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Chelating phosphines with low coordinated phosphorus atoms Part I. Phosphaalkenes associated with phosphine moieties — X-ray structure of *cis*-$(CO)_4Mo[$*ortho*-$Ph_2P–C_6H_4–CH{=}P(t\text{-}Bu_3C_6H_2)]\cdot C_7H_{16}$

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Abstract

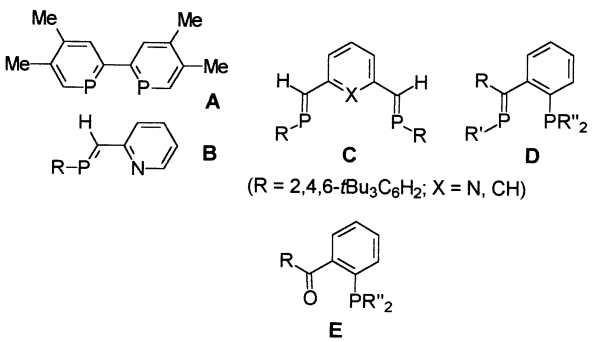
Condensation of *ortho*-diphenylphosphinobenzaldehyde with 2,4,6-tri-*t*-butyl-phenylphosphine yields the λ^2,λ^3-diphosphorus chelating agent **2a** with an *E*-configurated phosphaalkene unit as indicated by the analysis of the NMR data. On irradiation with UV light **2a** is transformed to the *Z*-isomer (**2b**). *E*-**2a** forms stable Mo(0), Pd(II) and Pt(II) chelate complexes (**3**–**5**). The X-ray structure of the molybdenum complex $\mathbf{3}\cdot C_7H_{16}$ (space group $P2_12_12_1$) has been determined showing the phosphaalkene moiety to be coordinated in a η^1-mode to molybdenum within a distorted six-membered chelate ring. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Phosphaalkenes; Diphenylphosphino groups; Mo(0), Pd(II), Pt(II) complexes; Ligand properties; X-ray structure

1. Introduction

The synthesis and coordination chemistry of monodentate organophosphorus compounds containing low coordinated phosphorus atoms (e.g. phosphaalkenes, phosphaalkynes and λ^3-phosphinines) have been developed in great detail in the past decades [1,2]. In contrast to the vast number of polydentate λ^3-phosphine ligands [3] there are only a very few reports in the literature on di- and tridentate ligands containing phosphorus in low coordination numbers, e.g. **A**–**C** [4,5].

Chelating agents of type **D** comprise donor properties of phosphaalkenes and tertiary phosphines in one molecule and should therefore show interesting coordination chemistry. There is only one report (patent literature) [6] claiming the application of a type **D** ligand in Pd catalyzed copolymerization of CO and olefins. No experimental details for the preparation and characterization of the ligand are given, however.



For the synthesis of λ^2,λ^3-phosphorus donor systems **D** aromatic phosphine ligands with appropriate O=C(R) functional groups in the *ortho*-position to the PR''_2 group, e.g. **E**, may be employed as starting materials. Phosphines of the type **E** with R″ = Ph and R = H, Me, Pr have already been reported in the literature [7a]. Recently, we have developed a convenient high yield synthesis for these *ortho*-functionalized derivatives of triphenylphosphine [7b].

Due to the pronounced reactivity of the prochiral P=C double bond [1,8,9], ligands of the type **D** may be used for the synthesis of novel chiral chelating phos-

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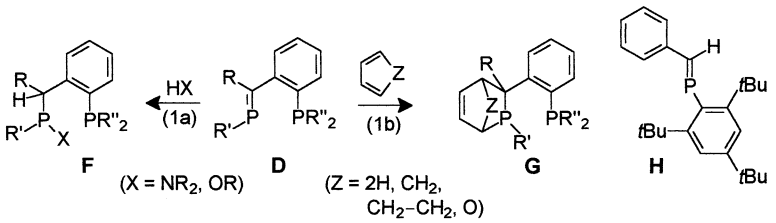
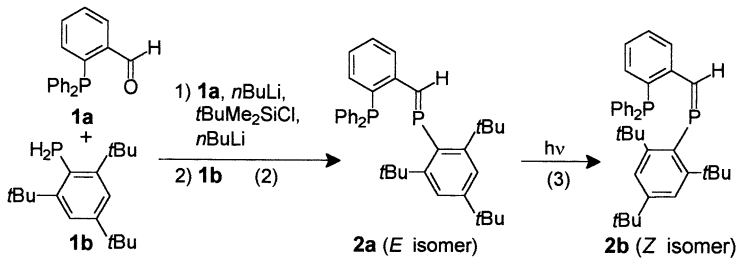


Scheme 1.



Scheme 2.

phines. Thus, addition of proton active compounds HX ($X = OR, NR_2$) yields chiral chelating agents **F** while by [2 + 4]-cycloaddition of 1,3-dienes mono- or bicyclic phosphine ligands **G** ($Z = 2H, CH_2, CH_2–CH_2, O$) are accessible (Eqs. (1a) and (1b) in Scheme 1).

The prochiral phosphaalkenes **D** are thus a potential source of optically active phosphines provided that face selectivity can be achieved by chiral substituents R, R′ or R″ during the additions and cycloadditions. Here we report on the synthesis of Ph_2P derivatives of **D** with a C(H)=PR′ group.

2. Syntheses of the phosphaalkene-phosphine ligands 2a, 2b

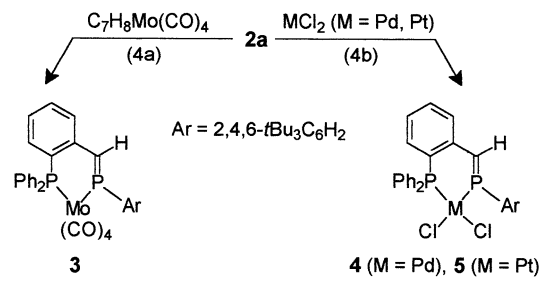
For the synthesis of the ligand **2a** easily accessible *ortho*-diphenylphosphino benzaldehyde (**1a**) [7] was used as the starting material. The phosphaalkene moiety could be introduced by the Yoshifuji procedure [10] employing 2,4,6-*t*-$Bu_3C_6H_2$-PH_2 (**1b**) [11] as the primary phosphine (Eq. (2) in Scheme 2). After workup conventional of the reaction mixture the phosphaalkene-phosphine ligand **2a** was obtained in high yield as a yellow crystalline solid.

In the $^{31}P\{^1H\}$-NMR spectrum **2a** shows two doublets at $\delta P = 268.2$ and -14.0 ($^4J(PP) = 20.4$ Hz). The δP value of the low field resonance is in the range typical for phosphaalkenes R–P=C–H)R′ bearing aromatic or aliphatic substituents R and R′ [12]. The resonance at $\delta P = 268.2$ appears as a doublet of doublets due to additional P–H coupling in the ^{31}P-NMR spectrum ($^2J(PH) = 24.7$ Hz) with broadened center lines. The $^{13}C\{^1H\}$-NMR signals of **2a** could be assigned by comparison with the corresponding data of **H** [10] and related compounds and by making use of ^{13}C-DEPT-NMR spectra. For the carbon atom of the P=C double bond a resonance at $\delta C = 174.5$ is observed showing a doublet of doublet P–C coupling fine structure ($^1J(PC) = 23.4$, $^3J(PC) = 13.2$ Hz).

Correspondingly the ^1H-NMR resonance of the vinylic α-hydrogen atom ($\delta H = 9.29$) shows doublet of doublet splitting ($^2J(PH) = 24.7$, $^4J(PH) = 5.8$ Hz). These data are in agreement with the structure proposed for **2a** with an *E*-configurated phosphaalkene substituent in *ortho*-position to the Ph_2P group. The assignment of an *E*-configuration to the ArP=C(H) unit in **2a** is supported by comparison with the pertinent NMR data of the *E*-isomers of phosphaalkenes of type **H** [10,13].

The mass spectrum of **2a** shows the peak for the molecular ion at $m/e = 550$ and peaks for fragment ions at $m/e = 494$ ($M^+ - C_4H_8$), 474 ($M^+ - C_6H_4$) with the basis peak at $m/e = 305$ corresponding to $M^+ - t$-$Bu_3C_6H_2$.

On irradiation of **2a** in benzene solution with a mercury lamp photoisomerization to **2b**, the *Z*-isomer



Scheme 3.

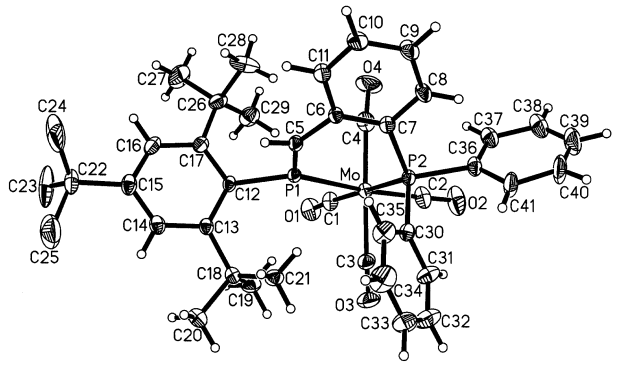


Fig. 1. Molecular structure of $3 \cdot C_7H_{16}$. Selected bond lengths (Å) and angles (°): Mo–P(1) 2.4729(14), Mo–P(2) 2.5239(14), Mo–C(1) 1.985(6), Mo–C(2) 1.965(7), Mo–C(3) 2.039(7), Mo–C(4) 2.031(8), P(1)–C(5) 1.668(5), P(1)–C(12) 1.857(5), P(2)–C(7) 1.837(5), C(5)–C(6) 1.443(7), C(6)–C(7) 1.423(7); P(1)–Mo–P(2) 81.89(5), Mo–P(1)–C(5) 121.8(2), Mo–P(1)–C(12) 139.3(2), C(5)–P(1)–C(12) 98.7(2), Mo–P(2)–C(7) 116.6(2), P(1)–C(5)–C(6) 131.4(4), C(5)–C(6)–C(7) 126.5(5), C(5)–C(6)–C(11) 116.3(5).

of **2a** occurs. The *Z*- and *E*-isomers are obtained in a ca. 1:1 ratio (Eq. (3) in Scheme 2). UV light induced *E*/*Z* isomerization of phosphaalkenes has been reported in the literature before [10,13]. The ^{1}H-NMR resonances of the vinylic protons of **2b** ($\delta H = 9.25$, $^2J(PH) = 35.8$, $^4J(PH) = 8.9$ Hz) and the aromatic hydrogens of the 2,4,6-*t*-$Bu_3C_6H_2$ substituent appear at higher field ($\delta H = 7.61$). The same applies for the *t*-Bu group in *ortho*-position, while the signals of the *t*-Bu groups in *para*-position are shifted to low field. The $^{13}C\{^1H\}$-NMR resonance of the P=C unit in **2b** ($\delta C =$ 159.9) appears at higher field compared with that of **2a**. This is in agreement with the corresponding $^{13}C\{^1H\}$-NMR data obtained for the *E*/*Z* isomers of a series of phosphaalkenes [10,13,14]. As for **2a** the carbon atom of the P=C moiety in **2b** shows a doublet of doublet fine structure, the P–C coupling constants ($^1J(PC) = 51.4$, $^3J(PC) = 31.0$ Hz) being somewhat larger than those in **2a**. On isomerization of **2a** to **2b** the δP value of the phosphaalkene unit is shifted to high field ($\delta P = 248.7$). The assignment of the $^{13}C\{^1H\}$-NMR resonances to the *Z*-isomer in the reaction mixture obtained after UV irradiation of **2a** was achieved by comparison with the pertinent NMR data of structurally related phosphaalkenes for which *E*- and *Z*-isomers are known [10,13,14]. The $^{31}P\{^1H\}$ signals of **2b** at $\delta P = 248.7$ and -13.2 are split into doublets through P–P coupling ($^4J(PP) = 12.7$ Hz).

3. Formation of Mo(0), Pd(II), Pt(II) complexes of 2a

In order to demonstrate the capability of **2a** to function as a chelating agent, complexes with transition metals (Mo(0), Pd(II), Pt(II)) in different oxidation states and coordination geometries have been synthesized. Analysis of the IR and NMR spectroscopic data of the complexes obtained should reveal the bonding mode and the ligand properties of this novel λ^2,λ^3-phosphorus donor system.

Thus on reaction of **2a** with $C_7H_8Mo(CO)_4$ [15] at ambient temperature red crystalline **3** was obtained in high yield (Eq. (4a) in Scheme 3). The $^{31}P\{^1H\}$ resonance of the PPh_2 group in **3** ($\delta P = 34.5$) is shifted by ca. 50 to low field compared with the corresponding δP value of **2a**. The chemical shift value δP ($\delta P = 256.5$) and the small negative coordination chemical shift [16a] $\Delta\delta P = \delta P(\text{complex}) - \delta P(\text{ligand}) = -11.7$ of the signal of the λ^2-phosphorus is in agreement with a η^1-coordination mode of the phosphaalkene moiety to the metal [17]. On coordination to Mo(0) the P–P coupling constant of the ligand **2a** ($^4J(PP) = 30.5$ Hz) increases significantly ($^2J(PP) = 20.4$ Hz in **3**). The η^1-coordination mode of the phosphaalkene unit is also supported by the small coordination chemical shift $\Delta\delta C$ (-5.4) in the $^{13}C\{^1H\}$-NMR spectrum of **2a**.

The IR spectrum of **3** displays four bands in the carbonyl stretching region at 2027, 1942, 1928, 1920 cm^{-1} placing **3** with its averaged electronic parameter *v* [18a] in between Ph_2PH and Ph_3P [18b].

The mass spectrum of **3** shows peaks centered at $m/e = 757$ derived from the molecular ion ($m/e = 760$, ^{98}Mo) by hydrogen abstraction and cluster of peaks for fragment ions at 730, 703, 676 and 647, which may be assigned to fragmentation of up to four CO ligands, the basis peak at $m/e = 231$ corresponding to {*t*-$Bu_3C_6H_2$-CH_2}.

When **2a** was allowed to react with palladium(II) or platinum(II) dichloride in methanol the yellow colored complexes **4** and **5** of composition MCl_2(**2a**) are formed (Eq. (4b)). Complex **4** may be obtained alternatively by the reaction of **2a** with K_2PdCl_4. While the $^{31}P\{^1H\}$ resonances of the PPh_2 groups in both cases are shifted to low field (**4**: $\delta P = 22.2$, **5**: 2.1) a high field shift is observed for the phosphaalkene moiety (**4**: $\delta P = 194.71$, **5**: 169.7) with respect to the corresponding data in **2a** ($\delta P = 268.2$). The $^{31}P\{^1H\}$ signals show doublet P–P coupling fine structure with a P–P coupling constant typical for *cis*-MCl_2L_2 (M = Pd, Pt; L = phosphine ligands) [19a] (**4**: $^2J(PP) = 24.2$, **5**: $^2J(PP) = 36.0$ Hz). The doublets in the $^{31}P\{^1H\}$-NMR spectra of **5** are accompanied by ^{195}Pt satellites. For the PPh_2 group the ^{195}Pt–^{31}P coupling constant ($^1J(^{195}Pt–^{31}P) = 3175.9$ Hz) is within the range typical for *cis*-$PtCl_2L_2$ complexes (L = mono- or bidentate phosphine ligands), e.g. *cis*-$PtCl_2(PTol_3)_2$: 3694 Hz [19b]; *cis*-$PtCl_2[Ph_2P–(CH_2)_n–PPh_2]$ ($n = 1–3$): 3078–3420 Hz [19c]. A significantly higher value is observed for the ^{195}Pt–^{31}P coupling constant of the phosphaalkene phosphorus atom ($^1J(^{195}Pt–^{31}P) = 4195.4$ Hz) in **5**. This value may well be compared with the one obtained for the structurally related *cis*-$PtCl_2(PEt_3)$(Mes-P=CPh_2) (4294 Hz) [20].

4. X-ray structure of 3

In order to get detailed information about the coordination mode of the phosphaalkene moiety and the mutual influence of the λ^2,λ^3-phosphorus donor groups in **3** a crystal structure investigation was performed. A view of the molecular structure of **3** is presented in Fig. 1, and relevant interatomic distances and angles are given in the caption of Fig. 1. This study clearly shows that the chelate ligand **2a** is coordinated to the metal by two σ-Mo–P bonds.

Of these, that formed by the three-coordinate P(1) atom is significantly (0.051(2) Å) shorter than that formed by the four-coordinate P(2) atom. The double bond character of the P(1)–C(5) interaction is demonstrated by its 1.668(5) Å length and the deviation of only 0.050(2) Å of the P(1) atom from the plane through its Mo, C(5) and C(12) substituents. A similar P=C bond length as in **3** has been found for $(CO)_5Cr(\eta^1$-Mes-P = $CPh_2)$ (**I**) (1.679(4) Å) [21]. The P=C distances in **3** and **I** do not differ significantly from that in the free phosphaalkenes [1]. For 2,4,6-$Me_3C_6H_2$–P = C(Ph)(2-*i*-PrC_6H_4) [22] with a similar substitution at the carbon and phosphorus atom of the P=C unit as in **3** a value of 1.682(2) Å was observed.

Despite the P(1)–C(5) multiple bond, the C(5)–P(1)–C(12) angle is 40.6(3)° smaller than the Mo–P(1)–C(12) angle. This asymmetry may in part be due to the steric interactions between the $Mo(CO)_4$ group and the bulky 2,4,6-tri-*t*-butylphenyl residue. The aromatic ring of the latter forms an angle of 80.5(2)° with the substituent plane of the P(1) atom. As is evident in Fig. 1, the six-membered chelate ring is nonplanar, a twist boat conformation being adopted. In accordance with the multiple bond nature of the P(1)–C(5) and C(6)–C(7) linkages, the C(5)–C(6)–C(7)–P(2) and Mo–P(1)–C(5)–C(6) fragments of the chelate ring are planar within ± 0.034 Å. Apparently π-conjugation between these two fragments is not disrupted by the $-25.2(8)°$ torsion along the P(1)–C(5)–C(6)–C(6)–C(7) sequence, the C(5)–C(6) bond length of 1.443(7) Å indicating a significant degree of multiple bonding.

5. Experimental

The starting materials were characterized by ^{1}H-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR spectroscopy and mass spectrometry. ^{1}H-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR spectra were recorded on a Bruker AC 400 or AM 250 and a JEOL FX90 Q Fourier transform spectrometer. Mass spectra were obtained on a Varian MAT 311A. The compounds 2,4,6-*t*-$Bu_3C_6H_2$–PH_2 (**1b**) [11], $C_7H_8Mo(CO)_4$ [15] and 2-PPh_2–C_6H_4–CHO [7b] were prepared according to literature methods. *t*-$BuMe_2SiCl$ was purchased from Aldrich GmbH.

5.1. Synthesis of *2a* and *2b*

5.1.1. Synthesis of *2a*

To a stirred solution of 5.00 g (17.9 mmol) of **1b** in 100 ml of THF 17.9 mmol of *n*-butyllithium dissolved in *n*-hexane was added at -78°C. The solution was allowed to warm up to ambient temperature and 2.70 g (17.9 mmol) of *t*-$BuMe_2SiCl$ dissolved in 50 ml of THF were added. After cooling to -30°C the second equivalent of *n*BuLi (17.9 mmol) was added. Thereafter the red colored reaction mixture was charged at ambient temperature with 3.62 g (12.5 mmol) of **1a**, dissolved in 50 ml of THF, until the color of the lithium phosphide had disappeared. All volatiles were then removed in vacuo (20°C, 0.01 mbar). The residue obtained was dissolved in ether and washed with 200 ml of a dilute solution of $NaHCO_3$. Thereafter the organic phase was separated and dried over $MgSO_4$ and the solvent was evaporated in vacuo. The yellow colored solid thus obtained was washed with 20 ml of hot methanol and recrystallized from a 60:5 ethanol–methanol mixture. Yield: 5.5 g (80%).

2a: Anal. Found: C, 79.93; H, 8.00. Calc. for $C_{37}H_{44}P_2$ (550.7): C, 80.69; H, 7.99%. — MS: (m/e) = 550 $[M^+]$, 494 $[M^+ - C_4H_9]$, 474 $[M^+ - C_6H_5]$, 305 $[M^+ - t\text{-}Bu_3C_6H_2]$; — ^{1}H-NMR ($C_6H_6$-$d_6$, δ): 1.30 (*p*-*t*-Bu), 1.57 (*o*-*t*-Bu), 6.9–7.3, (arom. H), 7.63 (arom. H, 2,4,6-*t*-$Bu_3C_6H_2$), 8.32, 9.29 (J = 24.7, 5.8 Hz); — $^{13}C\{^1H\}$-NMR (C_6H_6-d_6, δ): 174.5 (J = 23.4, 13.2 Hz), 154.6, 149.9, 145.1 (J = 13.2, 13.2 Hz), 139.6 (J = 57.0 Hz), 137.5 (J = 11.2 Hz), 135.2 (J = 14.2, 14.2 Hz), 134.6, 134.3 (J = 19.2 Hz), 129.5, 128.7 (J = 7.1 Hz), 128.6, 128.5 (J = 6.1 Hz), 126.1 (J = 27.4, 4.1 Hz), 122.0, 38.4, 35.1, 34.2 (J = 6.1 Hz), 31.5; — $^{31}P\{^1H\}$-NMR (C_6H_6-d_6, δ): 268.2 (J = 20.4 Hz), -14.0 (J = 20.4 Hz).

5.1.2. Irradiation of *2a*

A benzene solution of 0.39 g (0.7 mmol) of **2a** in 20 ml of benzene was irradiated for 6 h with a mercury high pressure lamp with cooling. Thereafter the ^{1}H-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR spectra of the reaction mixture were taken. The resonances which could be assigned to the *Z*-isomer **2b** are collected below.

2b: ^{1}H-NMR (C_6H_6-d_6, δ): 1.45 (*p*-*t*-Bu), 1.55 (*o*-*t*-Bu), 7.2–8.3 (arom. H), 7.61 (arom. H, 2,4,6-*t*-$Bu_3C_6H_2$), 9.25 (J = 35.8, 8.9 Hz;) — ^{13}C-NMR (C_6H_6-d_6, δ): 159.9 (J = 51.4, 31.0 Hz), 154.2, 151.0, 142.9 (J = 22.9, 22.9 Hz), 137.1 (J = 11.2 Hz), 137.0 (J = 10.2 Hz), 136.4 (J = 13.2, 13.2 Hz), 134.6, 134.0 (J = 4.1 Hz), 129.9 (J = 9.7, 2.5 Hz), 128.8 (J = 5.1 Hz), 128.7 (J = 10.2 Hz), 128.5 (J = 2.0 Hz), 127.8 (J = 7.1 Hz), 122.6, 38.3, 35.2, 33.0, 31.7; — $^{31}P\{^1H\}$-NMR

(C_6H_6-d_6, δ): 248.7 ($J = 12.7$ Hz), −13.1 ($J = 12.7$ Hz).

5.2. Synthesis of the complexes **3**–**5**

5.2.1. Preparation of **3**

2,5-Norbornadiene-tetracarbonyl molybdenum(0) (0.06 g, 0.2 mmol) and **2a** (0.11 g, 0.2 mmol) were dissolved in 20 ml of benzene and the solution was stirred at ambient temperature for 1.5 days. Thereafter all volatiles were removed in vacuo (20°C, 0.01 mbar) and the remaining red colored residue was recrystallized from *n*-heptane. Yield: 0.09 g (60%).

3: Anal. Found: C, 65.74; H, 6.08. Calc. for $C_{41}H_{44}MoO_4P_2$ (758.7): C, 64.91; H, 5.84%. — MS: (m/e) = 757 [$^{98}M^+ - 3H$]; 730 [$^{98}M^+ - CO - 2H$], 703 [$^{98}M^+ - 2CO - H$], 676 [$^{98}M^+ - 3CO$], 647 [$^{98}M^+ - 4CO - 3H$]; — ^{1}H-NMR (C_6H_6-d_6, δ): 1.39 (*p*-*t*-Bu), 1.64 (*o*-*t*-Bu), 6.4–7.4 (arom. H); — ^{13}C-NMR (C_6H_6-d_6, δ): 209.4, 169.1 ($J = 36.1$, 7.6 Hz), 156.1, 151.4, 144.1 ($J = 15.3$ Hz), 137.9 ($J = 4.1$ Hz), 136.0 ($J = 34.6$, 4.1 Hz), 133.6 ($J = 13.2$ Hz), 133.2 ($J = 3.1$ Hz), 132.1 ($J = 22.4$, 7.1 Hz), 130.8, 130.0, 128.7 ($J = 9.2$ Hz), 128.7 ($J = 5.7$, 5.7 Hz), 125.1 ($J = 31.0$, 8.7 Hz), 122.9 ($J = 6.1$ Hz), 39.3, 35.1, 32.0, 31.3; — ^{31}P{^{1}H}-NMR (C_6H_6-d_6, δ): 256.5 ($J = 30.5$ Hz), 34.5 ($J = 30.5$ Hz); IR (hexane, cm^{-1}): 2027(s), 1942(m), 1928(s), 1920(s).

5.2.2. Preparation of **4** and **5**

To a suspension of 0.60 g (3.4 mmol) of $PdCl_2$ or 0.294 g (1.1 mmol) of $PtCl_2$ in 20 ml of methanol 1.87 g (3.4 mmol) or 0.607 g (1.1 mmol) of **2a** were added with stirring at ambient temperature. The yellow precipitate that formed after 3 days was separated by filtration through a suction funnel. In the case of **4** the solid was washed with three aliquots of 35 ml of hot ethanol. The residue was dried in vacuo. For the isolation of **5** the yellow solid was suspended in 10 ml of dichloromethane and filtered through a glasfritted funnel. The solvent was removed from the filtrate in vacuo and the residue was washed with 20 ml of hot ethanol. Yields: 2.1 g (85%) **4**, 0.7 g (78%) **5**.

For the preparation of **4** instead of $PdCl_2$ 0.23 g (0.7 mmol) of K_2PdCl_4 and 0.51 g (0.9 mmol) of **2a** could be used. The workup procedure is as above.

4: Anal. Found: C, 61.02; H, 6.01. Calc. for $C_{37}H_{44}Cl_2P_2Pd$ (728.0): C, 61.04; H, 6.09%. — ^{1}H-NMR (CD_2Cl_2, δ): 1.39 (*p*-*t*-Bu), 1.54 (*o*-*t*-Bu), 6.90 ($J = 11.2$, 8.1 Hz), 7.2–7.7 (arom. H); — ^{13}C-NMR (CD_2Cl_2, δ): 155.4 ($J = 2.0$ Hz), 153.9 ($J = 2.0$ Hz), 146.9 ($J = 63.1$, 17.3 Hz), 141.4 ($J = 12.7$, 4.6 Hz), 136.4 ($J = 4.6$ Hz), 134.5 ($J = 11.2$ Hz), 133.5, 132.6 ($J = 24.9$, 7.6 Hz), 132.1 ($J = 3.1$ Hz), 130.7 ($J = 8.7$ Hz), 129.1 ($J = 12.2$ Hz), 128.7 ($J = 60.0$ Hz), 124.8 ($J = 11.2$ Hz), 123.2 ($J = 30.5$ Hz), 116.8 ($J = 53.4$, 25.0 Hz), 39.5, 35.4, 35.1, 31.1; — ^{31}P{^{1}H}-NMR (CD_2Cl_2, δ): 194.7 ($J = 24.2$ Hz), 22.2 ($J = 24.2$ Hz).

5: Anal. Found: C, 54.10; H, 5.73. Calc. for $C_{37}H_{44}Cl_2P_2Pt$ (816.7): C, 54.43; H, 5.43%. — ^{1}H-NMR (CD_2Cl_2, δ): 1.58 (*p*-*t*-Bu), 1.37 (*o*-*t*-Bu), 6.90 ($J = 12.0$, 7.9 Hz), 7.2–7.8 (arom. H), 7.89 ($J = 17.8$, 2.5 Hz). — ^{13}C-NMR (CD_2Cl_2, δ): 155.7 ($J = 4.0$ Hz), 154.0 ($J = 3.1$ Hz), 142.1 ($J = 11.7$, 5.6 Hz), 138.1 ($J = 84.4$, 11.2 Hz), 136.3 ($J = 5.6$, 5.6 Hz), 134.5 ($J = 10.2$ Hz), 133.2, 132.0 ($J = 2.0$ Hz), 131.9 ($J = 28.0$, 6.6 Hz), 129.6 ($J = 8.7$, 8.7 Hz), 128.9 ($J = 12.2$ Hz), 128.9 ($J = 69.2$ Hz), 124.8 ($J = 11.2$ Hz), 121.2 ($J = 47.8$ Hz), 115.3 ($J = 63.1$, 19.3 Hz), 39.7, 35.5, 35.1, 31.1; — ^{31}P{^{1}H}-NMR (CD_2Cl_2, δ): 169.7 ($J = 4195.4$, 36.0 Hz), 2.1 ($J = 3175.9$, 36.0 Hz).

5.3. X-ray structure analysis of **3**·C_7H_{16}

Crystallization of the molybdenum complex **3** proved difficult — evaporation of solutions in a variety of solvents leading to microcrystalline material. Crystals suitable for X-ray structural analysis were only obtained when heptane was used as the solvent. Such a crystal was sealed in a glass capillary. X-ray measurements were made with a Siemens P3 diffractometer using Mo–K_α radiation (0.71073 Å) and a graphite monochromator. Intensities were extracted from the profiles of $\theta - 2\theta$ scans, and they were corrected for the slight shift of the three periodically monitored standard reflections and absorption. The data were merged in accordance with the Laue symmetry of the crystal to give unique reflections. Direct methods revealed a large fragment of the molybdenum complex, and its remaining non-hydrogen atoms were located in a subsequent difference Fourier map.

After these atoms were refined anisotropically, the associated hydrogen atoms were entered in calculated positions (C–H = 0.95 Å) and assigned isotropic temperature factors. After refinement of this model ($wR_2 = 0.177$), a difference Fourier synthesis was calculated in order to locate the heptane molecule. While the atomic positions could not be resolved, a banana-shaped region of continuous electron density between 0.2 and 0.9 e Å^{-1} was found to extent for about 8 Å in a channel lying parallel to the *a*-axis. Apparently the heptane molecule is disordered, and a disorder model was constructed from a planar C_7 chain by rotating this fragment by 90, 180, and 270° about an axis that runs through the midpoints of the six C–C bonds. The 28 atoms of this model were given occupancies of 0.25 and a common isotropic temperature factor, and the atomic assembly was refined as a rigid group. While the use of this disorder model lowered the standard deviations of the complex by about 20%, the coordinates of the heptane carbon atoms cannot be taken seriously. The planar chains seem to be extended in the channel —

Table 1
Crystallographic data for $3 \cdot C_7H_{16}$

Empirical formula	$C_{41}H_{44}MoO_4P_2 \cdot C_7H_{16}$
Formula weight	858.84
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	16.009(3)
b (Å)	16.358(4)
c (Å)	18.163(4)
V (Å^3)	4756.3(17)
Z	4
D_{calc} (g cm^{-3})	1.199
T (K)	290(2)
θ Range (°)	2.10–25.06
Limiting indices	$0 \leq h \leq 19,\ 0 \leq k \leq 19,\ -21 \leq l \leq 21$
Reflections collected	9344
Unique	8429
R_{int}	0.0215
Observed ($I > 2\sigma$)	6263
Crystal size (mm)	$0.31 \times 0.29 \times 0.24$
μ (mm^{-1})	0.382
Transmission	0.9248–0.9077
R_1 (all data)	0.0644
WR_2 (all data)	0.1259
Goodness-of-fit	0.954
Parameters	441
ΔF (e Å^{-3})	0.489/−0.300
Flack parameter	−0.02(5)

contacts between the end of one chain and the beginning of a symmetry-related molecule being as short as 2.7 Å. Crystal data are listed in Table 1. While the Flack parameter indicates that the absolute structure has been determined correctly, we note that the chirality of the structure results from the packing of the molecules that are achiral in solution. The structure was solved, refined and displayed with a SHELXTL program package [23].

6. Supplementary material

Additional crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-154254. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK [Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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