, 10H, Ph), novel signals were found: for **2** – a doublet at δ 3.60 ppm, 3H, with $^3J(^1H-^{31}P)$ 14.8 Hz (CH_3-O-P), for **3** – a triplet at δ 1.03 (3H), CH_3, and the signal of 6 lines, δ 4.04 (2H) with $^3J(^1H-^{31}P)$ 14.0 Hz ($-CH_2-O-P$). The exact molecular structures of **2** and **3** have been established by X-ray investigation.

The *P*-alkoxy derivatives of phospholyl complexes have been obtained for the first time in this work. On the first step of this pro-cess phosphorus is attacked by palladium to give an intermediate (or transition state) which is stabilized on the second step by the nucleophilic addition of OR to the phosphorus atom from *exo*-side to afford **2** or **3** as final products. Quantum chemical calculations have shown that in phosphacymantrenes LUMO orbital is largely localized on the P atom and therefore nucleophilic attack could be expected to perform on phosphorus [4]. Previously, Mathey
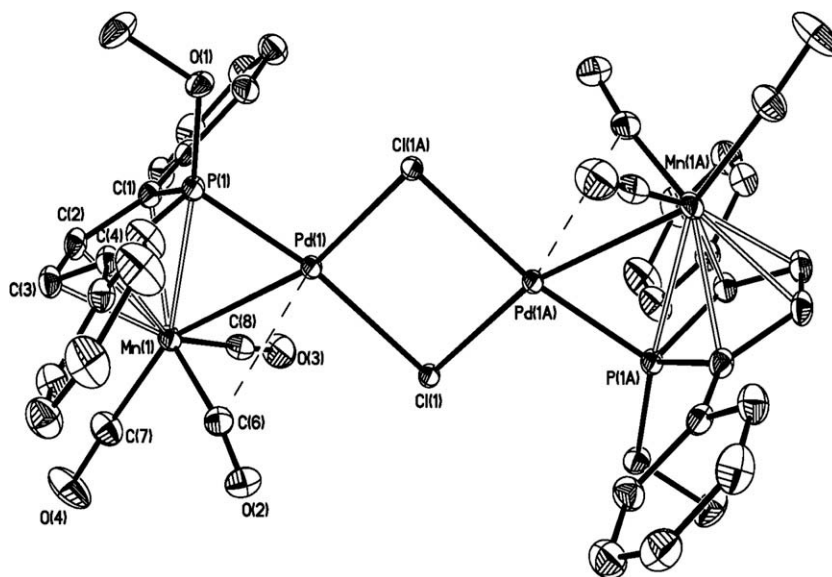

Fig. 1. ORTEP drawing of the molecular structure of complex **2** with thermal ellipsoids at 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond length (Å) and angles (°). Only one monomeric unit is described: Pd(1)–Mn(1) 2.6952(4); Pd(1)–Cl(1) 2.4561(5); Pd(1)–Cl(1A) 2.4168(5), symmetry transformation used to generate equivalent atoms is $-x - y - z + 2$; Pd(1)–P(1) 2.1574(6); Pd(1)···C(6) 2.639(2); Pd(1)···C(8) 2.990(2); Mn(1)–P(1) 2.4596(6); Mn(1)–C(1) 2.239(2); Mn(1)–C(2) 2.143(2); Mn(1)–C(3) 2.144(2); Mn(1)–C(4) 2.246(2); Mn(1)–C(6) 1.807(2); Mn(1)–C(7) 1.815(2); Mn(1)–C(8)1.811(2); P(1)–O(1) 1.604(2); P(1)–C(1) 1.788(2); P(1)–C(4) 1.779(2); C(1)–C(2) 1.411(2);C(2)–C(3)1.432(2); C(3)–C(4)1.407(2); P(1)–Pd(1)–Mn(1) 59.69(2); Cl(1)–Pd(1)–Cl(1A) 87.37(2); P(1)–Pd(1)–Cl(1) 169.68(2); P(1)–Pd(1)–Cl(1A) 102.96(2); Cl(1)–Pd(1)–Mn(1) 110.05(1); Mn(1)–Pd(1)–Cl(1A) 161.54(2); Pd(1)–Cl(1)–Pd(1A) 92.63(2); O(1)–P(1)–C(1) 115.9(1); O(1)–P(1)–C(4) 115.0(1); O(1)–P(1)–Pd(1) 114.22(6); C(1)–P(1)–Pd(1) 110.09(7); C(4)–P(1)–Pd(1) 107.42(8).
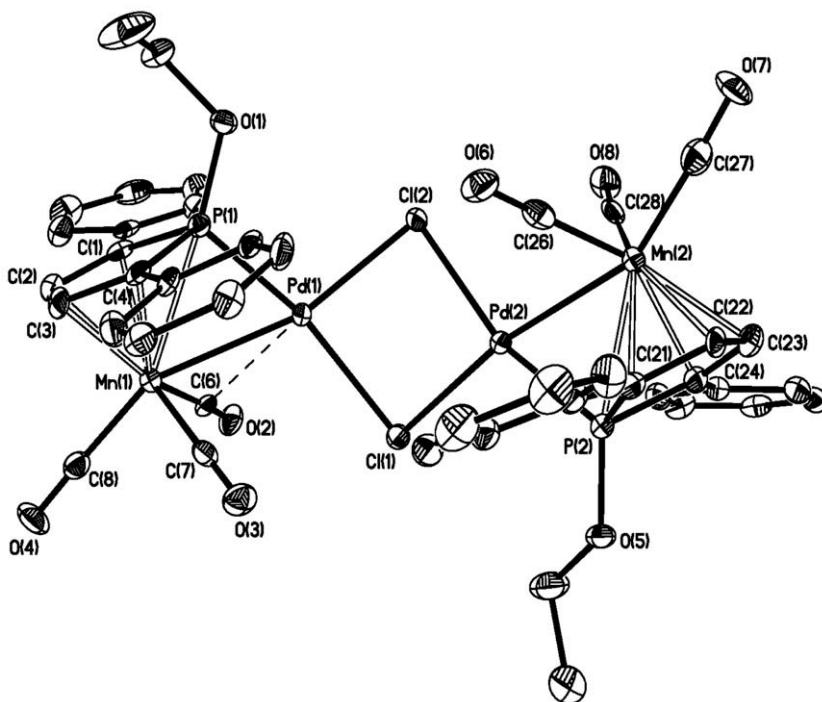

Fig. 2. ORTEP drawing of the molecular structure of one of two independent molecules of complex **3** with thermal ellipsoids at 50% probability level. Hydrogen atoms have been omitted for clarity.

et al. established that η^5-3,4-dimethylphosphacymantrene in the reactions with PhLi [5] or *t*-BuLi [6] added Ph or *t*-Bu group on phosphorus with the formation of unstable manganates which may be stabilized on the second stage by reacting with BrCH$_2$CH$_2$Z (Z = COOEt, CN) [5] or PdCl$_2$(cyclooctadiene) [6].

In the present case, both steps are united in the reaction that can be called "solvopalladation" by the analogy to the solvomercuration of olefins [7]. However, the special feature of this reaction is that *the same atom* (that of phosphorus) is attacked first by palladium, then by OR group. It is worth to note that palladium goes in from the site close to manganese atom and OR from the opposite site that suggests the initial interaction Pd···Mn. Probably, this is the reason why cyclopalladation is not realized because it requires the in-plane approach of the metal to close the nearly flat five-membered metallocycle. The ability of manganese atom to be coordinated with an electrophilic metal had been found before [8]. Preliminary data show that similar products are formed from **1** with *i*-PrOH or PhCH$_2$OH (in CH$_2$Cl$_2$ solution).

2.1. X-ray crystal structures of compounds **2** and **3**

The molecular structures of **2** and **3** are similar but not identical. Complex **2** in crystal (Fig. 1) is in a special position (centre of inversion is situated in the middle of the four-membered planar cycle Pd$_2$Cl$_2$). Atom P(1) lays in the same plane whereas Mn(1) goes out of it by 0.276 Å. As a result, the tetrahedral distortion of a pla-

nar square environment is observed for 4-coordinated palladium, dihedral angle between two planes Pd(1)Cl(1)Cl(1A) and Pd(1)P(1)Mn(1) is 6.8°. There is a slight semi-bridged interaction between palladium atom and one of the carbonyl ligands of Mn(CO)$_3$. Distances Pd(1)···C(6) and Pd(1)···C(8) are non-equivalent and the metal carbonyl moiety C(6)O(2) is non-linear. Dihedral angle around the line C(1)···C(4) is 2.5°, phosphorus atom goes out of the four-carbon plane away from Mn atom by 0.055 Å. The planes of both phenyl groups are rotated by 14.9° and 10.1° in respect to the middle plane of the phospholyl cycle.

In the crystal of complex **3** (Fig. 2) there are two crystallographically independent molecules (A and B) whose structures are very close to that of complex **2**. The main difference is that both molecules of **3** are in the general position and the central 4-membered cycle Pd$_2$Cl$_2$ deviates substantially from the planarity. It has the butterfly geometry with dihedral angle around the line Cl(1)···Cl(2) 143.6° (in A) and 136.1° (in B). In the molecule A both palladium atoms have planar square environment (the deviation out of plane of four bonded atoms are 0.068 and 0.002 Å for Pd(1) and Pd(2), respectively). In the molecule B atom Pd(1) is square planar but Pd(2) undergoes tetrahedral distortion, the dihedral angle between the planes Pd(2)Cl(1)Cl(2) and Pd(2)P(2)Mn(2) being 16.1°. Semi-bridged interactions are realized only for three of four independent palladium atoms (see Table 1). The bends along the line C(1)···C(4) in four independent phospholyl cycles are 2.2, 3.7, 2.4, 0.5°. On the whole, the structures of **2** and **3** including

Table 1
Selected bond lengths (Å) and angles (°) for two independent molecules (A and B) of complex **3**.

	A	B		A	B
Pd(1)–Mn(1)	2.6519(9)	2.6710(9)	Pd(2)–Mn(2)	2.6539(9)	2.6867(9)
Pd(1)–P(1)	2.161(1)	2.163(1)	Pd(2)–P(2)	2.174(1)	2.154(1)
Pd(1)–Cl(1)	2.454(1)	2.454(1)	Pd(2)–Cl(1)	2.399(1)	2.413(1)
Pd(1)–Cl(2)	2.374(1)	2.408(1)	Pd(2)–Cl(2)	2.436(1)	2.457(1)
Pd(1)···C(6)	2.557(5)	2.647(5)	Pd(2)···C(26)	2.749(5)	2.654(5)
Pd(1)···C(7)	2.869(5)	2.860(5)	Pd(2)···C(28)	2.735(5)	2.886(5)
Mn(1)–P(1)	2.466(2)	2.455(2)	Mn(2)–P(2)	2.475(2)	2.447(2)
Mn(1)–C(1)	2.233(5)	2.242(5)	Mn(2)–C(21)	2.234(5)	2.264(5)
Mn(1)–C(2)	2.136(5)	2.141(5)	Mn(2)–C(22)	2.135(5)	2.158(5)
Mn(1)–C(3)	2.135(5)	2.155(6)	Mn(2)–C(23)	2.151(5)	2.142(5)
Mn(1)–C(4)	2.251(5)	2.249(6)	Mn(2)–C(24)	2.245(5)	2.253(5)
Mn(1)–C(6)	1.799(6)	1.809(6)	Mn(2)–C(26)	1.822(6)	1.806(6)
Mn(1)–C(7)	1.822(6)	1.813(6)	Mn(2)–C(27)	1.808(6)	1.808(6)
Mn(1)–C(8)	1.823(6)	1.812(6)	Mn(2)–C(28)	1.826(6)	1.812(6)
P(1)–O(1)	1.593(4)	1.603(4)	P(2)–O(5)	1.600(4)	1.604(4)
P(1)–C(1)	1.787(5)	1.783(6)	P(2)–C(21)	1.788(5)	1.789(5)
P(1)–C(4)	1.792(5)	1.777(6)	P(2)–C(24)	1.782(5)	1.787(5)
C(1)–C(2)	1.383(7)	1.432(7)	C(21)–C(22)	1.412(7)	1.414(7)
C(2)–C(3)	1.427(7)	1.407(8)	C(22)–C(23)	1.429(7)	1.410(7)
C(3)–C(4)	1.411(7)	1.401(7)	C(23)–C(24)	1.402(7)	1.402(7)
P(1)–Pd(1)–Mn(1)	60.63(4)	59.96(4)	P(2)–Pd(2)–Mn(2)	60.71(4)	59.52(4)
Cl(2)–Pd(1)–Cl(1)	86.96(5)	86.16(4)	Cl(1)–Pd(2)–Cl(2)	86.81(4)	86.00(4)
P(1)–Pd(1)–Cl(2)	103.60(5)	106.70(5)	P(2)–Pd(2)–Cl(1)	109.26(5)	104.12(5)
P(1)–Pd(1)–Cl(1)	167.93(5)	167.06(5)	P(2)–Pd(2)–Cl(2)	163.92(5)	169.02(5)
Cl(2)–Pd(1)–Mn(1)	164.23(4)	166.32(4)	Cl(1)–Pd(2)–Mn(2)	169.96(4)	158.91(4)
Cl(1)–Pd(1)–Mn(1)	108.71(4)	107.27(4)	Cl(2)–Pd(2)–Mn(2)	103.23(4)	111.60(4)
Pd(2)–Cl(1)–Pd(1)	86.75(4)	85.38(4)	Pd(1)–Cl(2)–Pd(2)	87.72(4)	85.33(4)
O(1)–P(1)–C(1)	115.0(2)	115.6(3)	O(5)–P(2)–C(21)	109.2(2)	116.1(2)
O(1)–P(1)–C(4)	117.9(2)	114.2(2)	O(5)–P(2)–C(24)	113.1(2)	114.8(2)
O(1)–P(1)–Pd(1)	114.5(2)	115.5(2)	O(5)–P(2)–Pd(2)	123.8(2)	112.9(2)
O(1)–P(1)–Mn(1)	175.5(2)	174.1(2)	O(5)–P(2)–Mn(2)	166.7(2)	175.9(2)
C(1)–P(1)–Pd(1)	110.4(2)	108.4(2)	C(21)–P(2)–Pd(2)	108.0(2)	109.5(2)
C(4)–P(1)–Pd(1)	105.2(2)	108.5(2)	C(24)–P(2)–Pd(2)	106.3(2)	110.0(2)
C(1)–P(1)–C(4)	91.3(2)	92.0(3)	C(24)–P(2)–C(21)	91.7(2)	91.8(2)
C(2)–C(1)–P(1)	110.9(4)	108.9(4)	C(22)–C(21)–P(2)	109.9(4)	109.6(4)
C(1)–C(2)–C(3)	114.2(5)	114.5(5)	C(21)–C(22)–C(23)	113.9(5)	114.2(5)
C(4)–C(3)–C(2)	113.6(5)	113.6(5)	C(24)–C(23)–C(22)	113.5(5)	114.2(5)
C(3)–C(4)–P(1)	110.0(4)	110.8(5)	C(23)–C(24)–P(2)	110.7(4)	110.2(4)
O(2)–C(6)–Mn(1)	171.8(5)	175.5(5)	O(6)–C(26)–Mn(2)	175.1(5)	175.5(5)
O(3)–C(7)–Mn(1)	177.0(5)	177.2(5)	O(7)–C(27)–Mn(2)	177.0(5)	177.5(5)
O(4)–C(8)–Mn(1)	175.9(5)	179.5(6)	O(8)–C(28)–Mn(2)	176.1(5)	176.4(5)

Table 2
Crystal data, data collection and structure refinement parameters for **2** and **3**.

Compound	2	3
Molecular formula	$C_{40}H_{30}Cl_2Mn_2O_8P_2Pd_2$	$C_{42}H_{34}Cl_2Mn_2O_8P_2Pd_2 \cdot 1.25(C_3H_6O)$
Formula weight	1094.16	1194.81
Dimension (mm)	$0.33 \times 0.17 \times 0.08$	$0.25 \times 0.12 \times 0.04$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	9.5962(5)	32.258(2)
b (Å)	16.0702(8)	13.782(1)
c (Å)	13.1991(6)	21.172(2)
α (°)	90	
β (°)	98.598(1)	98.310(2)
γ (°)	90	
V (Å^3)	2012.6(2)	9313.4(12)
Z	2	8
ρ_{calc} (g cm^{-3})	1.806	1.704
Linear absorption (μ) (cm^{-1})	17.56	15.28
T_{min}/T_{max}	0.595/0.872	0.636/0.941
$2\theta_{max}$ (°)	58	52
No. unique reflections [$R_{(int)}$]	5347 (0.0421)	18 212 (0.1089)
No. of observed reflections ($I > 2\sigma(I)$)	4544	11 812
No. of parameters	254	1143
R_1 (on F for observed reflections)[a]	0.0249	0.0456
wR_2 (on F^2 for all reflections)[b]	0.0654	0.0894
Goodness-of-fit (GOF)	1.046	0.988

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.
[b] $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2) \}^{1/2}$.

the bond lengths Mn–P, Pd–P and Mn–Pd are close to that of a dimeric complex with Pd_2Cl_2 core and *tert*-butyl group on phosphorus [6].

3. Experimental

2,5-Diphenylphosphacymantrene (**1**) was obtained according to procedure [9]. NMR spectra ^1H and ^{31}P-{^1H} were registered using spectrometer Bruker Avance-300, ^{13}C NMR spectra were obtained with Bruker Avance-600. Chemical shifts were measured relative to H_3PO_4 (^{31}P) or TMS (^1H, ^{13}C).

3.1. Synthesis of complexes **2** (or **3**)

37.4 mg (0.1 mM) of **1**, 29.4 mg (0.1 mM) of Na_2PdCl_4 and 13.6 mg (0.1 mM) of NaOAc were stirred in methanol (or ethanol) (30 ml) under argon at 20 °C under TLC control (eluent hexane–dichloromethane 3:1). When reaction proceeds, the initial yellow colour gradually changes to red colour. After ~40 min complex **1** disappeared and reaction was interrupted by pouring into cold water. The product was extracted with benzene or CH_2Cl_2, washed with water, dried (Na_2SO_4) and solvent removed *in vacuo* to give **2** (or **3**) as orange-red crystals stable in air and soluble in organic solvents except alkanes. Yield 45–50 mg (83–90%).

Spectral data for **2**: NMR ^{31}P-{^1H} narrow singlet, δ 89.50 ppm (for starting **1** δ −30.1 ppm). ^1H (acetone-d_6): δ 3.653 (3H), d, $^3J(^1H$–$^{31}P)$ 14.8 Hz, OCH$_3$; δ 6.054, (2H), d, $J(^1H$–$^{31}P)$ 22.5 Hz, Cp-H; δ 7.267 (6H), s, (m+p)-C_6H_5; δ 7.915 (4H), m, o-C_6H_5.

NMR ^{13}C: δ (acetone-d_6): 55.635, d, $J(^{13}C$–$^{31}P)$ 12 Hz, OCH$_3$; δ 73.643, d, $J(^{13}C$–$^{31}P)$ 62 Hz, two C-atoms in α-position to P; δ 75.174, d, $J(^{13}C$–$^{31}P)$ 18 Hz, two C-atoms in β-position to P; δ 127.915, d, $J(^{13}C$–$^{31}P)$ 8 Hz, one of two C-atoms in o-position C_6H_5; δ 128, 015, s, another C-atom in o-position C_6H_5; δ 129,169, s, C-atoms of (m+p)-positions; δ 132,67, $J(^{13}C$–$^{31}P)$ 13 Hz, key-C-atoms of C_6H_5; δ 226.0, broad, (CO)$_3$Mn. Assignment of signals in ^1H spectra of **3** has been made using 2D correlation spectra ^1H–^{13}C COSY and HSQC.

Spectral data for **3**: NMR ^{31}P-{^1H} narrow singlet, δ 84.43 ppm. ^1H (acetone-d_6): δ 1.032, t (3H), $J(H$–$H)$ 7.3 Hz, CH$_3$; δ 4.043 (2H), 6 lines, two overlapped quadruplets with $J(H$–$H)$ 7.3 Hz and

$^3J(^1H$–$^{31}P)$ 14 Hz; OCH$_2$; δ 6.219 (2H), d, $J(^1H$–$^{31}P)$ 23,4 Hz, Cp-H; δ 7.513 (6H), (m+p) C_6H_5; δ 8,233, m, (4H), o-C_6H_5.

3.2. X-ray studies of **2** and **3**

Single crystals of the complexes **2** and **3** were obtained by slow diffusion of pentane into the solutions of **2** in CH_2Cl_2 or **3** in acetone-d_6 in NMR tubes at room temperature.

The single crystal X-ray diffraction experiment was carried out with a Bruker SMART APEX II diffractometer (graphite monochromated Mo Kα radiation, $\lambda = 0.71073$ Å, ω-scan technique, $T = 100$ K). The APEX II software [10] was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, scaling and absorption correction, and SHELXTL [11] for space group and structure determination, refinements, graphics, and structure reporting. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 with the anisotropic thermal parameters for all non- hydrogen atoms. In the crystal **3**, one of four independent OEt groups is disordered over two positions with 0.6/0.4 occupancies, and there are three solvent molecules of acetone, two of which are disordered. All hydrogen atoms in structures of **2** and **3** were placed geometrically and refined in the riding motion approximation. The principal experimental and crystallographic parameters of **2** and **3** are presented in Table 2.

Supplementary material

CCDC 694601 and 694602 contain the supplementary crystallographic data for **2** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] V.V. Dunina, O.N. Gorunova, Russ. Chem. Rev. 73 (2004) 309.
[2] V.V. Dunina, O.N. Gorunova, Russ. Chem. Rev. 74 (2005) 871.
[3] A.G. Ginzburg, A.S. Batsanov, Yu.T. Struchkov, Organometal. Chem. USSR 4 (1991) 417.
[4] C. Guimon, G. Pfister-Guilliouso, F. Mathey, Nouv. J. Chim. 3 (1979) 725.
[5] B. Deschamps, P. Toullec, L. Ricard, F. Mathey, J. Organometal. Chem. 634 (2001) 131.
[6] B. Deschamps, L. Ricard, F. Mathey, J. Organometal. Chem. 689 (2004) 4647.
[7] R.C. Larock, Solvomercuration – Demercuration Reactions in Organic Synthesis, Springer, Berlin, 1986.
[8] L.G. Kuzmina, A.G. Ginzburg, Yu.T. Struchkov, D.N. Kursanov, J. Organometal. Chem. 253 (1983) 329.
[9] A. Breque, F. Mathey, C. Santini, J. Organometal. Chem. 165 (1979) 129.
[10] APEX II Software Package, Bruker AXS Inc., 5465, East Cheryl Parkway, Madison, WI, 2005, p. 5317.
[11] SHELXTL v. 5.10, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA, 1998.