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

Jochen Krause, Karl-Josef Haack, Günter Cestaric, Richard Goddard and Klaus-Richard Pörschke*†

Max-Planck-Institut für Kohlenforschung, Postfach 10 13 53, D-45466 Mülheim an der Ruhr, Germany

With hepta-1,6-diene and diallyl ether, Pd^0 and Pt^0 form highly reactive homoleptic dinuclear M_2(1,6-diene)$_3$ complexes, which are cleaved by donors L (*e.g.* C_2H_4, phosphanes, phosphites, isonitriles) to afford mononuclear derivatives L–M(1,6-diene); the X-ray structure of $(Me_3P)Pd\{(\eta^2\text{-}CH_2{=}CHCH_2)_2O\}$ has been determined.

Although d^{10} 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, Pr^i, Ph, and Cy is known for the parent ethene complexes $(R_3P)M(C_2H_4)_2$ (M = Ni, Pt), $(Cy_3P)Pd(C_2H_4)_2$[1] is apparently the only reported Pd derivative. In view of their potential importance as a source of the [L–Pd^0] 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.

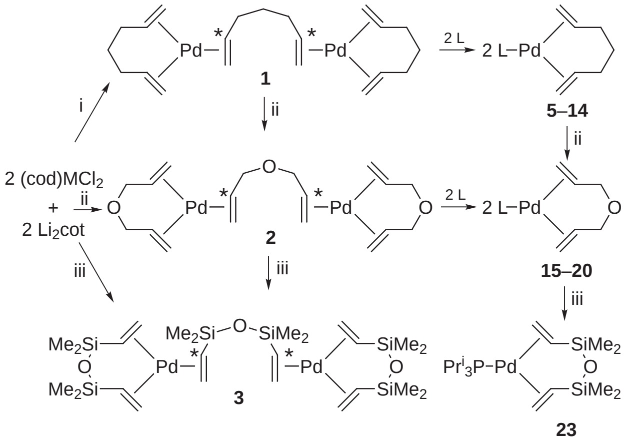
Following on from our synthesis of *rac*/*meso*-$(\mu\text{-}\eta^2,\eta^2\text{-}C_7H_{12})\{Ni(\eta^2,\eta^2\text{-}C_7H_{12})\}_2$,[3] we have reacted (cod)$PdCl_2$ with Li_2cot in hepta-1,6-diene and obtained a colorless precipitate of the Pd derivative **1** (61%). Analogously, reaction in diallyl ether yields complex **2** and in tetramethyldivinyldisiloxane complex **3** (Scheme 1). The latter corresponds to the already known $\{\mu\text{-}(\eta^2\text{-}CH_2{=}CHSiMe_2)_2O\}[M\{(\eta^2\text{-}CH_2{=}CHSiMe_2)_2O\}]_2$ (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 $Pd(C_2H_4)_3$.[1,5] In the case of Pt^0, 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 C_2H_4, PR_3 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 divinyldisiloxane (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

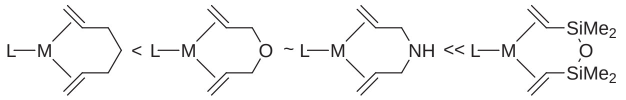
Table 1 Pd^0 and Pt^0 1,6-diene complexes§

Complex	Formula[a]	Selected identifying data[b,c,d]
$Pd_2(C_7H_{12})_3$ **1**	$C_{21}H_{36}Pd_2$ (501.4)	Voluminous precipitate, insoluble in thf; slowly decomp. ≈0 °C
$Pd_2(C_6H_{10}O)_3$ **2**	$C_{18}H_{30}O_3Pd_2$ (507.3)	Poorly soluble in thf (−30 °C); slowly decomp. >0 °C
$Pd_2\{(CH_2{=}CHSiMe_2)_2O\}_3$ **3**	$C_{24}H_{54}O_3Pd_2Si_6$ (772.0)	Off-white crystals; mp 55 °C
$(C_2H_4)Pd(C_7H_{12})$ **5**	$C_9H_{16}Pd$ (230.7)	Light yellow; extremely soluble; C_2H_4: δ(H) 3.39
$(Me_3P)Pd(C_7H_{12})$ **6**	$C_{10}H_{21}PPd$ (278.7)	Mp ≈27 °C; δ(P) −22.3
$(Pr^i_3P)Pd(C_7H_{12})$ **7**	$C_{16}H_{33}PPd$ (362.8)	Mp 52 °C; M^+ 362; δ(P) 53.6
$(Cy_3P)Pd(C_7H_{12})$ **8**	$C_{25}H_{45}PPd$ (483.0)	Mp 131 °C; M^+ 482; δ(P) 40.3
$(Bu^t_3P)Pd(C_7H_{12})$ **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)
$(Ph_3P)Pd(C_7H_{12})$ **10**	$C_{25}H_{27}PPd$ (464.9)	Mp 87 °C decomp.; δ(P) 30.6
$\{(4\text{-}MeC_6H_4)_3P\}Pd(C_7H_{12})$ **11**	$C_{28}H_{33}PPd$ (507.0)	Mp 114 °C; δ(P) 28.2
$\{(PhO)_3P\}Pd(C_7H_{12})$ **12**	$C_{25}H_{27}O_3PPd$ (512.9)	Stable at 20 °C for several days; δ(P) 150.3
$\{(2,6\text{-}Me_2C_6H_3O)_3P\}Pd(C_7H_{12})$ **13**	$C_{31}H_{39}O_3PPd$ (597.0)	Mp 131 °C decomp.; δ(P) 156.1
$\{(2,6\text{-}Pr^i_2C_6H_3O)_3P\}Pd(C_7H_{12})$ **14**	$C_{43}H_{63}O_3PPd$ (765.4)	Mp 142 °C; δ(P) 155.9
$(Me_3P)Pd(C_6H_{10}O)$ **15**	$C_9H_{19}OPPd$ (280.6)	Mp 79 °C decomp.; δ(P) −21.8
$(Pr^i_3P)Pd(C_6H_{10}O)$ **16**	$C_{15}H_{31}OPPd$ (364.8)	Mp 63 °C; δ(P) 55.2
$(Ph_3P)Pd(C_6H_{10}O)$ **17**	$C_{24}H_{25}OPPd$ (466.9)	Mp 112 °C decomp.; δ(P) 31.3
$(Cy_3P)Pd(C_6H_{10}O)$ **18**[6]	$C_{24}H_{43}OPPd$ (485.0)	Mp 145 °C; M^+ 484; δ(P) 41.8
$\{(PhO)_3P\}Pd(C_6H_{10}O)$ **19**	$C_{24}H_{25}O_4PPd$ (514.9)	Mp 92 °C decomp.; δ(P) 151.4
$(Bu^tNC)Pd(C_6H_{10}O)$ **20**	$C_{11}H_{19}NOPd$ (287.7)	Tan; ν(N≡C) 2148 cm^{-1}
$(Pr^i_3P)Pd(C_6H_{10}NH)$ **21**	$C_{15}H_{32}NPPd$ (363.8)	M^+ 363; δ(P) 54.7
$(Ph_3P)Pd(C_6H_{10}NH)$ **22**	$C_{24}H_{26}NPPd$ (465.9)	δ(P) 31.2
$(Pr^i_3P)Pd\{(CH_2{=}CHSiMe_2)_2O\}$ **23**	$C_{17}H_{39}OPPdSi_2$ (453.1)	Mp 75 °C decomp.; δ(P) 48.6
$Pt_2(C_7H_{12})_3$ **4**	$C_{21}H_{36}Pt_2$ (678.7)	Voluminous precipitate, poorly soluble in thf; mp 110 °C decomp.
$(C_2H_4)Pt(C_7H_{12})$ **24**	$C_9H_{16}Pt$ (319.3)	Light yellow; extremely soluble; C_2H_4: δ(H) 2.91, ^2J(PtH) 59 Hz
$(Pr^i_3P)Pt(C_7H_{12})$ **25**	$C_{16}H_{33}PPt$ (451.5)	Orange; mp 75 °C; M^+ 451; δ(P) 46.5, ^1J(PtP) 3393 Hz
$(Ph_3P)Pt(C_7H_{12})$ **26**	$C_{25}H_{27}PPt$ (553.5)	Yellow; mp 110 °C decomp.; M^+ 553; δ(P) 25.8, ^1J(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 ^{106}Pd and ^{195}Pt. [d] ^{31}P NMR shifts (downfield positive) relative to external 85% aqueous H_3PO_4; solvent is [$^2H_8$]thf.



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



Scheme 2 Sequence of increasing stability (decreasing reactivity) of L–M(1,6-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-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-diene) moiety adopts the expected chair-like conformation, and the C=C bonds [mean 1.38(1) Å] are only slightly lengthened as compared with an uncoordinated C=C bond (1.34 Å), indicating that back-bonding is rather weak for Pd^0.

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-ynes to 1,4,6-trisubstituted *cis*-hexa-1,3-dien-5-ynes between −30 and 20 °C (Scheme 3).[7]

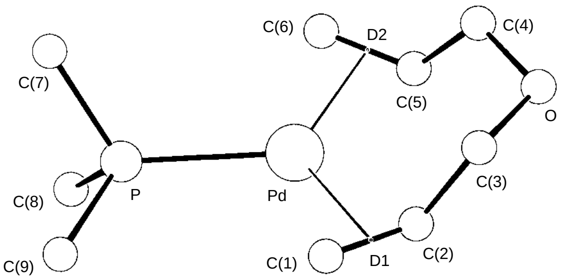
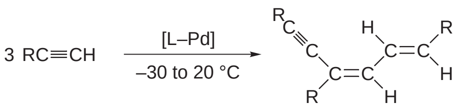


Fig. 1 Molecular structure of **15**. Selected bond lengths (Å): Pd–P 2.303(1), Pd–C(1) 2.151(5), Pd–C(2) 2.155(5), Pd–C(5) 2.157(5), Pd–C(6) 2.160(5), C(1)–C(2) 1.364(8), C(5)–C(6) 1.386(9), D1···D2 3.57(1). Selected bond angles (°): D1–Pd–D2 121.8(6), P–Pd–D1 119.4(3), P–Pd–D2 118.6(3).



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

Notes and References

† E-mail: poerschke@mpi-muelheim.mpg.de

‡ 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^i_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 ether[6] and hepta-1,6-diene-type ligands[10] have been reported previously.

‖ *Crystal data* for **15**: $C_9H_{19}OPPd$, M_r = 280.6, colorless prism, crystal size 0.28 × 0.42 × 0.46 mm, a = 10.050(2), b = 9.194(2), c = 13.053(1) Å, β = 101.866(10)°, V = 1180.2(4) Å^3, T 293 K, monoclinic, space group $P2_1/n$ (No. 14), Z = 4, D_c = 1.58 g cm^{-3}, μ = 1.67 mm^{-1}. Enraf-Nonius CAD4 diffractometer. Mo-Kα X-radiation, λ = 0.710 69 Å. 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 ρ_{max} = 1.95 e Å^{-3}, 0.8 Å from Pd. CCDC 182/845.

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