

Hepta-1,6-diene and diallyl ether complexes of palladium(0) and platinum(0): a route to L–M(alkene)₂ complexes containing non-activated alkenes

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With hepta-1,6-diene and diallyl ether, Pd⁰ and Pt⁰ form highly reactive homoleptic dinuclear M₂(1,6-diene)₃ complexes, which are cleaved by donors L (e.g. C₂H₄, phosphanes, phosphites, isonitriles) to afford mononuclear derivatives L–M(1,6-diene); the X-ray structure of (Me₃P)Pd{(η²-CH₂=CHCH₂)₂O} has been determined.

Although d¹⁰ L–M(alkene)₂ complexes with non-activated alkenes are well known for M = Ni, Pt, they are scarce for M = Pd. Indeed, whereas the full series of phosphane derivatives with R = Me, Et, Prⁱ, Ph, and Cy is known for the parent ethene complexes (R₃P)M(C₂H₄)₂ (M = Ni, Pt), (Cy₃P)Pd(C₂H₄)₂¹ is apparently the only reported Pd derivative. In view of their potential importance as a source of the [L–Pd⁰] moiety for stoichiometric and catalytic reactions in homogeneous solutions under mild conditions,² it is clearly highly desirable to have a convenient route to reactive L–Pd(alkene)₂ complexes.

Following on from our synthesis of *rac/meso*-(μ-η²,η²-C₇H₁₂){Ni(η²,η²-C₇H₁₂)₂},³ we have reacted (cod)PdCl₂ with Li₂cot in hepta-1,6-diene and obtained a colorless precipitate of the Pd derivative **1** (61%). Analogously, reaction in diallyl ether yields complex **2** and in tetramethyldivinylsiloxane complex **3** (Scheme 1). The latter corresponds to the already known {μ-(η²-CH₂=CHSiMe₂)₂O}[M{(η²-CH₂=CHSiMe₂)₂O}]₂

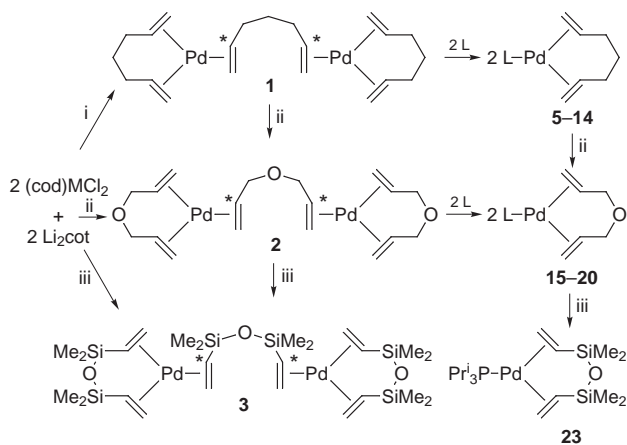
(M = Ni, Pt; the Pt *rac*-derivative is structurally characterized).⁴ Although complexes **1** and **2** slowly decompose around 0 °C, they are significantly more stable and easier to handle than, e.g., the comparable homoleptic Pd(cod)₂ or Pd(C₂H₄)₃.^{1,5} In the case of Pt⁰, we have prepared complex **4** (65%; mp 110 °C) by the same route as for **1**.

When **1–4** are reacted with π- or σ-donor molecules L, such as C₂H₄, PR₃ and P(OR)₃ (R = alkyl, aryl), and isonitriles,[‡] the bridging 1,6-diene ligand is displaced and complexes of the type L–M(1,6-diene) are obtained in 80–95% yield (Table 1). The products have been characterized by elemental analyses, mass spectra, IR and NMR spectra. In addition, the crystal structure of **15** has been determined (see below). Displacement reactions show that the hepta-1,6-diene ligands are readily replaced by diallyl ether or diallylamine and the latter by the divinylsiloxane (Scheme 2). The hepta-1,6-diene complexes are the most reactive and hence preferential starting materials. However, for many purposes the diallyl ether complexes are most convenient because of (i) good stability and easy isolation and handling, (ii) high reactivity, and (iii) low price of the ligand. A survey of the literature reveals that **18** has been previously obtained accidentally, but the excellent suitability of this class of complexes as starting materials for further reactions has apparently not been recognized.⁶ ¶ L–Pd(1,6-diene) complexes are generally stable

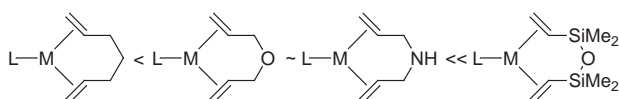
Table 1 Pd⁰ and Pt⁰ 1,6-diene complexes§

Complex	Formula ^a	Selected identifying data ^{b,c,d}
Pd ₂ (C ₇ H ₁₂) ₃ 1	C ₂₁ H ₃₆ Pd ₂ (501.4)	Voluminous precipitate, insoluble in thf; slowly decomp. ≈ 0 °C
Pd ₂ (C ₆ H ₁₀ O) ₃ 2	C ₁₈ H ₃₀ O ₃ Pd ₂ (507.3)	Poorly soluble in thf (–30 °C); slowly decomp. > 0 °C
Pd ₂ {(CH ₂ =CHSiMe ₂) ₂ O} ₃ 3	C ₂₄ H ₅₄ O ₃ Pd ₂ Si ₆ (772.0)	Off-white crystals; mp 55 °C
(C ₂ H ₄)Pd(C ₇ H ₁₂) 5	C ₉ H ₁₆ Pd (230.7)	Light yellow; extremely soluble; C ₂ H ₄ : δ(H) 3.39
(Me ₃ P)Pd(C ₇ H ₁₂) 6	C ₁₀ H ₂₁ PPd (278.7)	Mp ≈ 27 °C; δ(P) –22.3
(Pr ⁱ ₃ P)Pd(C ₇ H ₁₂) 7	C ₁₆ H ₃₃ PPd (362.8)	Mp 52 °C; M ⁺ 362; δ(P) 53.6
(Cy ₃ P)Pd(C ₇ H ₁₂) 8	C ₂₅ H ₄₅ PPd (483.0)	Mp 131 °C; M ⁺ 482; δ(P) 40.3
(Bu ^t ₃ P)Pd(C ₇ H ₁₂) 9	C ₁₉ H ₃₉ PPd (404.9)	Decomp. at 20 °C to give Pd(PBu ^t ₃) ₂ ; δ(P) 88.4 (–80 °C)
(Ph ₃ P)Pd(C ₇ H ₁₂) 10	C ₂₅ H ₂₇ PPd (464.9)	Mp 87 °C decomp.; δ(P) 30.6
{(4-MeC ₆ H ₄) ₃ P}Pd(C ₇ H ₁₂) 11	C ₂₈ H ₃₃ PPd (507.0)	Mp 114 °C; δ(P) 28.2
{(PhO) ₃ P}Pd(C ₇ H ₁₂) 12	C ₂₅ H ₂₇ O ₃ PPd (512.9)	Stable at 20 °C for several days; δ(P) 150.3
{(2,6-Me ₂ C ₆ H ₃ O) ₃ P}Pd(C ₇ H ₁₂) 13	C ₃₁ H ₃₉ O ₃ PPd (597.0)	Mp 131 °C decomp.; δ(P) 156.1
{(2,6-Pr ⁱ ₂ C ₆ H ₃ O) ₃ P}Pd(C ₇ H ₁₂) 14	C ₄₃ H ₆₃ O ₃ PPd (765.4)	Mp 142 °C; δ(P) 155.9
(Me ₃ P)Pd(C ₆ H ₁₀ O) 15	C ₉ H ₁₉ OPPd (280.6)	Mp 79 °C decomp.; δ(P) –21.8
(Pr ⁱ ₃ P)Pd(C ₆ H ₁₀ O) 16	C ₁₅ H ₃₁ OPPd (364.8)	Mp 63 °C; δ(P) 55.2
(Ph ₃ P)Pd(C ₆ H ₁₀ O) 17	C ₂₄ H ₂₅ OPPd (466.9)	Mp 112 °C decomp.; δ(P) 31.3
(Cy ₃ P)Pd(C ₆ H ₁₀ O) 18 ^e	C ₂₄ H ₄₃ OPPd (485.0)	Mp 145 °C; M ⁺ 484; δ(P) 41.8
{(PhO) ₃ P}Pd(C ₆ H ₁₀ O) 19	C ₂₄ H ₂₅ O ₄ PPd (514.9)	Mp 92 °C decomp.; δ(P) 151.4
(Bu ⁿ NC)Pd(C ₆ H ₁₀ O) 20	C ₁₁ H ₁₉ NOPd (287.7)	Tan; ν(N≡C) 2148 cm ^{–1}
(Pr ⁱ ₃ P)Pd(C ₆ H ₁₀ NH) 21	C ₁₅ H ₃₂ NPPd (363.8)	M ⁺ 363; δ(P) 54.7
(Ph ₃ P)Pd(C ₆ H ₁₀ NH) 22	C ₂₄ H ₂₆ NPPd (465.9)	δ(P) 31.2
(Pr ⁱ ₃ P)Pd{(CH ₂ =CHSiMe ₂) ₂ O} 23	C ₁₇ H ₃₉ OPPdSi ₂ (453.1)	Mp 75 °C decomp.; δ(P) 48.6
Pt ₂ (C ₇ H ₁₂) ₃ 4	C ₂₁ H ₃₆ Pt ₂ (678.7)	Voluminous precipitate, poorly soluble in thf; mp 110 °C decomp.
(C ₂ H ₄)Pt(C ₇ H ₁₂) 24	C ₉ H ₁₆ Pt (319.3)	Light yellow; extremely soluble; C ₂ H ₄ : δ(H) 2.91, ² J(PtH) 59 Hz
(Pr ⁱ ₃ P)Pt(C ₇ H ₁₂) 25	C ₁₆ H ₃₃ Pt (451.5)	Orange; mp 75 °C; M ⁺ 451; δ(P) 46.5, ¹ J(PtP) 3393 Hz
(Ph ₃ P)Pt(C ₇ H ₁₂) 26	C ₂₅ H ₂₇ Pt (553.5)	Yellow; mp 110 °C decomp.; M ⁺ 553; δ(P) 25.8, ¹ J(PtP) 3513 Hz

^a Satisfactory elemental analyses (C, H, P, Pd, Pt) were obtained for all compounds with the exception of non-isolated **5** and **24**. ^b All compounds are colorless, if not indicated otherwise. ^c EI mass spectra at 70 eV; the data refer to ¹⁰⁶Pd and ¹⁹⁵Pt. ^d ³¹P NMR shifts (downfield positive) relative to external 85% aqueous H₃PO₄; solvent is [D₂H₆]thf.



Scheme 1 Reagents and conditions: i, hepta-1,6-diene; ii, diallyl ether; iii, tetramethyldivinylsiloxane



Scheme 2 Sequence of increasing stability (decreasing reactivity) of $L-M(1,6\text{-diene})$ complexes ($M = Ni, Pd, Pt$)

and we have found that other 1,6-dienes, such as diallylsilanes, are equally applicable. In contrast, $L-M(1,6\text{-enyne})$ complexes ($M = Ni, Pd, Pt$) are apparently not stable.

The X-ray structure determination of **15** (Fig. 1) reveals a trigonal-planar ($TP-3$) coordination of the Pd atom by the phosphorus atom and the C=C bonds of the diallyl ether ligand. The geometry indicates that the 1,6-diene moiety is able to chelate two coordination sites at a $d^{10} TP-3 M^0$ center with little strain. Thus, the angles D1–Pd–D2, P–Pd–D1, and P–Pd–D2 (D1, D2 are the mid-points of the C=C bonds) are all very close to 120° , and the C=C carbon atoms lie exactly in the coordination plane. Moreover, the $Pd^0(1,6\text{-diene})$ moiety adopts the expected chair-like conformation, and the C=C bonds [mean $1.38(1) \text{ \AA}$] are only slightly lengthened as compared with an uncoordinated C=C bond (1.34 \AA), indicating that back-bonding is rather weak for Pd⁰.

These complexes find application in homogeneous catalysis in those cases where an unsaturated complex fragment [$L-Pd^0$] (L e.g. PPh_3), rather than a coordinatively saturated complex like $Pd(PPh_3)_4$, is expected to catalyze the reaction. For example, we have observed that [$L-Pd$] complexes (e.g. **7** and **16**) catalyze regio- and stereo-selectively the linear trimerization of alk-1-yne to 1,4,6-trisubstituted *cis*-hexa-1,3-dien-5-yne between -30 and 20°C (Scheme 3).⁷

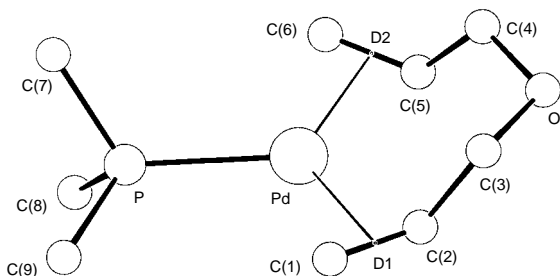
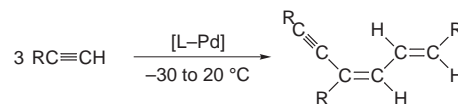


Fig. 1 Molecular structure of **15**. Selected bond lengths (\AA): Pd–P 2.303(1), Pd–C(1) 2.151(5), Pd–C(2) 2.155(5), Pd–C(5) 2.157(5), Pd–C(6) 2.160(5), C(1)–C(2) 1.364(8), C(5)–C(6) 1.386(9), D1...D2 3.57(1). Selected bond angles ($^\circ$): D1–Pd–D2 121.8(6), P–Pd–D1 119.4(3), P–Pd–D2 118.6(3).



Scheme 3 $R = Bu, CMe_2OH, Ph, Bu^t, SiMe_3$

Notes and References

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‡ It is expected that donors such as pyridines, phosphoranes, carbanions and heterocarbenes will coordinate together with 1,6-diene ligands on the Pd and Pt centers, as has already been shown for Ni.^{3,8,9}

§ *Representative synthesis protocols*: **1**: a 0.2 M solution of Li_2cot (150 ml, 30 mmol) in diethyl ether was slowly added to a suspension of $(cod)PdCl_2$ (8.57 g, 30 mmol) in 40 ml of hepta-1,6-diene at -78°C . When the temperature was raised to -40°C a voluminous precipitate began to form, consisting of **1** and $LiCl$. At -20°C the suspension was so dense that it could hardly be stirred. When diethyl ether was evaporated under vacuum at -10°C , **1** dissolved again. $LiCl$ was removed by filtration, and to the light green solution 50 ml of pentane was added (-30°C), whereupon pure, colorless **1** precipitated. The product was isolated by filtration, washed with cold pentane, and dried under vacuum (-30°C). Yield: 4.59 mg (61%).

7: a colorless solution of **1** (501 mg, 1.00 mmol) in 1 ml of hepta-1,6-diene was treated with a solution of PPr_3 (320 mg, 2.00 mmol) in 5 ml of pentane. When the mixture was cooled from -30 to -78°C colorless crystals separated. After disposal of the mother liquor the product was washed with cold pentane and dried under vacuum (20°C). Yield: 610 mg (84%).

16: a solution of **7** (363 mg, 1.00 mmol) in 5 ml of diethyl ether was treated with diallyl ether (0.13 ml, 1.05 mmol). After 1 h the colorless mixture was cooled to -78°C , whereupon the crystalline product separated (isolation as described for **7**). Yield: 347 mg (95%). For identifying data see Table 1.

¶ Other Pd complexes with substituted diallyl ether⁶ and hepta-1,6-diene-type ligands¹⁰ have been reported previously.

|| *Crystal data for 15*: $C_9H_{19}OPd$, $M_r = 280.6$, colorless prism, crystal size $0.28 \times 0.42 \times 0.46 \text{ mm}$, $a = 10.050(2)$, $b = 9.194(2)$, $c = 13.053(1) \text{ \AA}$, $\beta = 101.866(10)^\circ$, $V = 1180.2(4) \text{ \AA}^3$, $T 293 \text{ K}$, monoclinic, space group $P2_1/n$ (No. 14), $Z = 4$, $D_c = 1.58 \text{ g cm}^{-3}$, $\mu = 1.67 \text{ mm}^{-1}$. Enraf-Nonius CAD4 diffractometer. Mo-K α X-radiation, $\lambda = 0.71069 \text{ \AA}$. 5598 measured reflections, 2688 unique, 2315 observed [$I > 2.0\sigma(F_o^2)$]. The structure was solved by direct methods (SHELXS-86) and refined by full-matrix least-squares on F^2 for all data with Chebyshev weights to $R = 0.043$ (obs.), $wR = 0.118$ (all data), $S = 1.07$, H atoms isotropic, max. shift/error 0.001, residual $\rho_{\text{max}} = 1.95 \text{ e \AA}^{-3}$, 0.8 \AA from Pd. CCDC 182/845.

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Received in Cambridge, UK, 27th March 1998; 8/02381F