1,6-Diene Complexes of Palladium(0) and Platinum(0): Highly Reactive Sources for the Naked Metals and [L−M^0] Fragments

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Abstract: The complexes (cod)MCl_2 (M = Pd, Pt; cod = *cis*,*cis*-1,5-cyclooctadiene) react with Li_2(cot) (cot = cyclooctatetraene) in a 1,6-diene/diethyl ether mixture (1,6-diene = hepta-1,6-diene, diallyl ether, dvds (1,3-divinyl-1,1,3,3-tetramethyldisiloxane)) to afford the isolated homoleptic dinuclear Pd^0 and Pt^0 compounds $Pd_2(C_7H_{12})_3$ (**1**), $Pd_2(C_6H_{10}O)_3{\cdot}C_6H_{10}O$ (**2′**; **2**: $Pd_2(C_6H_{10}O)_3$), $Pd_2(dvds)_3$ (**3**), and $Pt_2(C_7H_{12})_3$ (**4**). When **1**−**4** are treated with additional 1,6-diene the equally homoleptic but mononuclear derivatives of type M(1,6-diene)$_2$ (**5**−**8**) and with ethene the mixed alkene complexes (C_2H_4)M(1,6-diene) (**9**−**12**) are obtained in solution. Complexes **1**−**12** react with donor ligands such as phosphanes, phosphites, or ^{t}BuNC to give isolated complexes of types L−M(1,6-diene) (**13**−**41**), which have also been prepared by other routes. In all complexes the metal centers are *TP*-3 coordinated: complexes **1**−**4** contain chelating and bridging 1,6-diene ligands, whereas the other complexes contain a chelating 1,6-diene ligand and an η^2-alkene (**5**−**12**) or η^1-donor ligand (**13**−**41**). Of the studied 1,6-diene complexes the hepta-1,6-diene derivatives are most reactive, while the diallyl ether complexes are often more convenient to handle. The readily isolable dinuclear hepta-1,6-diene and diallyl ether complexes **1**, **2′**, and **4**, and their mononuclear pure olefin derivatives are among the most reactive sources for naked Pd^0 and Pt^0. The corresponding L−M(1,6-diene) complexes are equally reactive precursor compounds for the generation of [L−M^0] fragments in solution, which for M = Pd are available otherwise only with difficulty. The results are significant for the operation of naked Pd^0 and L−Pd^0 catalysts in homogeneous catalysis.

Introduction

In organopalladium chemistry innumerable coupling reactions of organic substrates are known which are catalyzed by species derived from either $Pd(PR_3)_4$ (R, e.g., Ph)[1] or "$Pd(dba)_2$"[2] (dba = dibenzylideneacetone) as catalyst precursors.[3] It is generally agreed on that complexes such as $Pd(PPh_3)_4$[4] gradually dissociate in the course of the reactions to afford coordinatively unsaturated complexes such as 16e $(Ph_3P)_3Pd$,[5] 14e $(Ph_3P)_2Pd$,[6] and the elusive 12e [$(Ph_3P)Pd$].[7] Similarly, when mixtures of "$Pd(dba)_2$"[8] and PPh_3 are applied as catalysts, the dba ligands are gradually displaced or eliminated to afford $(Ph_3P)_2Pd(dba)$[9] and eventually $(Ph_3P)_2Pd$ and [$(Ph_3P)Pd$]. It appears that for many reactions in fact the usually nonisolable complex fragments [$(R_3P)_2Pd^0$], [{$(RO)_3P$}$_2Pd^0$], [$(R_3P)Pd^0$], and [{$(RO)_3P$}Pd^0] (R = alkyl, aryl) are the "true catalysts".

Additional insight into the importance of coordinative unsaturation was gained from an investigation by Hartwig on the function of isolated {(2-$MeC_6H_4)_3P$}$_2$Pd as a catalyst precursor for various coupling reactions. It was demonstrated through kinetic studies that the reactions were initiated by a loss of a P(*o*-tolyl)$_3$ ligand to generate 12e [{(2-$MeC_6H_4)_3P$}Pd] as a

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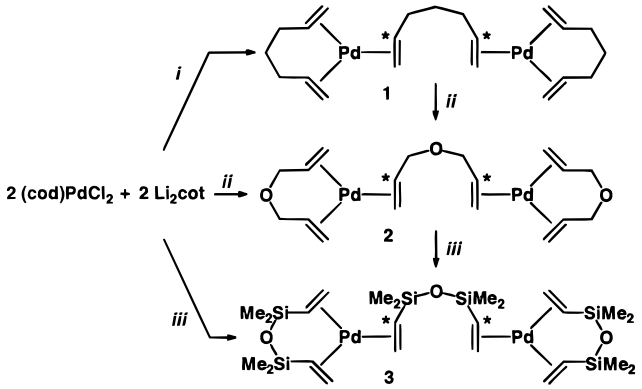
catalytically active intermediate.[10] [$(R_3P)Pd^0$]-type complexes are assumed to be also the "true catalysts" for the telomerization of butadiene.[11] Similarly, we have shown that $(^iPr_3P)_2Pd$[5b] is a catalyst for various coupling reactions (formation of germa- and stannacyclopentadienes by (2+2+1) cycloadditions; trimerization of terminal alkynes) and that phosphane dissociation is an essential step on the reaction path.[12,13]

Palladium complexes, in which the elusive [$(R_3P)Pd^0$] and [$\{(RO)_3P\}Pd^0$] (R = alkyl, aryl) fragments are stabilized by readily displaceable alkene ligands, are scarce. $(Cy_3P)Pd(C_2H_4)_2$[14a] is apparently the only ethene complex mentioned in the literature, although the series of phosphane derivatives $(R_3P)M(C_2H_4)_2$, R = Me, Et, ^{i}Pr, Ph, Cy, is known for M = Ni and Pt. However, some rare reports have appeared in which 1,6-diene ligands are coordinated to L−Pd^0 moieties. Thus, in the context of the Pd-catalyzed telomerization of butadiene with methanol, Jolly isolated complexes such as $(Me_3P)Pd\{C_7H_{11}(CH_2OMe)\}$ with a substituted hepta-1,6-diene ligand.[11] Continuing a related study on Ni^0 complexes,[15a] Yamamoto reported that allyl alcohol undergoes a dehydration reaction with $(Cy_3P)_2Pd$ to give the diallyl ether complex $(Cy_3P)Pd(C_6H_{10}O)$ (**26**), and with 1-methylallyl alcohol a substituted derivative $(Cy_3P)Pd(C_6H_8Me_2O)$ was obtained.[15b] It has apparently not been recognized in these studies that the L−Pd^0 complexes with heptadiene- and diallyl ether-type ligands are excellent starting materials to provide 12e [$(R_3P)Pd^0$] moieties under mild reaction conditions.

Our own studies on Pd^0− and Pt^0−1,6-diene complexes commenced with the finding that Ni^0 forms the dinuclear homoleptic hepta-1,6-diene complex *rac-/meso*-(μ-C_7H_{12})$\{Ni(C_7H_{12})\}_2$ in which the bridging hepta-1,6-diene ligand is easily replaced by donor ligands to produce a broad variety of L−$Ni(C_7H_{12})$ complexes.[16] Recognizing that 1,6-dienes also provide a general access to both the "naked" metals and 12e [L−M^0] fragments of palladium and platinum, and in view of their potential for stoichiometric and catalytic reactions under mild conditions, we set out to synthesize corresponding homoleptic complexes M_2(1,6-diene)$_3$ and donor ligand adducts L−M(1,6-diene) (M = Pd, Pt) and to study their reactivity. The focus of this work is primarily on palladium for which stable and yet highly reactive M^0 complexes are still missing. Part of this work[13] has already been communicated.[17]

Scheme 1[a]



[a] Reagents: (i) hepta-1,6-diene; (ii) diallyl ether; (iii) 1,3-divinyl-1,1,3,3-tetramethyldisiloxane.

Results

I. Homoleptic M_2(1,6-diene)$_3$ (1−4) and M(1,6-diene)$_2$ (5−8) (M = Pd, Pt). *rac-/meso*-$Ni_2(C_7H_{12})_3$[16a] and *rac-/meso*-$Pt_2(dvds)_3$[18a] are readily synthesized from Ni(cdt)[19] (cdt = *trans,trans,trans*-1,5,9-cyclododecatriene) and $Pt(cod)_2$[14,20] by displacement of the alkene ligands. In contrast, corresponding Pd^0 starting complexes to be considered for the synthesis of **1**−**3** are either thermally labile, i.e., accessible only with great difficulty ($Pd(cod)_2$, $Pd(C_2H_4)_3$),[14] or not sufficiently reactive ("$Pd(dba)_2$")[8] to be employed in practice. However, complexes **1**−**3** can be synthesized[21] from $(cod)PdCl_2$ by a route similar to Stone's synthesis of $Pd(cod)_2$.[14]

When the yellow suspension of $(cod)PdCl_2$ in a mixture of hepta-1,6-diene and diethyl ether is reacted with $Li_2(cot)$ between −78 and −10 °C, a thick slurry of **1** and LiCl precipitates. After evaporation of the diethyl ether, complex **1** dissolves in the neat hepta-1,6-diene. LiCl is removed by filtration, and after addition of an about equal volume of pentane pure colorless **1** (60%) precipitates between −30 and −78 °C (Scheme 1). Using diallyl ether as the 1,6-diene component affords **2′** in a similar reaction. Pure pale yellow **2′** (42%) slowly crystallizes from the diallyl ether/pentane mixture at ≤−30 °C. **2′** contains one molecule of cocrystallized diallyl ether (**2**: solvent-free $Pd_2(C_6H_{10}O)_3$). The synthesis of **3** follows that of **1** and **2′** by using dvds (20 °C) as a 1,6-diene. After removal of LiCl the dvds solution of **3** is evaporated to form a sticky oil, and addition of some pentane affords (−78 °C) microcrystalline, almost colorless **3** in 75% yield. Finally, in a synthesis

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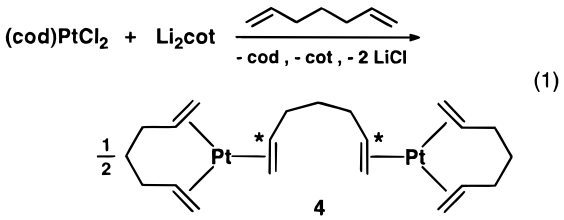
(21) Thermolysis of Pd(η^3-C_3H_5)$_2$ and (tmeda)$PdMe_2$ in neat hepta-1,6-diene results in deposition of elemental palladium, instead of the formation of **1**.

corresponding to that of **1**, (cod)$PtCl_2$ reacts with Li_2(cot) in hepta-1,6-diene to yield colorless microcrystalline **4** (40%) (eq 1), which is also obtained from $Pt(cod)_2$ and hepta-1,6-diene



by the displacement of the cod ligands. Compounds **1**−**4** supplement and complete the series of homologous d^{10} M^0−1,6-diene complexes $M_2(C_7H_{12})_3$ (M = Ni,[16a] Pd (**1**), Pt (**4**)), $M_2(C_6H_{10}O)_3$ (M = Ni,[16c] Pd (**2**), Pt[22]), and $M_2(dvds)_3$ (M = Ni,[16c,23] Pd (**3**), Pt[18a]).

Complex **2′** is also formed by displacing the hepta-1,6-diene ligands of **1**. Similarly, the diallyl ether ligands in **2** are displaced by dvds to yield **3** (Scheme 1). Thus, there is an increasing thermodynamic stability (decreasing reactivity) of the complexes in solution in the series **1** < **2** < **3**. The thermal stability of the solids also increases in the above series **1** (≈0 °C dec) < **2′** (>0 °C dec) < **3** (mp 55 °C dec). The Pt−hepta-1,6-diene complex **4** is more stable (indefinitely at ambient temperature; mp 110 °C dec) than any of the Pd complexes.

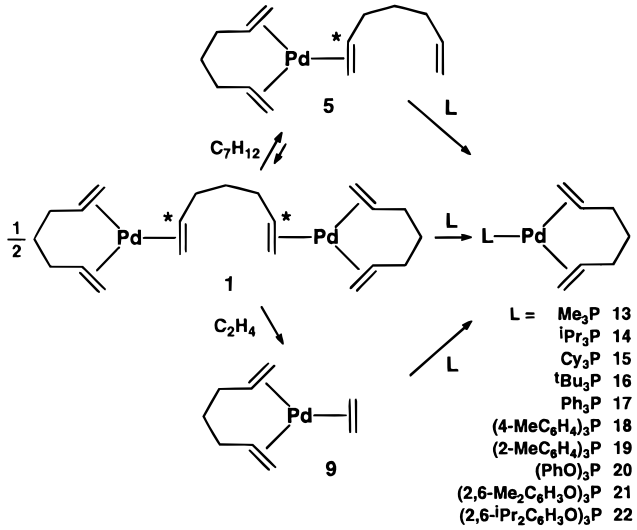
The dinuclear hepta-1,6-diene complexes **1** and **4** are only sparingly soluble in the usual solvents such as diethyl ether, THF, or toluene, whereas the dvds complex **3** dissolves quite well. The diallyl ether complex **2′** is moderately soluble; in solution dinuclear **2** and the diallyl ether contained in the crystal are in equilibrium with mononuclear **6** (NMR, see below). The low solubility of **1**, **2′**, and **4** is advantageous for the isolation of the compounds but impedes recording of informative NMR spectra for **1** and **4**. In contrast, dinuclear **1**−**4** dissolve very well in an *excess of the corresponding 1,6-dienes.* Such solutions of **1** and **2′** in hepta-1,6-diene or diallyl ether are more stable than the isolated complexes and decompose only after several days, and a dvds solution of **3** appears to be stable at ambient temperature for months. In these solutions the dinuclear complexes are in equilibrium with the excess of 1,6-diene to produce *mono*nuclear derivatives: dinuclear **1**, **2**, and **4** are quantitatively converted into mononuclear **5**, **6**, and **8**, respectively (Schemes 2, 3, and 5), whereas the dinuclear dvds complex **3** forms only little mononuclear **7** (Scheme 4). A similar equilibrium has been established for $Pt_2(dvds)_3$ and dvds, giving rise to $Pt(dvds)_2$.[24] The mononuclear complexes **5**−**8** can be considered to be the primary reaction products when the synthesis of **1**−**4** is carried out in 1,6-diene solution according to Scheme 1 and eq 1.

NMR Spectroscopic Characterization. The 300 MHz ^1H and 75.5 MHz ^{13}C NMR spectra of **1**−**8** have been recorded in THF-d_8 between −80 and 27 °C. In the following the spectra of the homoleptic dinuclear M_2(1,6-diene)$_3$ and corresponding mononuclear M(1,6-diene)$_2$ complexes are described in the order of the individual 1,6-dienes.

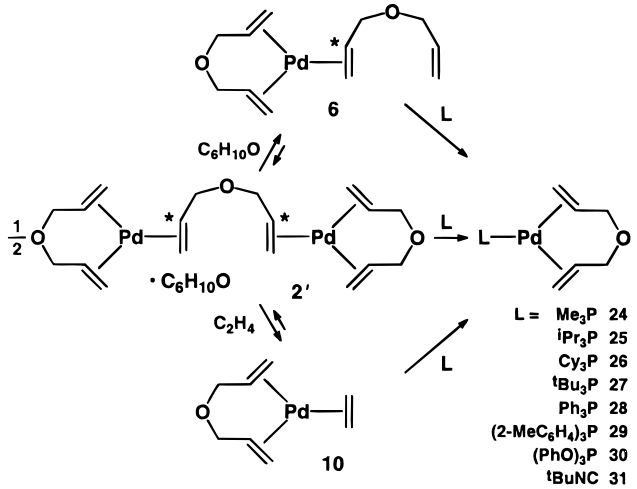
For the homoleptic dinuclear *hepta-1,6-diene* complexes **1** and **4** no meaningful NMR spectra have been obtained due to the poor solubility. It can be assumed that in analogy to the corresponding *rac-/meso*-$Ni_2(C_7H_{12})_3$[16a] the Pd and Pt atoms in dinuclear **1** and **4** are *TP*-3 coordinated by a chairlike chelating and a bridging hepta-1,6-diene ligand and that the complexes represent a mixture of *rac/meso* diastereomers. However, when an excess of hepta-1,6-diene is added to **1** and **4**, solutions of the mononuclear derivatives **5** and **8**, respectively, are obtained.

Complex **5** exhibits in the −80 °C ^{13}C NMR spectrum 14 signals (each 1C) of which two signals are attributed to an

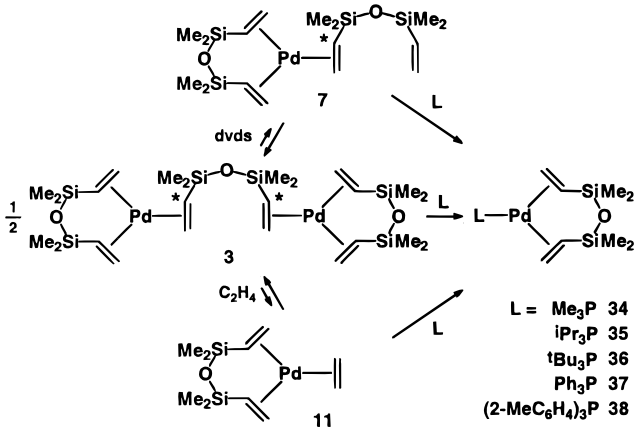
Scheme 2



Scheme 3



Scheme 4



(22) Preliminary experiments have shown that beige microcrystals of *rac-/meso*-$Pt_2(C_6H_{10}O)_3$, $C_{18}H_{30}O_3Pt_2$ (684.6), can be prepared by reaction of either **4** or $Pt(cod)_2$ with diallyl ether. The identity was determined by elemental analysis and the ^{13}C NMR spectrum (27 °C).

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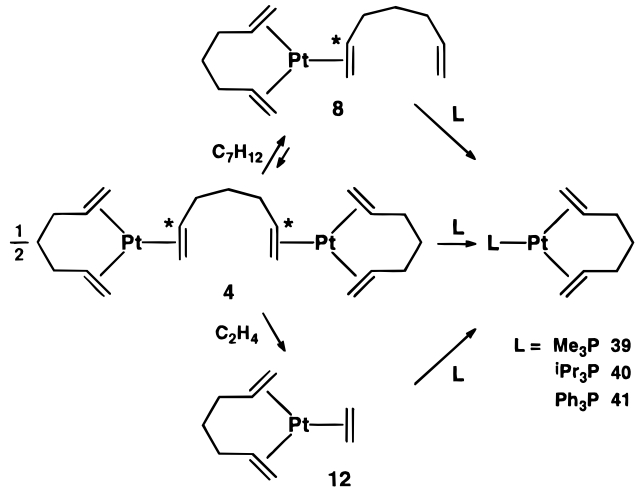
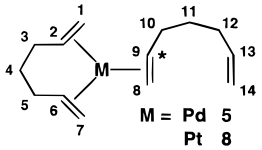
Scheme 5

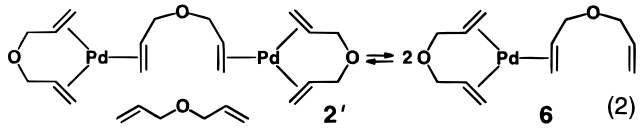


uncoordinated vinyl group (δ(C) 139.6 (=CH−) and 115.1 (H_2C=)), two sets of three signals to three differently coordinated vinyl groups (δ(C) 84.4, 84.2, 84.0 (=CH−) and 62.8, 62.4, 61.6 (H_2C=)), and further six signals to the inequivalent allylic and aliphatic methylene groups (δ(C) 35.6−32.4). The spectrum of the Pt derivative **8** (−30 °C) is analogous, but the resonances of the coordinated vinyl groups (δ(C) 70.0, 69.8, 65.6 (=CH−) and 48.5, 48.1, 46.8 (H_2C=)) are at markedly higher field than for **5**. In **8** the J(^{195}PtC) couplings allow an assignment of most resonances. The spectra show that in **5** and **8** a *TP*-3 M^0 center (M = Pd, Pt) is coordinated by a chairlike[25a] chelating and a η^2-bound C_7H_{12} ligand; the latter renders the complexes chiral.[25b] The ^{1}H NMR spectra of **5** (−80 °C) and **8** (−30 °C) are very complex because of 24 inequivalent protons, giving rise to as many partially overlapping multiplets.



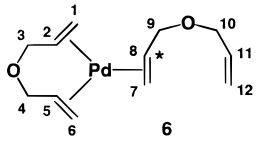
When the temperature is raised, the ^{1}H and ^{13}C NMR resonances of **5** and **8** broaden and partially coalesce but a full equilibration of the corresponding signals does not occur up to 0 (**5**) and 27 °C (**8**). The sharp solvent hepta-1,6-diene resonances are seemingly unaffected. The spectra show that for **5** at about −30 °C and for **8** at about 27 °C *intra*molecular structural dynamics become relevant which are explained by an exchange of the coordinated and uncoordinated vinyl groups of the hepta-1,6-diene ligands. Exchange reactions of the hepta-1,6-diene ligands with uncoordinated hepta-1,6-diene (solvent) are much slower and become noticeable only at a higher temperature (for **5** at about 27 °C).

The ^{1}H and ^{13}C NMR spectra of a THF-d_8 solution of the *diallyl ether* complex **2′** display signals for **2**, for an equal amount of uncoordinated diallyl ether (contained in crystalline **2′**), and for twice the amount of **6** (formed by partial reaction of **2** with diallyl ether), corresponding to a balanced equilibrium according to eq 2.



For dinuclear **2** the −80 to −30 °C ^{1}H NMR spectrum is very complex. A total of 30 equally intense signals (each 2H) for six different diallyl ether moieties H_EH_ZC=CH−CH_aH_bO− is expected, and these signals overlap with 4 signals of uncoordinated diallyl ether and 20 signals of **6** (see below). In the −80 to −30 °C ^{13}C NMR spectrum **2** exhibits for the diallyl ether ligands 18 (partially isochronous) signals of equal intensity (2C). The signals are arranged in three signal groupings of six signals each in the ranges δ(C) 84−79 (=CH−), 73−70 (CH_2O), and 63−59 (=CH_2). The ^{13}C NMR spectrum is consistent with a diastereomeric mixture of dinuclear complexes in which the *TP*-3 Pd atoms are coordinated by both a chelating and a bridging diallyl ether ligand (Figure 1). There are two types each of chelating and bridging diallyl ether ligands (four types altogether). Both halves of the bridging diallyl ether ligands are equivalent as is also the case for the corresponding Pd(η^2,η^2-$C_6H_{10}O$) moieties, but all carbon atoms of a single Pd-(η^2,η^2-$C_6H_{10}O$) moiety are inequivalent due to the asymmetry (*R* or *S* stereochemistry) of the substituted olefinic C atoms of the bridging diene ligands. The *R*,*S* stereocenter combination of the central diallyl ether ligand furnishes a C_s symmetrical *meso* isomer, whereas the *R*,*R* and *S*,*S* combinations give rise to a *rac* mixture of spectroscopically equivalent C_2 symmetrical isomers. The interpretation of the NMR spectra of **2** is in compliance with the detailed discussion of the spectra of the structurally related hepta-1,6-diene complex *rac-/meso*-Ni_2-(C_7H_{12})$_3$.[16a]

When an excess of diallyl ether is added to a THF-d_8 solution of **2′**, dinuclear **2** is almost completely converted into **6**. In the −80 °C ^{13}C NMR spectrum, **6** displays 12 discrete signals of equal intensity (each 1C). There are two pairs of signals for the vinyl groups (δ(C) 85.6, 85.4 (=CH−), 59.6, 59.4 (H_2C=)) of an unsymmetrical, chelating $C_6H_{10}O$ ligand, and another two sets of signals for the coordinated (δ(C) 77.3 (=CH−), 63.9 (H_2C=)) and the uncoordinated vinyl groups (δ(C) 136.4 (=CH−), 115.7 (H_2C=)) of an η^2-coordinated $C_6H_{10}O$ ligand; four further close signals arise from inequivalent allylic C atoms (δ(C) 73.4, 70.5, 69.9, 69.6 (CH_2O)). In the ^{1}H NMR spectrum (−80 °C) the expected 20 proton multiplets of **6** strongly overlap. Similar as for **5**, in the diallyl ether derivative **6** a *TP*-3 Pd^0 center is coordinated by both a chairlike chelating and a singly coordinating $C_6H_{10}O$ ligand, the latter imposing chirality. On raising the temperature to −30 °C the signals of **6** broaden significantly and partially coalesce, whereas the resonances of residual **2** and uncoordinated diallyl ether remain sharply resolved. At 0 °C the signals of **2** and **6** are coalesced (the solvent diallyl ether resonances are still very sharp) and at 27 °C are hardly observable any more (the solvent diallyl ether resonances are now broadened).



The ^{13}C NMR spectra of **2** and **6** indicate that with respect to the coordination of the vinyl groups the structure of **2** is static between −80 and −30 °C and the structure of **6** is static at −80 but fluxional at −30 °C on the NMR time scale. For **6** a

(25) (a) If the chelating 1,6-diene ligand in complexes **5**−**8** were of local C_2 symmetry, fewer ^{1}H and ^{13}C NMR signals would be expected as compared to the chairlike conformation of local C_s symmetry. In fact, the spectra prove that the chelating 1,6-diene ligands assume a locally C_s symmetrical, chairlike conformation in the ground state. (b) Paiaro, G. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 319.

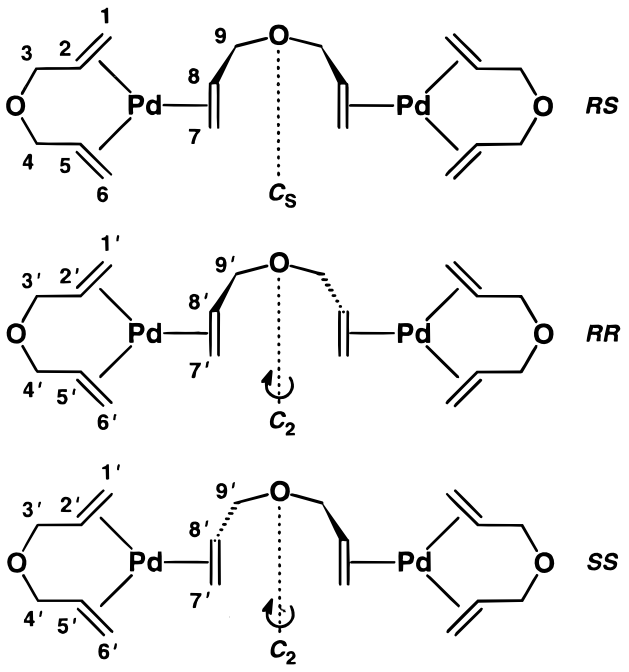
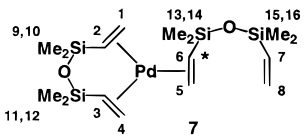


Figure 1. Stereoisomers of *rac-/meso*-$Pd_2(C_6H_{10}O)_3$ (**2**); the numbering refers to inequivalent C atoms. The $(C_6H_{10}O)Pd$ moieties rotate about the Pd−C═C bond axes of the bridging diene ligand. Corresponding stereoisomers are formed by the hepta-1,6-diene complexes **1** and **4** and the dvds complex **3**.

rapid intramolecular exchange of the coordinated and uncoordinated vinyl groups proceeds at −30 °C. Ligand exchange reactions between **2** and **6** are observable only at ≥0 °C and exchange reactions between **2** or **6** and free diallyl ether become rapid only at 27 °C.

For a solution of the dinuclear *dvds* complex **3** in THF-d_8 the −80 °C ^{13}C NMR spectrum exhibits 12 signals each for vinyl C atoms and for silicon bound Me groups; all signals have the same intensity (2C) (some of them are isochronous). In the ^1H NMR spectrum the multiplets of the vinyl protons (18 resonances expected, each 2H) largely overlap, whereas for the Si−Me groups 12 singlets are observed (each 6H; four signals are isochronous). The spectra are almost unchanged at −30 °C but are broad at ambient temperature. The low-temperature spectra of **3** agree with a mixture of diastereomeric dinuclear complexes, similar to the homologous complexes *rac-/meso*-$M_2(dvds)_3$ (M = Ni,[16c] Pt[18a]).

When **3** is dissolved in a THF-d_8/dvds mixture, the ^1H and ^{13}C NMR signals of **3** are consistently sharp between −80 and −30 °C as are the resonances of uncoordinated dvds. At −80 °C additional *broad* resonances are observed for a minor amount (20−40%) of mononuclear **7**. In the −80 °C ^{13}C NMR spectrum **7** displays signals at δ(C) 140 (═CH−) and 133 (H_2C═) for an uncoordinated vinyl group, two sets of three signals each at δ(C) ≈75 (═CH−) and ≈73 (H_2C═) for three differently coordinated vinyl groups, and eight resonances (of which 6 signals are resolved) between δ(C) 3.1 and −1.1 for four inequivalent $SiMe_aMe_b$ groups. At −30 °C the signals of **7** are so broad that they can hardly be located any longer.



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It is concluded from these results that (a) the equilibrium between dinuclear **3** and mononuclear **7** in dvds solution is in favor of **3** (Scheme 4), (b) the equilibrium between **3** and **7** and their ligand exchange with uncoordinated dvds are slow at −30 °C, (c) in **7** a *TP*-3 Pd^0 center is coordinated by a chelating dvds and a η^2-dvds ligand and the complex is chiral (similar as for **5** and **6**), and (d) in **7** the intramolecular exchange of the coordinated and uncoordinated vinyl groups is fast below −30 °C. The rigidity of the structures of the $M(1,6\text{-diene})_2$ complexes thus follows the order **7** < **6** < **5** < **8**.

II. (Ethene)Pd(1,6-Diene) (9−12). When suspensions of dinuclear **1**−**4** in a usual solvent are saturated with ethene at −78 °C and the mixtures are warmed to −60 (**1**−**3**) or −20 °C (**4**), clear solutions are obtained. In equilibrium reactions the bridging 1,6-diene ligands are replaced by ethene and the mononuclear, 1,6-diene ligated M^0−ethene complexes **9**−**12** are formed. As shown by NMR (see below), the reactions of **1** and **4** to afford the hepta-1,6-diene ligated Pd^0− and Pt^0−ethene complexes **9** and **12** are quantitative (Schemes 2 and 5). Thus, for $(C_7H_{12})M^0$ fragments (M = Ni,[16a] Pd, Pt) ethene is a much better coligand than a further C_7H_{12} vinyl group. The diallyl ether complex **2′** also reacts completely when treated with ethene, but in addition to the ethene adduct **10** some homoleptic mononuclear **6** is obtained due to the competing reaction of **2** with the released 1,6-diene (Scheme 3). In contrast, the dvds complex **3** reacts only partially with an excess of ethene and such a solution contains residual **3**, the ethene adduct **11**, and some additional **7** (Scheme 4). Complexes **9**−**12** are extremely soluble, also in pentane at −78 °C, and only **12** has been isolated. The platinum complex **12** is very volatile and decomposes at >15 °C. In the EI mass spectrum (15 °C) the molecular ion (*m/e* 319, 36%) is observed; cleavage of the ethene ligand generates the base ion $[(C_7H_{12})Pt)]^+$ (291).

NMR Spectroscopic Characterization. Corresponding to the synthesis routes, the THF-d_8 solutions of **9**−**11** (−80 to −30 °C) and **12** (27 °C) display sharp ^1H and ^{13}C NMR signals for the chelating 1,6-diene (Table 1) and coordinated ethene of **9**−**12**, and additional signals for 1 half-equiv of displaced 1,6-diene and the excess of uncoordinated ethene. For a solution of **10** (obtained from **2′**) further signals are found for about 10% of residual **2** (or **6** at −80 °C), and similarly, for a solution of **11** (obtained from **3**) additional signals are observed for about 30% of residual **3** and a small amount of **7**.

The spectra of **9**−**12** are in agreement with the presence of a C_s symmetrical *TP*-3 coordination of the metals by ethene and a chelating 1,6-diene ligand in a chairlike conformation. The ^1H NMR singlets observed for the ethene ligands indicate that the latter are rapidly rotating even at −80 °C (an AA′BB′ spin system was to be expected for the static structure), whereas a possible exchange of the ethene ligands with uncoordinated ethene is slow (for **12** even at 27 °C), as evidenced both by the sharp separate signals for coordinated and uncoordinated ethene and, for **12**, by the flanking of the ethene ^1H and ^{13}C signals by ^{195}Pt spin−spin coupling satellites.

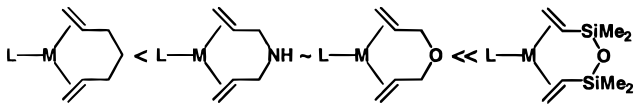
The ethene ligand ^1H and ^{13}C NMR resonances (uncoordinated ethene: δ(H) 5.40, δ(C) 123.7) are shifted to high-field when the 1,6-diene ligands are exchanged in the series **11** (δ(H) 3.79, δ(C) 73.3) → **10** (δ(H) 3.53, δ(C) 63.0) → **9** (δ(H) 3.39, δ(C) 61.9) → **12** (δ(H) 2.95, δ(C) 44.3), indicative of an increasing $M^0-C_2H_4$ back-bonding. Thus, the $[(dvds)Pd^0]$ moiety is only weakly back-bonding to the ethene ligand, more so $[(C_6H_{10}O)Pd^0]$, and the most $[(C_7H_{12})Pd^0]$, in agreement with a decreasing acceptor strength of the 1,6-diene ligands in that order (Scheme 6). In the (hepta-1,6-diene)$M(C_2H_4)$ complexes back-bonding to the ethene ligand, as expected, is stronger for Pt^0 than for Pd^0. Nevertheless, for all (1,6-diene)$M(C_2H_4)$

Table 1. ^{1}H and ^{13}C NMR Data (1,6-diene ligands) and ^{31}P NMR Data of L−M(C_7H_{12}) (M = Pd, Pt), L−Pd($C_6H_{10}O$), L−Pd($C_6H_{10}NH$), and L−Pd(dvds) Complexes[a]

	δ(H)					δ(C)				
	=CH−	H_ZHC=	HH_EC=	$-CH_{eq}H_{ax}-$	$-CH_aH_b-$	=CH−	H_2C=	=$CHCH_2$−	$-CH_2-$	δ(P)
C_7H_{12}	5.80	5.01	4.94	2.02	1.43	139.0	114.9	33.4	28.5	
9[b]	4.03	3.24	3.35	2.50, 0.66	1.96[d]	84.3	60.0	32.4	34.4	
13	3.44	2.54	2.76	2.22, 0.49	1.78[d]	74.2	52.1	33.0	34.0	−22.3
14	3.48	2.62	2.73	2.32, 0.57	1.85[d]	74.0	52.4	33.0	33.6	53.6
15	3.52	2.63	2.74	2.36, 0.63	–[d]	74.2	52.7	33.3	33.8	40.3
16[c]	3.64	2.80	2.83	2.33, 0.66	1.84[d]					88.4
17	3.79	2.70	2.85	2.36, 0.77	1.94, 1.84	79.2	58.7	33.2	33.2	30.6
18	3.78	2.69	2.83	2.35, 0.76	1.87[d]	78.7	58.5	33.5	33.6	28.2
19[50]	3.84	2.25	2.73	2.33, 0.70	1.85[d]	79.0	59.8	33.6	33.1	22.4
20[b]	3.52	2.53	2.59	2.09, 0.16	1.74, 1.68					150.9
21	3.63	2.56	2.81	2.13, 0.22	1.80, 1.70	82.2	59.0	32.4	32.5	156.1
22	3.53	2.49	2.44	2.24, 0.60	1.85, 1.76	83.8	58.2	32.6	33.1	155.9
23[b]	3.51	2.65	2.78	2.27, 0.59	1.88, 1.84					44.3
$C_6H_{10}O$	5.87	5.24	5.09	3.93		136.2	116.0	71.4		
10[b]	4.11	3.14	3.49	4.54, 2.29		84.2	57.1	70.0		
24	3.54	2.50	2.82	4.35, 2.13		74.3	49.4	70.3		−21.8
25	3.60	2.58	2.81	4.35, 2.15		73.9	49.1	70.4		55.2
26	3.62	2.57	2.79	4.38, 2.20		73.9	49.3	70.4		41.8
27[c]	3.69	2.71	2.87	4.38, 2.28		76.6	52.7	70.3		89.8
28	3.92	2.69	2.94	4.42, 2.37		78.9	55.5	70.6		31.3
29	3.93	2.17	2.76	4.35, 2.24		78.5	56.9	71.0		23.7
30	3.64	2.48	2.67	4.17, 1.82						151.4
31[b]	3.56	2.65	2.95	4.33, 2.17		74.7	50.7	70.2		
$C_6H_{10}NH$[f]	5.86	5.16	5.00	3.18		138.6	115.7	52.5		
32	3.53	2.63	2.75	3.53, 1.63		75.8	48.8	51.7		54.7
33	3.91	2.74	2.88	3.60, 1.84		81.0	56.2	52.0		31.2
dvds	6.12	5.73	5.91	0.17[e]		140.3	132.0	0.48[e]		
11[b]	3.50	3.86	3.82	0.24, −0.32[e]		72.0	68.8	1.5, −1.2[e]		
34	2.84	3.05	3.30	0.18, −0.30[e]		63.1	63.0	1.4, −0.8[e]		−19.9
35	2.82	3.09	3.36	0.19, −0.26[e]		63.8	62.6	1.6, −0.7[e]		48.6
36[c]	3.11	3.44	3.39	0.18, −0.22[e]		69.2	66.9	1.8, −0.3[e]		90.7
37	3.20	3.04	3.33	0.19, −0.24[e]		68.7	69.9	1.4, −0.9[e]		30.2
38	3.17	3.00	2.93	0.18, −0.16[e]		68.9	70.8	1.4, −1.1[e]		25.2
12	3.53	2.82	3.07	2.57, 0.42	1.97, 1.95	70.4	46.0	31.3	34.0	
	^2J(PtH) 54	^2J(PtH) 59	^2J(PtH) 61	^3J(PtH) 44, ...		^1J(PtC) 110	^1J(PtC) 128	^2J(PtC) 29	^3J(PtC) 36	
39	2.77	1.75	2.13	2.17, 0.32	1.84, 1.69	54.7	37.5	32.1	35.7	−23.3
	^2J(PtH) 57	^2J(PtH) 58	^2J(PtH) 58	^3J(PtH) 49, 27		^1J(PtC) 143	^1J(PtC) 165	^2J(PtC) 33	^3J(PtC) 53	^1J(PtP) 3305
40	2.81	1.85	2.11	2.20, 0.34	1.76, 1.73	54.5	37.9	32.2	35.2	46.5
	^2J(PtH) 57	^2J(PtH) 58	^2J(PtH) 58	^3J(PtH) 54, ...		^1J(PtC) 139	^1J(PtC) 173	^2J(PtC) 31	^3J(PtC) 50	^1J(PtP) 3393
41	3.17	1.86	2.17	2.28, 0.51	1.81, 1.78	59.7	44.3	32.4	34.8	25.8
	^2J(PtH) 62	...	^2J(PtH) 57	^3J(PtH) 57, ...		^1J(PtC) 139	^1J(PtC) 168	^2J(PtC) 34	^3J(PtC) 56	^1J(PtP) 3513

[a] Solvent THF-d_8. Temperature 27 °C, if not indicated otherwise. Coupling constants in hertz. [b] Temperature −30 °C. [c] Temperature −80 °C. [d] Not resolved. [e] $SiMe_2$ resonances. [f] δ(H) 1.67 (NH).

Scheme 6. Sequence of Increasing Reactivity and Increasing Acceptor Strength of the 1,6-Dienes and of Increasing Stability (decreasing reactivity) of the Corresponding L−M(1,6-diene) Complexes (M = Ni, Pd, Pt)



complexes $M^0-C_2H_4$ back-bonding is considerably weaker as compared to ($R_2PC_2H_4PR_2$)M(C_2H_4) complexes.[26]

III. L−Pd(1,6-diene) (13−38) and L−Pt(1,6-diene) (39−41). In dinuclear **1**−**4** and in mononuclear **5**−**12** the nonchelating alkene ligands are readily displaced by a broad variety of donors such as phosphanes, phosphites, and isocyanides.[27] In a typical reaction aimed at the synthesis of L−Pd(C_7H_{12}) in homogeneous solution, dinuclear **1** is dissolved in some hepta-1,6-diene and to the in situ generated **5** the stoichiometric amount of phosphane PR_3 or phosphite $P(OR)_3$ (R = alkyl, aryl) is added. When the mixture is cooled to −78 °C colorless crystals of the phosphane complexes **13**−**15**, **17**, and **18** and the phosphite complexes **20**−**22** separate in 70−80% yield. Alternatively, to avoid the excess of 1,6-diene, a suspension of **1** in diethyl ether or pentane is first treated with ethene (0 °C) to produce a solution of **9** that is then reacted further with L (Scheme 2).

In analogous reactions the dinuclear diallyl ether complex **2′** is solubilized with diallyl ether or ethene to intermediately afford mononuclear **6** and **10**, respectively, which are reacted further with PR_3 (R = alkyl, aryl), $P(OPh)_3$, and ^{t}BuNC to produce the L−Pd($C_6H_{10}O$) derivatives **24**−**31** (Scheme 3). Reaction of the dinuclear dvds complex **3** with PR_3 affords the L−Pd(dvds) complexes **34**−**38** (Scheme 4).

Problems arise for sterically *very* demanding ligands such as (2-MeC_6H_4)$_3$P (cone angle: $\theta = 194°$)[28] and ^{t}Bu$_3$P ($\theta = 182°$)[28a] for which crystallization of the products is retarded by excess of alkene. Isolation of the (*o*-tolyl)$_3$P derivatives **19**, **29**, and **38** is so far possible only by evaporating the 1,6-diene solution to dryness. The isolated complexes readily dissolve again in the corresponding 1,6-dienes but poorly in other solvents. We assume that the extraordinary solubility of the complexes is caused by polarity effects of the 1,6-dienes (the NMR spectra gave no indication for the formation of solvent adducts).

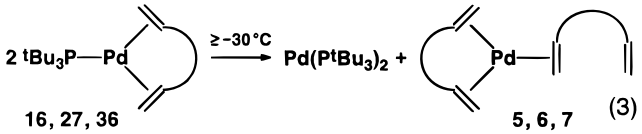
The synthesis of the ^{t}Bu$_3$P complexes **16**, **27**, and **36** is furthermore complicated by thermal instability and, hence, needs to be carried out at low temperatures (<−30 °C) as described in the Experimental Section. At 20 °C solid **16** decomposes very quickly and **27** in the course of a day, whereas **36** (>100 °C dec) is stable for a long time. In solution, these complexes

(26) (^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Pd(C_2H_4): δ(H) 2.30, δ(C) 38.4;[26a] (^{i}Pr$_2$PC$_2$H$_4$P-^{i}Pr$_2$)Pt(C_2H_4): δ(H) 1.63, δ(C) ≈25.[26b] The coordination of the ethene ligand in these complexes is static as compared to the NMR time scale. (a) Krause, J.; Bonrath, W.; Pörschke, K.-R. *Organometallics* **1992**, *11*, 1158. (b) Schager, F.; Haack, K.-J.; Mynott, R.; Rufinska, A.; Pörschke, K.-R. *Organometallics* **1998**, *17*, 807.

(27) Attempts to react **3** with pyridine to produce (C_5H_5N)Pd(dvds) have failed.

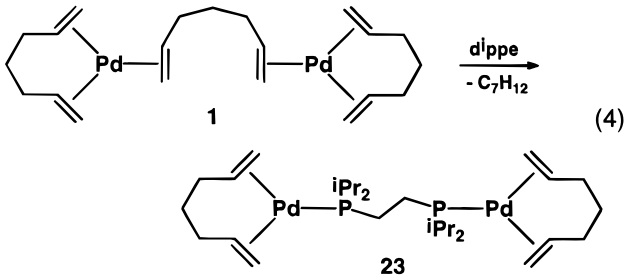
(28) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (b) For (2-MeC_6H_4)$_3$P the given cone angle of 194° appears to be overestimated, and on the basis of chemical experience a value of about 170° reflects the steric bulk of this phosphane more reasonably.

undergo ligand redistribution reactions to afford the very stable $Pd(P^tBu_3)_2$[29] together with (decomposing) **5** or **6** or (stable) **7** (eq 3). For **16** this ligand redistribution starts already at −30



°C (and is fast at 20 °C), and for **27** and **36** it starts slowly at about 0 °C. This reaction cannot be completely suppressed in the synthesis of highly soluble **16** and **27**, which therefore contain about 10% of $Pd(P^tBu_3)_2$ as a byproduct.[30]

When **1** is reacted with 1 equiv of bidentate d^{i}ppe (bis-(diisopropylphosphino)ethane) the bridging hepta-1,6-diene ligand is replaced by d^{i}ppe but the chelating 1,6-diene ligands are maintained to form the equally dinuclear **23** (eq 4). This

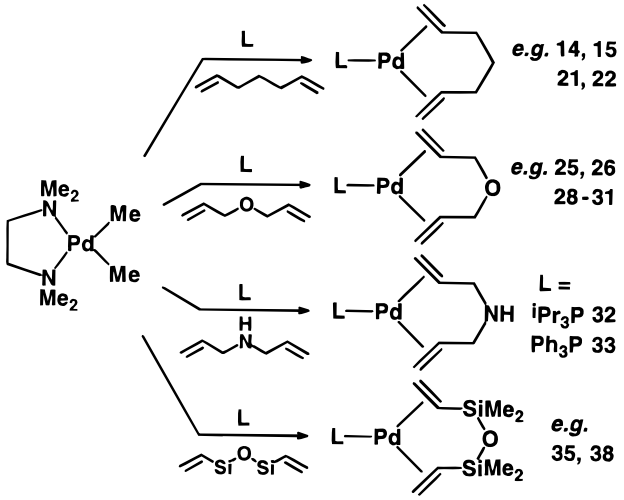


reaction shows that the chelate effect of a 1,6-diene ligand can outdo that of a bidentate phosphane, affording the latter in a nonchelating binding mode.

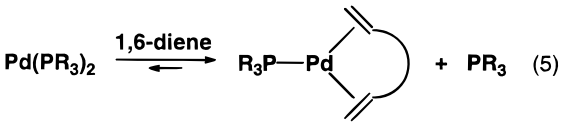
Alternative Routes to L−Pd(1,6-diene) Complexes. L−Pd-(1,6-diene) complexes can also be prepared by substituting L in L_2Pd^0 by 1,6-dienes. An early example of such a reaction was the synthesis of **26** from $Pd(PCy_3)_2$ and diallyl ether, although no details were given.[15b] $Pd(PCy_3)_2$ completely dissociates in 1,6-diene solution to give equimolar mixtures of the corresponding (Cy_3P)Pd(1,6-diene) complexes (**15**, **26**) and uncoordinated PCy_3 as evidenced by the sharp ^{31}P NMR signals. The same holds for the otherwise sparingly soluble Pd{P(*o*-tolyl)$_3$}$_2$, yielding the {(*o*-tolyl)$_3$P}Pd(1,6-diene) complexes **19**, **29**, and **38** and free P(*o*-tolyl)$_3$.

$Pd(P^iPr_3)_2$ in 1,6-diene solution is subjected to a double equilibrium. It predominantly dissociates to give about equimolar mixtures of the corresponding (^{i}Pr$_3$P)Pd(1,6-diene) complexes **14**, **25**, and **35** and uncoordinated P^iPr_3, but part of it also forms an adduct with the released P^iPr_3 to give $Pd(P^iPr_3)_3$.[5b] With respect to the formation of **14** and **25** the ^{31}P NMR signals of $Pd(P^iPr_3)_2$, P^iPr_3, and $Pd(P^iPr_3)_3$ are broad due to an exchange reaction, whereas for a solution of $Pd(P^iPr_3)_2$ in neat dvds a small amount of $Pd(P^iPr_3)_3$ precipitates. After separation of the latter, the ^{31}P NMR spectrum displays sharp signals of **35** and some uncoordinated P^iPr_3. Evaporation of the volatiles (dvds, P^iPr_3) or crystallization affords pure **35**. The rather stable $Pd(P^tBu_3)_2$ dissolves unchanged in hepta-1,6-diene, and even in dvds it only reluctantly liberates P^tBu_3 to form a small amount of **36** (10%).

Scheme 7



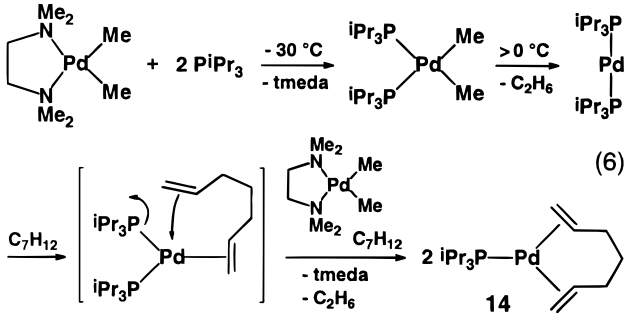
Hence, $Pd(PR_3)_2$ as well as $(R_3P)_2$Pd(alkene) complexes (R = alkyl, aryl) react with 1,6-dienes to give (R_3P)Pd(1,6-diene) complexes in an equilibrium reaction (eq 5), and the applicability



as a synthesis route depends on the special PR_3 ligand. Coordinatively saturated complexes such as $Pd(PMe_3)_4$ and $Pd(PPh_3)_4$ react with 1,6-dienes to yield (R_3P)Pd(1,6-diene) only if the displaced PR_3 is trapped by a further complex (see below).

Additional synthesis routes for L−Pd(1,6-diene) start from either (tmeda)$PdMe_2$, Pd(η^3-C_3H_5)$_2$, Pd(η^3-MeC_3H_4)$_2$, or CpPd(η^3-C_3H_5) by inducing reductive elimination of the organic ligands. (tmeda)$PdMe_2$[31] suspended in the corresponding 1,6-diene reacts with tri*alkyl*phosphanes PR_3 (R, e.g., ^{i}Pr, Cy) at 20−30 °C and with tri*aryl*phosphanes PR_3 (R, e.g., Ph) or phosphites $P(OR)_3$ (R, e.g, C_6H_3-2,6-Me_2, C_6H_3-2,6-^{i}Pr$_2$) at 70−80 °C with elimination of ethane to yield the corresponding L−Pd(1,6-diene) (Scheme 7). For the synthesis of the diallylamine complexes **32** and **33** this route (or the displacement of hepta-1,6-diene from the L-Pd(C_7H_{12}) complexes **14** and **17** by diallylamine) is the method of choice since a homoleptic Pd^0−diallylamine complex $Pd(C_6H_{10}NH)_n$, related to **1**−**3**, has not been isolated.

To gain insight into the mechanism of the L−Pd(1,6-diene) syntheses from (tmeda)$PdMe_2$, the synthesis of **14** was studied in detail (eq 6). (tmeda)$PdMe_2$ reacts with *two* ^{i}Pr$_3$P already at −30 °C by tmeda displacement[31b,c] to give a suspension of *cis*-



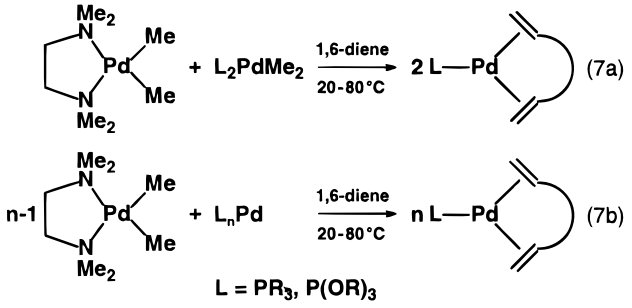
(29) (a) Matsumoto, M.; Yoshioka, H.; Nakatsu, K.; Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1974**, *96*, 3323. Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. *J. Am. Chem. Soc.* **1976**, *98*, 5850. Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 101. Tanaka, M. *Acta Crystallogr., Part C* **1992**, *48*, 739. (b) The shift of the ^{31}P NMR signal of $Pd(P^tBu_3)_2$ in THF-d_8 is temperature dependent: δ(P) 85.8 (27 °C), 83.6 (−30 °C), 82.0 (−80 °C).

(30) For ^{t}Bu$_3$P/Pd catalyst systems, see: (a) Nishiyama, M.; Yamamoto, T.; Koie, Y. *Tetrahedron Lett.* **1998**, *39*, 617 and 2367. (b) Littke, A. F.; Fu, G. C. *Angew. Chem.* **1998**, *110*, 3586; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3387. (c) Mann, G.; Incarvito, C.; Rheingold, A. L.; Hartwig, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 3224.

(^{i}Pr$_3$P)$_2$PdMe$_2$.[32] If only one ^{i}Pr$_3$P is used, half of the (tmeda)-PdMe$_2$ remains unreacted. Isolated *cis*-(^{i}Pr$_3$P)$_2$PdMe$_2$, when heated in an inert solvent to >0 °C, eliminates ethane and homoleptic Pd(P^{i}Pr$_3$)$_2$ is obtained. When the reaction is carried out in undiluted hepta-1,6-diene,[33a] a part of the Pd(P^{i}Pr$_3$)$_2$ reacts further to **14** while the other traps the released P^{i}Pr$_3$ to form Pd(P^{i}Pr$_3$)$_3$. The latter is not obtained in the presence of further (tmeda)PdMe$_2$ which consumes the liberated P^{i}Pr$_3$, thereby affording a total of 2 equiv of **14**.[33b] Thus, the over-all reaction of (tmeda)PdMe$_2$ with *one* P^{i}Pr$_3$ and hepta-1,6-diene to give **14** involves *cis*-(^{i}Pr$_3$P)$_2$PdMe$_2$ and Pd(P^{i}Pr$_3$)$_2$ as intermediates and the reaction is formally catalyzed by P^{i}Pr$_3$.

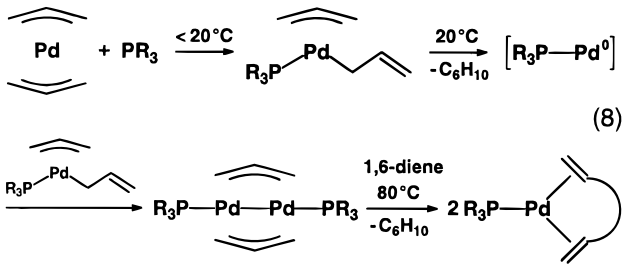
Reductive ethane elimination from the (R$_3$P)$_2$PdMe$_2$ intermediate is rate-determining. For example, *cis*-(Ph$_3$P)$_2$PdMe$_2$ is readily obtained from (tmeda)PdMe$_2$ and PPh$_3$ (≤20 °C).[31b] In 1,6-diene solution (or toluene) it undergoes reductive ethane elimination to produce (Ph$_3$P)$_2$Pd only at 80 °C.[34] The reaction of (Ph$_3$P)$_2$Pd with (tmeda)PdMe$_2$ and 1,6-dienes to give (Ph$_3$P)-Pd(1,6-diene) products (e.g. **28)** likewise proceeds readily (≤20 °C).

The mechanism shown in eq 6 has two consequences. First, the (tmeda)PdMe$_2$ route is practicable only for phosphane and phosphite ligands of intermediate bulk, excluding, for example, PMe$_3$ and P^{t}Bu$_3$ for which the reactions stop at the stages of the intermediates. With regard to PMe$_3$, *cis*-(Me$_3$P)$_2$PdMe$_2$[35] does not undergo reductive elimination under the given conditions, not even at 80 °C and in the presence of (tmeda)PdMe$_2$. Concerning P^{t}Bu$_3$, the readily formed Pd(P^{t}Bu$_3$)$_2$ is thermodynamically too stable to react further. Second, reactions of L$_2$-PdMe$_2$ complexes (L = phosphane (excluding PMe$_3$), phosphite) (20−80 °C; eq 7a) as well as L$_n$Pd^0 complexes (n = 2−4;

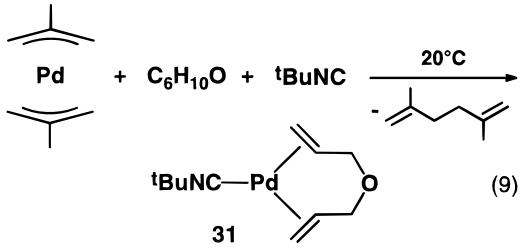


excluding Pd(P^{t}Bu$_3$)$_2$ and Pd(PMe$_3$)$_4$) (20 °C; eq 7b) *with the stoichiometric quantity of (tmeda)PdMe$_2$* in 1,6-diene solution also produce L-Pd(1,6-diene) complexes.

Pd(η^3-C$_3$H$_5$)$_2$, Pd(η^3-MeC$_3$H$_4$)$_2$, and CpPd(η^3-C$_3$H$_5$) are of similar reactivity and applicability. They react with PR$_3$ (R = alkyl, aryl) in hepta-1,6-diene at 80 °C by elimination of hexa-1,5-diene, 2,5-dimethylhexa-1,5-diene, or allylcyclopentadiene[36a] to yield the corresponding (R$_3$P)Pd(C$_7$H$_{12}$) complexes (R, e.g., Me (**13**), ^{i}Pr (**14**)) in the course of several hours. The mechanism of these reactions (eq 8) involves the initial formation of (R$_3$P)-



Pd(η^3-allyl)(η^1-allyl) or (R$_3$P)PdCp(η^1-allyl) adducts,[36,37] which partially thermolyze (20 °C) to generate [(R$_3$P)Pd^0] intermediates. The latter are trapped by the so far unreacted Pd^{II} complexes to produce rather stable dinuclear Pd^I complexes,[38] of which the new {(Me$_3$P)Pd}$_2$(μ-η^5-C$_5$H$_5$)(μ-η^3-C$_3$H$_5$)[39a] and {(^{i}Pr$_3$P)Pd}$_2$(μ-η^3-C$_3$H$_5$)$_2$[39b] have been isolated. Only the dinuclear Pd^I complexes, when thermolyzing at 80 °C, react with hepta-1,6-diene to give the products. Similarly, in diallyl ether the complexes (R$_3$P)Pd(C$_6$H$_{10}$O) (R, e.g., Me (**24**), ^{i}Pr (**25**), Ph (**28**)) are obtained. It is interesting to note that the formation of **24** proceeds rapidly already at ambient temperature. There is no doubt that phosphite derivatives {(RO)$_3$P}Pd(1,6-diene) and dvds ligated complexes L−Pd(dvds) are also accessible from the Pd^{II,I}−allyl complexes. Furthermore, the Pd^{II}−allyl complexes react with ^{t}BuNC and diallyl ether already at 20 °C to give the isocyanide complex **31** (eq 9).[40]



In short, there are now numerous, well-understood synthesis routes to L−Pd(1,6-diene) complexes.

General Properties of L−Pd(1,6-Diene). Displacement reactions, similar to those in Scheme 1, have shown that in L−Pd(C$_7$H$_{12}$) the hepta-1,6-diene ligand is readily replaced by stoichiometric amounts of diallylamine or diallyl ether to afford L−Pd(C$_6$H$_{10}$NH) and L−Pd(C$_6$H$_{10}$O), respectively, and for all these complexes the 1,6-diene ligands are displaced by dvds to

(31) (a) Nakazawa, H.; Ozawa, F.; Yamamoto, A. *Organometallics* **1983**, *2*, 241. (b) de Graaf, W.; Boersma, J.; Grove, D.; Spek, A. L.; van Koten, G. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 299. de Graaf, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907. (c) de Graaf, W.; Boersma, J.; van Koten, G. *Organometallics* **1990**, *9*, 1479.

(32) *cis*-(^{i}Pr$_3$P)$_2$PdMe$_2$: C$_{20}$H$_{48}$P$_2$Pd (457.0). ^{1}H NMR (−30 °C): δ 2.52 (6H, PCH), 1.28 (36H, PCH*Me*$_2$), 0.08 (6H, PdMe$_2$). ^{31}P NMR (−30 °C): δ 33.6.

(33) (a) At the given temperature neither (tmeda)PdMe$_2$ nor Pd(P^{i}Pr$_3$)$_3$ react with neat hepta-1,6-diene. A reaction between Pd(P^{i}Pr$_3$)$_2$ and (tmeda)-PdMe$_2$ does not occur in the absence or in a dilluted hepta-1,6-diene solution, nor in neat hexa-1,5-diene, cod, or other dienes with a C=C bond sequence different from 1,6. (b) The reaction of Pd(P^{i}Pr$_3$)$_2$ and (tmeda)PdMe$_2$ in neat diallyl ether and dvds produces the (^{i}Pr$_3$P)Pd(1,6-diene) complexes **25** and **35**, respectively.

(34) Reductive ethane elimination from *cis*-(Ph$_3$P)$_2$PdMe$_2$ is solvent dependent. In THF solution, the typical dark-green solution of (Ph$_3$P)$_2$Pd (δ(P) 23.2) is obtained already at 20 °C.

(35) Tooze, R.; Chiu, K. W.; Wilkinson, G. *Polyhedron* **1984**, *3*, 1025.

(36) (a) Werner, H. *Angew. Chem.* **1977**, *89*, 1; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 1. (b) Werner, H.; Kühn, A. *Angew. Chem.* **1977**, *89*, 427; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 412.

(37) Henc, B.; Jolly, P. W.; Salz, R.; Stobbe, S.; Wilke, G.; Benn, R.; Mynott, R.; Seevogel, K.; Goddard, R.; Krüger, C. *J. Organomet. Chem.* **1980**, *191*, 449.

(38) (a) Werner, H. *Adv. Organomet. Chem.* **1981**, *19*, 155 and references therein. (b) Jolly, P. W.; Krüger, C.; Schick, K.-P.; Wilke, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35*, 926. Benn, R.; Jolly, P. W.; Mynott, R.; Raspel, B.; Schenker, G.; Schick, K.-P.; Schroth, G. *Organometallics* **1985**, *4*, 1945.

(39) (a) Büch, H. M. Dissertation (P. Binger), Universität Kaiserslautern (Germany), 1982, p 27. (b) {(^{i}Pr$_3$P)Pd}$_2$(μ-η^3-C$_3$H$_5$)$_2$: Yellow columns. Anal. Calcd for C$_{24}$H$_{52}$P$_2$Pd$_2$ (615.4): C, 46.84; H, 8.52; P, 10.07; Pd, 34.58. Found: C, 46.96; H, 8.78; P, 10.06; Pd, 34.28. ^{31}P NMR: δ 47.3.

(40) For the reaction of CpPd(η^3-allyl) complexes with isocyanides RNC, see: Otsuka, S.; Nakamura, A.; Tatsuno, Y. *J. Am. Chem. Soc.* **1969**, *91*, 6994 and ref 4b.

give the thermodynamically and thermally most stable L−Pd(dvds). The 1,6-diene displacements are equilibrium reactions. For example, when the $C_6H_{10}O$ complex **25** is dissolved in hepta-1,6-diene (and some THF-d_8 is added), a mixture of equal amounts of **14** and **25** is formed as shown by ^{31}P NMR. Similarly, the dvds derivative **35** partially reacts in neat $C_6H_{10}O$ to give a mixture of **25** and **35**. Thus, the L−Pd(1,6-diene) complexes are related to each other by the sequence of increasing stability (decreasing reactivity) depicted in Scheme 6,[41] which reflects also an increasing acceptor strength of the 1,6-diene ligands (see NMR).

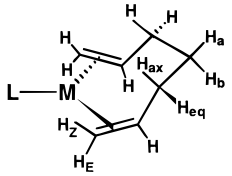
The L−Pd(C_7H_{12}) complexes are most reactive and preferential starting complexes for [L−Pd] reactions. For many purposes, however, L−Pd($C_6H_{10}O$) complexes are more convenient. The latter are more polar and thus easier to isolate from nonpolar solvents by crystallization and they are thermally more stable and easier to handle. For example, (Me_3P)Pd(C_7H_{12}) (**13**) melts slightly above ambient temperature and needs to be handled at low temperature, whereas the melting point of (Me_3P)Pd($C_6H_{10}O$) (**24**) is at 79 °C. Similarly, ($^tBu_3P$)Pd(C_7H_{12}) (**16**) is difficult to isolate but ($^tBu_3P$)Pd($C_6H_{10}O$) (**27**) crystallizes nicely at −78 °C. The reactivity of the L−Pd($C_6H_{10}O$) complexes is somewhat lower than that of the L−Pd(C_7H_{12}) complexes but still very high. In addition, diallyl ether is inexpensive, whereas hepta-1,6-diene is precious. L−Pd($C_6H_{10}O$) complexes are preferred over L−Pd($C_6H_{10}NH$) derivatives because isolation of the latter is sometimes impeded by adhering diallylamine.

The compounds have been isolated and characterized by elemental analyses, mass spectra, and IR and NMR spectra, including a single-crystal structure determination for **24**.[17] With the exception of the ($^tBu_3P$)Pd(1,6-diene) complexes **16** and **27** and low-melting **13**, all solids are at least temporarily stable at ambient temperature. Although in solution (THF, ether, pentane) the Pd complexes slowly deposit metallic Pd, such solutions can generally be stabilized by the addition of 1,6-diene. Solutions of some L−Pd(C_7H_{12}) complexes in boiling hepta-1,6-diene (90 °C) did not indicate decomposition over at least 1 h.

L−Pt(1,6-diene). L−Pt(C_7H_{12}) complexes have been prepared according to Scheme 5 by immediate reaction of **4** with P^iPr_3 (**40**) and PPh_3 (**41**) or by first dissolving dinuclear **4** in hepta-1,6-diene (to give **8**) and subsequent reaction with PMe_3 (**39**). As expected, the platinum complexes are sufficiently stabilized by the hepta-1,6-diene ligand and we found no reason to prepare other 1,6-diene derivatives.[18]

Spectroscopic Characterization of L−M(1,6-diene) (M = Pd, Pt). The 1,6-diene ligand IR data of the complexes are compiled and commented in Table 2. The EI mass spectra reflect the relative stabilities and volatilities of the complexes. The molecular ion M^+ is found only for the tri*alkyl*phosphane derivatives (R_3P)Pd(1,6-diene). Here, M^+ is observed the better the smaller the R_3P ligand. For example, M^+ is readily observed for (Me_3P)Pd(C_7H_{12}) (**13**; 31%) and ($^iPr_3P$)Pd(C_7H_{12}) (**14**; 28%) but less so for (Cy_3P)Pd(C_7H_{12}) (**15**; 1%). For the ($^tBu_3P$)Pd(1,6-diene) complexes M^+ is observable only for ($^tBu_3P$)Pd(dvds) (**36**; <1%). A stabilization of M^+ with increasing 1,6-diene acceptor strength (Scheme 6) is largely offset by the opposing increase in molecular weight. Fragmentation of the (R_3P)Pd(1,6-diene) derivatives occurs by loss of the 1,6-diene to produce $[L-Pd]^+$. For (Me_3P)Pd($C_6H_{10}O$) (**24**) elimination of diallyl ether from M^+ proceeds stepwise via $[(Me_3P)Pd(C_3H_5)]^+$ by extruding C_3H_5O. The thermally rather robust L−Pt(C_7H_{12}) complexes furnish intense M^+ peaks for all L. While $\mathbf{41}^+$ (L = PPh_3) preferentially eliminates hepta-1,6-diene to give $[(Ph_3P)Pt]^+$, degradation of $\mathbf{39}^+$ (L = PMe_3) and $\mathbf{40}^+$ (L = P^iPr_3) is more complex due to a series of hydrogen (C_7H_{12} ligand) and propene ($^iPr_3P$ ligand) elimination steps.

The ^1H and ^{13}C NMR data of the 1,6-diene ligands (Table 1) are very characteristic. For L−M(C_7H_{12}), data of the complete homologous series M = Ni,[16a] Pd, and Pt are now available. In the ^1H NMR spectrum uncoordinated C_7H_{12} gives rise to five signals, whereas for C_s symmetrical *TP*-3 L−M(C_7H_{12}) seven hepta-1,6-diene signals are expected because of the inequivalence of the geminal methylene protons $=CHCH_{eq}H_{ax}-$ and $-CH_aH_b-$ of the chairlike M(C_7H_{12}) moiety.[42,43]



As compared to uncoordinated C_7H_{12}, both signals of the central aliphatic protons $-CH_aH_b-$ are shifted to lower field by 0.3−0.5 ppm; the signal splitting is small and usually resolved only in the 400 MHz spectra. In contrast, for the allylic protons $=CHCH_{eq}H_{ax}-$ the signal of H_{eq} is shifted to lower field by 0.1−0.5 ppm and that of H_{ax} to higher field by 1.2−1.9 ppm, resulting in a signal separation of up to 2 ppm. These shifts are explained by anisotropic effects of the metal center,[15b] and it is interesting to note that they appear to be independent of the respective metal Ni,[16a] Pd, or Pt. The shifts of the corresponding $-CH_2-$ and $=CHCH_2-$ ^{13}C nuclei are almost unaffected by coordination. The olefinic ^1H and ^{13}C resonances $H_ZH_EC=CH-$ are all shifted to higher field due to $M^0-C=C$ back-bonding, and as expected the shifts are smallest for Pd, intermediate for Ni,[16a] and largest for Pt. The assignment of $H_ZH_EC=CH-$ is based on the vicinal couplings, which are 12−14 Hz for H_Z (trans to $=CH-$) and 8−9 Hz for H_E (cis). For (R_3P)Pd(C_7H_{12}) the hepta-1,6-diene ^{13}C nuclei are all spin−spin coupled to ^{31}P, and interestingly, the couplings are largest for $=CH-$ ($^2J(PC)$ = 10−12 Hz) and the aliphatic $-CH_2-$ group ($^4J(PC)$ = 7−8 Hz) but smallest (and sometimes not resolved) for $H_2C=$ ($^2J(PC)$ < 5.5 Hz) and $=CHCH_2-$ ($^3J(PC)$ < 4 Hz). For {$(RO)_3P$}Pd(C_7H_{12}) the hepta-1,6-diene ^{13}C,^{31}P spin−spin couplings are about 50% larger. For L−Pt(C_7H_{12}) complexes, spin−spin couplings with ^{195}Pt were observed for most of the hepta-1,6-diene ^1H and all ^{13}C nuclei, but unexpectedly, not for the allylic H_{ax} protons which are directed toward Pt.

The diallyl ether ligand in L−Pd($C_6H_{10}O$) and the diallylamine ligand in L−Pd($C_6H_{10}NH$) give rise to five (six) proton signals due to the inequivalence of the allylic protons $=CHCH_{eq}H_{ax}-$. Of these, H_{eq} is deshielded by 0.2−0.6 ppm and H_{ax} is shielded by 1.6−2.1 ppm as compared to uncoordi-

(41) In addition, we have shown that other 1,6-dienes such as diallylsilanes serve also as ligands in L−Pd(1,6-diene) complexes, so that the applicability of 1,6-dienes as a stabilizing coligand for the [L−Pd^0] moiety seems to be very general.

(42) Corresponding to the chairlike conformation of the M(1,6-diene) moiety,[16a] allylic protons are designated equatorial or axial, $=CHCH_{eq}H_{ax}-$. An equally applicable designation is exo or endo,[15b] taking into account that the equatorial (exo) protons point away from the metal center and the axial (endo) protons come close to it. The same holds for the Me substituents $=CHSiMe_{eq}Me_{ax}-$ in M(dvds) complexes.

(43) The inequivalence of the aliphatic protons $-CH_aH_b-$ excludes a C_2 symmetrical as well as a dynamic structure of the L−M(C_7H_{12}) complexes. For the ($^iPr_3P$)M(1,6-diene) complexes **14**, **25**, **32**, **35**, and **40** C_s symmetry is also indicated by the enantiotopic Me groups of the $^iPr_3P$ ligand (as opposed to diastereotopic Me groups expected for C_2 symmetry).

Table 2. Characteristic 1,6-Diene Ligand IR Data (KBr, cm^{-1}) of the M_2(1,6-diene)$_3$ Complexes **1**−**4** and of the L−M(1,6-diene) Complexes **13**−**41** as Well as Frequencies of the Uncoordinated 1,6-Diene for Comparison

		=C−H def						
	ν(=C−H)	in-plane[a]	out-of-plane	ν(−CH_2−)	ν(C=C)	$SiMe_2$	COC or SiOSi	others
C_7H_{12}	3080, 3000, 2980		992, 912	2930, 2860	1643			
$C_6H_{10}O$	3082, 3016, 2984		990, 923	2915, 2851	1648		1139 sh, 1090	
$C_6H_{10}NH$	3078, 3010, 2980		994, 918	2915, 2814	1644			3285 ν(NH)
dvds	3052, 3013		1009, 955		1596	2960, 1255, 840, 787	1060	
1	3058, 2991	1240	1014, 896	2918, 2875, 2848, 2820	1523			
2′	3064, 3004	1237	946	2905, 2841	1522 (1646)		1085/1055	
3	3045, 3013	1235 sh	1015		1496	2958, 1249, 830, 785	1055	
4	3044, 2979	1219	1021	2915, 2880, 2852, 2830	1489			
13	3040	1223	1008	*c*	1498			
14	3050	1227	1005	*c*	1496			
15	3049	1225	1009	*c*	1498			
16	3062	1242	*b*	*c*	1522			
17	*b*	1235	*b*	2918, 2878, 2862, 2815	1505			
18	*b*	1229	*b*	*c*	*d*			
19	*b*	1228	*b*	*c*	1503			
20	*b*	1235	*b*	2912, 2880, 2855, 2820	1513			
21	*b*	1236	1012	*c*	1515			
22	*b*	1245	*b*	*c*	1519			
23	3054, 3017	1230	1009	*c*	1501			
24	3047	1240	1008, 922	*c*	1497		1215,[a] 1072	
25	3052	1238	1010, 930	*c*	1498		1218,[a] 1070	
26	3054, 3013, 2998	1237	*b*	*c*	1493		1215,[a] 1070	
27	3056	1240	*b*	*c*	1506		1231,[a] 1086	
28	*b*	1238	932	2908, 2885, 2835	1502		1220,[a] 1068	
30	*b*	1230	*b*	2940, 2915, 2890, 2842	1510 sh		1218,[a] 1072	
31	3060	1240	934	*c*	1494		1215,[a] 1065	2150 ν(CN)
32	3051	1220	933	*c*	1500			3266 ν(NH)
34	3028	1214	*b*		1480	2955, 1249, 837, 781	994	
35	3032	1217	*b*		1481 sh	*c*, 1245, 835, 785	990	
36	3055, 3001	*b*	997		1485 sh	2954, 1245, 835, 783	997	
37	*b*	1220	937		1485 sh	2952, 1249, 836, 787	999	
39	3031	1195	1017	*c*	1466			
40	3033/3025	1194	1010 sh	*c*	1470 sh			
41	*b*	1202	*b*	2972, 2911, 2870, 2821	*d*			

[a] Strong bands which are typical of the coordinated 1,6-diene. [b] Not assigned because bands of the 1,6-diene and the coligand L are located in the same range. [c] Obscured by absorptions of other aliphatic groups. [d] Overlapped by C−C arene absorptions.

nated diallyl ether. Strong =CHC$H_{eq}H_{ax}$− signal splittings have been described before for L−M($C_6H_{10}O$) (M = Ni, Pd) (e.g. **26**).[15] The ^2J(PC) and ^3J(PC) couplings of the diallyl ether ^{13}C nuclei are of the same magnitude as for hepta-1,6-diene ligands.

For the dvds ligand in L−Pd(dvds) separate ^1H and ^{13}C NMR signals are observed for =CHSi$Me_{eq}Me_{ax}$−, in agreement with other L−M(dvds) complexes (M = Ni,[16c,23] Pt[18b−d]). Here, the vicinal couplings for H_ZH_EC=CH− amount to 15−17 Hz for H_Z and 12−13 Hz for H_E. The couplings ^2J(PC) of =CH− (7−8 Hz) and H_2C= (2−4.5 Hz) are relatively small.

For the L−M(1,6-diene) complexes of a given 1,6-diene ligand the ^{13}C coordination chemical shift (absolute value)[44] of the =CH− and H_2C= vinyl group C atoms increases with an increasing donor strength of L in the order of eq 10. When for

$$C_2H_4 < (ArO)_3P < Ar_3P < {}^tBuNC < R_3P \qquad (10)$$

a given R_3P ligand the 1,6-diene ligands of (R_3P)M(1,6-diene) are changed in the sequence of increasing acceptor strength according to Scheme 6, the ^{31}P NMR resonances are shifted downfield in agreement with an increased electron withdrawal from the [L−M] moiety (**35** is an unexplained exception from this rule).

Structural Dynamics of L−M(1,6-diene) Complexes. It has already been shown for ($^tBu_3P$)Pt(dvds) that the dvds ligand undergoes slow structural dynamics.[18d] In the ^1H and ^{13}C NMR spectra, recorded at 22 °C, the $SiMe_{eq}Me_{ax}$ groups give rise to broad singlets which coalesce at a higher temperature,[45] indicating that a stepwise dissociation−reassociation process with a rotation of the decoordinated C=C bond takes place (cp Scheme 8). The dynamics are due to the exceeding bulk of the $^tBu_3P$ ligand[46] which weakens the coordination of the dvds ligand. We have previously described a similar process for a Cu^I−1,5-hexadiene complex.[47]

As compared to Pt^0, back-bonding is weaker for Pd^0 which a priori renders the Pd−1,6-diene coordination more labile. Furthermore, considering that Pd (single-bond radius 1.283 Å) is somewhat smaller than Pt (1.295 Å),[48] steric strain is expected to be more severe for L−Pd(1,6-diene) than for the Pt derivatives. In general, it can be expected for L−M(1,6-diene) (M = Ni, Pd, Pt) that dynamic processes of the 1,6-diene ligands proceed the more facile (i) the smaller M, (ii) the larger L, (iii) the weaker back-bonding the [L−M^0] moiety, and (iv) the weaker electron accepting the 1,6-diene ligand.

(44) The ^1H and ^{13}C coordination chemical shift, i.e., the change in chemical shift which the alkene experiences upon coordination to a metal center, is defined by $\Delta\delta = \delta_{ligand} - \delta_{free\ alkene}$. Thus, typical alkene coordination shifts to higher field are negative. Jolly, P. W.; Mynott, R. *Adv. Organomet. Chem.* **1981**, *19*, 257.

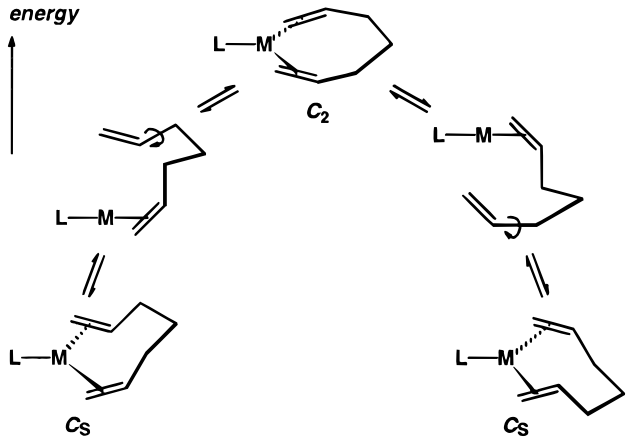
(45) ^1H NMR (89.6 MHz): T_c = 48 °C. ^{13}C NMR (22.5 MHz): T_c = 52 °C.[18d]

(46) (Cy_3P)Pt(dvds) (Cy_3P: θ = 170°) is stereochemically rigid.[18d]

(47) Nickel, T.; Pörschke, K.-R.; Goddard, R.; Krüger, C. *Inorg. Chem.* **1992**, *31*, 4428.

(48) Pauling, L. *Die Natur der Chemischen Bindung*, 3rd ed.; VCH: Weinheim, Germany, 1976.

Scheme 8

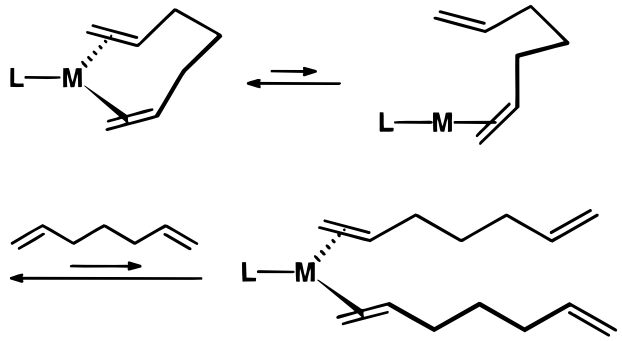


There are three potential dynamic processes of the 1,6-diene ligand which should be considered for L−M(η^2,η^2-diene) complexes: (a) Reversible cleavage of one of the M−C═C coordination bonds of the chelating 1,6-diene ligand gives rise to a *L*-2 L−M(η^2-diene) intermediate. When the decoordinated C═C bond is recoordinated by the *same* face, the original C_s symmetrical structure is retained (see lower part of Scheme 8). This process by itself is not detected by NMR unless the equilibrium is shifted markedly in favor of the L−M(η^2-diene) intermediate. (b) If the cleaved C═C bond of the *L*-2 L−M(η^2-diene) intermediate is recoordinated by the *reverse* face, a C_2 symmetrical L−M(η^2,η^2-diene) intermediate is formed. Repeating such a face-exchange for the second C═C bond leads back to a C_s symmetrical L−M(η^2,η^2-diene) complex (Scheme 8). In the course of this process for the hepta-1,6-diene ligand the protons ═CHC$H_{eq}H_{ax}$− and −CH_aH_b−, for the diallyl ether and diallylamine ligands the protons ═CHC$H_{eq}H_{ax}$−, and for the dvds ligand the methyl groups ═CHSi$Me_{eq}Me_{ax}$− swap positions and become equivalent. This process is evidenced by broadening and eventual coalescence of the corresponding NMR signals while the vinyl resonances remain sharp. (c) The *L*-2 L−M(η^2-diene) intermediate may reversibly coordinate a further 1,6-diene molecule to produce a L−M(η^2-diene)$_2$ intermediate. Dissociation of the initial 1,6-diene ligand results in its replacement at the L−M(1,6-diene) complex (Scheme 9). This process is indicated by a broadening of all resonances of the coordinated and uncoordinated 1,6-dienes. Alternative associative mechanisms involving the intermediate formation of an 18e species[49] to explain the fluxionality of L−M(1,6-diene) complexes are discarded because of steric and electronic reasons.

As the experiments show, at ambient temperature sharply resolved 1,6-diene NMR resonances are observed for those L−M(1,6-diene) complexes of Table 1 in which the ligands L are *predominantly electron-donating* (tri*alkyl*phosphanes) and not exceedingly large. Typical ligands of this type are PMe_3, P^iPr_3, and PCy_3. The 1,6-diene resonances of the given complexes are unaffected by the presence of additional 1,6-diene. This is also true for (Ph_3P)Pd(dvds) (**37**) in which dvds represents the strongest electron-withdrawing 1,6-diene of Scheme 6. For these (R_3P)M(1,6-diene) complexes the 1,6-diene coordination appears to be static on the NMR time scale. A reversible chelate ring cleavage, which would be a prerequisite for dynamics according to Schemes 8 and 9, is seemingly insignificant.

The situation is different for *weaker donors* L. For (Ph_3P)-Pd(C_7H_{12}) (**17**), {(4-MeC_6H_4)$_3$P}Pd(C_7H_{12}) (**18**), and (Ph_3P)-Pd($C_6H_{10}O$) (**28**) the ambient temperature 1,6-diene ^{1}H and ^{13}C resonances are sharp as long as additional 1,6-diene is absent. For {(RO)$_3$P}Pd(C_7H_{12}) (**20**−**22**) some broadening of the hepta-1,6-diene ═CHC$H_{eq}H_{ax}$− and −CH_aH_b− resonances is observed in the ambient temperature ^{1}H NMR spectra, but the resonances are sharply resolved when the temperature is lowered to −30 °C. For these compounds in the presence of uncoordinated 1,6-diene *all* 1,6-diene resonances are broad at ambient temperature. Thus, a decreasing donor strength of L (eq 10) destabilizes the 1,6-diene coordination, resulting in structural dynamics according to Schemes 8 and/or 9.

Scheme 9



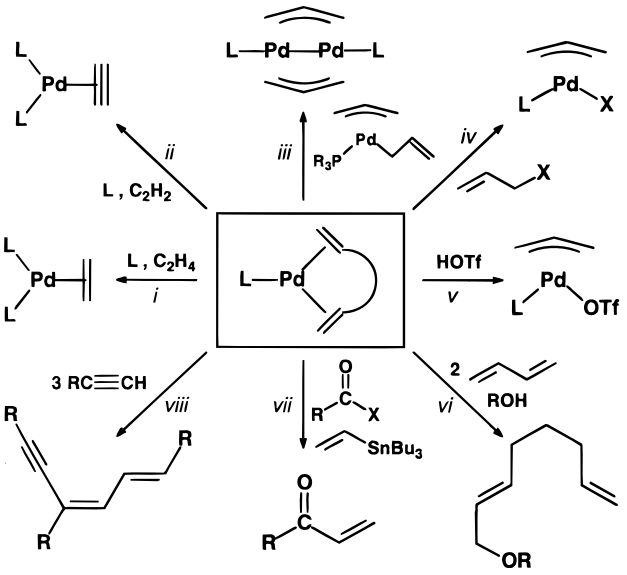
Concerning *sterically encumbered* {(2-MeC_6H_4)$_3$P}Pd(1,6-diene) (**19**, **29**, **38**),[50] for the hepta-1,6-diene derivative **19** the ^{1}H NMR signals of ═CHC$H_{eq}H_{ax}$− and −CH_aH_b−, for the diallyl ether derivative **29** the ^{1}H NMR signals of ═CHC$H_{eq}H_{ax}$−, and for the dvds derivative **38** the ^{1}H and ^{13}C NMR signals of ═CHSi$Me_{eq}Me_{ax}$− are distinct but broad at ambient temperature, while the vinyl resonances are sharply resolved. In the presence of uncoordinated 1,6-diene the spectra of the complexes are unchanged and additional sharp resonances of the free 1,6-diene are observed. The spectra show that the 1,6-diene ligands in these complexes undergo slow intramolecular face-exchange dynamics of the vinyl groups according to (b) (Scheme 8).

These dynamics are even more rapid for ($^tBu_3P$)Pd(1,6-diene) (**16**, **27**, **36**). The hepta-1,6-diene derivative **16** displays broad ═CHC$H_{eq}H_{ax}$− resonances as low as −80 °C. Unfortunately, recording of the coalesced signal at higher temperature was impeded by the thermolability of this complex. In the ^{1}H NMR spectra of the diallyl ether complex **27** the ═CHC$H_{eq}H_{ax}$− resonances are sharp at −80 °C but broad at −30 °C, and in the ^{1}H and ^{13}C NMR spectra of the dvds complex **36** the $SiMe_{eq}$-Me_{ax} resonances are sharply resolved at −80 °C but coalesced at −30 °C; the vinyl resonances are constantly sharp at these temperatures. For added 1,6-diene separate sharp signals are observed, showing that an exchange of coordinated and uncoordinated 1,6-diene is slow. Thus, the ($^tBu_3P$)Pd(1,6-diene) complexes likewise undergo intramolecular vinyl group face-exchange dynamics according to (b) (Scheme 8), and these dynamics, detectable for **16** at −80 °C and for **27** and **36** at −30 °C, are markedly more rapid than for other L−Pd(1,6-diene) complexes and the platinum derivative ($^tBu_3P$)Pt(dvds).[18d] At 27 °C all 1,6-diene resonances of **27** and **36** are broad and so are the resonances of added 1,6-diene, giving evidence of an exchange of coordinated and uncoordinated 1,6-diene. Furthermore, increasing the temperature from −80 to 27 °C shifts the ^{31}P NMR signals of **27** and **36** downfield by about 5

(49) Dreher, E.; Gabor, B.; Jolly, P. W.; Kopiske, C.; Krüger, C.; Limberg, A.; Mynott, R. *Organometallics* **1995**, *14*, 1893.

(50) In the −80 °C ^{13}C NMR (75.5 MHz) spectrum of **19** seven hepta-1,6-diene resonances are observed (δ(C) 78.0, 77.4 (═CH−), 59.5, 59.0 (H_2C═), 33.8, 33.4 (═CHCH_2−), 33.0 (−CH_2−)), indicating chirality of the complex. This is explained by the propeller-like conformation of the (*o*-tolyl)$_3$P ligand with locked handedness.

Scheme 10



ppm, which we attribute to occurrence of Pd−1,6-diene chelate ring cleavage and an increased population of an *L*-2 ($^tBu_3P$)-Pd(η^2-1,6-diene) intermediate.[51] These spectral features are explained by structural dynamics according to (c) (Scheme 9), becoming relevant at ambient temperature in addition to those of (b).

IV. Applications of L−Pd(1,6-Diene) Complexes (Scheme 10). L−Pd(1,6-diene) complexes represent versatile building blocks for the deliberate synthesis of a large variety of Pd^0, Pd^I, and Pd^{II} complexes. Examples include (i, ii) the formation of L_2Pd−alkene and L_2Pd−alkyne complexes,[52] (iii) the formation of dinuclear Pd^I complexes,[13a,53] and (iv, v) the formation of [L−Pd(allyl)] moieties from L−Pd($C_6H_{10}O$) by oxidative addition of allyl halides or protonation.[13a,53] Apart from these stoichiometric reactions, L−Pd(1,6-diene) complexes are effective catalysts for a variety of coupling reactions under mild conditions. Examples are given by (vi) the linear telomerization of butadiene with MeOH to give 1-methoxy-octa-2,7-diene[11] above −10 °C,[54] (vii) the Stille coupling of organoelectrophiles and organostannanes[55a] at 20 °C,[55b] and (viii) the regio- and stereoselective linear trimerization of alk-1-ynes to give 1,4,6-trisubstituted *cis*-hexa-1,3-dien-5-ynes between −30 and 20 °C.[13a,c,17,52] Promising candidates are furthermore Pd-catalyzed cross-coupling reactions such as Heck reactions, Suzuki couplings, and aryl halide amination.[56]

(51) The ^{31}P NMR downfield shift indicates an enlarged charge withdrawal from P. Apparently, in a 14e *L*-2 ($^tBu_3P$)Pd(η^2-alkene) complex the charge withdrawal from phosphorus by the trans coordinated C═C group is larger than that in 16e *TP*-3 **27** and **36** by two C═C groups.

(52) (a) Krause, J.; Pörschke, K.-R. 5th International Conference on the Chemistry of the Platinum Group Metals, St. Andrews, U.K., July 11−16, 1993, A199. (b) Krause, J.; Schager, F.; Pörschke, K.-R. 32nd International Conference on Coordination Chemistry (ICCC), Santiago, Chile, Aug 24−29, 1997, 7O4. Cestaric, G.; Krause, J.; Pörschke, K.-R. Manuscript in preparation.

(53) Krause, J.; Pörschke, K.-R. To be submitted for publication.

(54) Vollmüller, F.; Krause, J.; Klein, S.; Mägerlein, W.; Beller, M. Submitted.

(55) (a) Stille, J. K. *Angew. Chem.* **1986**, *98*, 504; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033. Mitchell, T. N. *Synthesis* **1992**, 803. (b) The reactions apparently proceed without an induction period or deposition of palladium. The results confirm that in the L_nPd^0 catalyzed Stille reaction phosphane dissociation gives rise to [L−Pd^0] species as the "true catalyst". No second phosphane ligand is necessary to act in the catalytic cycle. Krause, J.; Pörschke, K.-R. Unpublished results.

(56) Hartwig, J. F. *Synlett* **1998**, 329.

Conclusions

This work describes the development of a general and efficient access to 1,6-diene stabilized "naked palladium" and L−Pd^0 complexes as fundamental and highly reactive building units in palladium chemistry. In the homoleptic olefinic complexes **1**−**12** the metal atoms (Pd and Pt) are *TP*-3 coordinated (in contrast to, e.g., the *T*-4 geometry predicted for the elusive Pd(cod)$_2$). This feature and the properties of the chelating 1,6-diene moiety, which chelates a *TP*-3 d^{10} M^0 center with little strain, are the clue for the stability of this class of complexes.

As exemplified by **13**−**38**, there is now a broad range of 16e *TP*-3 L−Pd(η^2,η^2-1,6-diene) complexes available which may be prepared by numerous routes. For complexes with weakly electron-donating (P(OR)$_3$) or sterically demanding (P(*o*-tolyl)$_3$, P^tBu_3) ligands it is anticipated that the chelate ring opens easily to generate 14e *L*−2 L−Pd(η^2-diene) intermediates from which the 1,6-diene ligand can be displaced.

Besides for stoichiometric reactions, L−Pd(1,6-diene) complexes may play an important role in the "soft" catalytic Pd^0 chemistry under nonforcing conditions, in particular when high selectivities are desired. Moreover, the complexes are readily formed as intermediates from a Pd^0 source in the presence of a donor L simply by running reactions in a 1,6-diene solvent (e.g. diallyl ether). It is to be expected that the complexes find general application in homogeneous catalysis in those cases where an unsaturated complex fragment [L−Pd^0], which is easily developed from the complexes, acts as the "true catalyst". This concept has already been proven for the reactions cited above.

Although our study focused on the 1,6-dienes given in Scheme 6, the principle of stabilization of "naked palladium" and [L−Pd^0] fragments by 1,6-positioned ene functions is presumingly quite general. Thus, 1,6-heterodienes (C═NR, C═O) are also expected to form stable *TP*-3 L−M(diene) complexes (M = Ni, Pd, Pt). In contrast, L−M(1,6-diyne) complexes are significantly less stable and so far confined to M = Ni,[57] and L−M(1,6-enyne) complexes seem to be unstable for all metals of the d^{10} triad.

Experimental Section

To exclude oxygen and moisture, all operations were conducted under an atmosphere of argon by standard Schlenk techniques. (cod)$PdCl_2$,[58a] (cod)$PtCl_2$,[58b] Pd(η^3-C_3H_5)$_2$,[26a] Pd(η^3-2-MeC_3H_4)$_2$,[26a] CpPd(η^3-C_3H_5),[59] and (tmeda)$PdMe_2$[31a,b] were prepared by published procedures. Microanalyses were performed by the Mikroanalytisches Labor Kolbe, Mülheim, Germany. ^1H NMR spectra (δ relative to internal TMS) were measured at 200, 300, and 400 MHz, ^{13}C NMR spectra (δ relative to internal TMS) at 50.3, 75.5, and 100.6 MHz, and ^{31}P NMR spectra (δ relative to external 85% aqueous H_3PO_4) at 81, 121.5, and 162 MHz on Bruker AM-200, WM-300, and WH-400 instruments. For all NMR spectra solutions of the compounds in THF-d_8 were used. EI mass spectra (the data refer to ^{28}Si, ^{106}Pd, and ^{195}Pt) were recorded at 70 eV on a Finnigan MAT 8200, and IR spectra on Nicolet FT 7199 and Magna-IR 750 spectrometers.

(μ-η^2,η^2-C_7H_{12}){Pd(η^2,η^2-C_7H_{12})}$_2$ (1). A suspension of (cod)$PdCl_2$ (8.57 g, 30.0 mmol) in 40 mL of hepta-1,6-diene was treated slowly at −78 °C with a 0.2 M solution of Li_2(cot) (150 mL, 30.0 mmol) in diethyl ether. When the temperature was raised to −40 °C a voluminous

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(58) (a) Chatt, J.; Vallarino, L. M.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 3413. (b) Chatt, J.; Vallarino, L. M.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 2496. McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521.

(59) (a) Shaw, B. L. *Proc. Chem. Soc., London* **1960**, 247. (b) Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 220.

precipitate formed, consisting of **1** and LiCl. At −20/−10 °C the suspension was so dense that it could hardly be stirred. When diethyl ether was evaporated under vacuum, **1** dissolved again. LiCl was removed by D4-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 g (61%); ∼0 °C dec. Anal. Calcd for $C_{21}H_{36}Pd_2$ (501.4): C, 50.31; H, 7.24; Pd, 42.45. Found: C, 50.41; H, 7.35; Pd, 42.45.

(μ-η^2,η^2-$C_6H_{10}O$){Pd(η^2,η^2-$C_6H_{10}O$)}$_2$·$C_6H_{10}O$ (2′). The reaction was performed as for **1** by treating a suspension of (cod)$PdCl_2$ (2.86 g, 10.0 mmol) in diallyl ether (20 mL) with a 0.2 M ethereal solution of Li_2(cot) (50 mL, 10.0 mmol) at −78 °C. After warming the mixture to 0 °C the ether was evaporated under vacuum. Pentane (40 mL) was added at −30 °C to precipitate LiCl, which was removed by an immediate D4-filtration. The product crystallized between −30 and −78 °C, and the mother liquor was removed by cannulation. The pale yellow solid was washed twice with cold pentane and dried under vacuum (−30 °C): yield 1.26 g (42%); >0 °C dec. EI-MS: The complex decomposed between 30 and 50 °C; no ions containing Pd were observed. ^{1}H NMR of **2** (300 MHz, −30 °C): δ 3.26, 3.26, 3.17, 3.13, 3.05, 3.04 (each 2H, H_ZHC═), 3.56, 3.56, 3.47, 3.46, 3.40, 3.40 (each 2H, HH_EC═), 4.43 (4H), 4.13 (8H, unresolved ═CH−), 4.52 (8H), 4.28 (4H, unresolved −CH_aHO−), 4.28, 4.28, 2.31, 2.30, 2.30, 2.29 (each 2H, −CHH_bO−). ^{13}C NMR of **2** (75.5 MHz, −30 °C): δ 85.7, 85.7, 85.5, 85.5, 79.3, 79.1 (═CH−), 72.8, 72.5, 70.3, 70.3, 70.1, 69.9 (−CH_2O−), 63.4, 63.4, 59.5, 59.5, 59.3, 59.25 (H_2C═); all signals have the same intensity (2C). The signals and intensities refer to the diastereomeric mixture. Additional signals are observed for uncoordinated $C_6H_{10}O$ (see Table 1) and **6**. Anal. Calcd for $C_{18}H_{30}O_3Pd_2$·$C_6H_{10}O$ (605.4): C, 47.61; H, 6.66; O, 10.57; Pd, 35.16. Found: C, 47.79; H, 6.62; Pd, 34.94.

{μ-(η^2-H_2C═CHSiMe_2)$_2$O}[Pd{(η^2-H_2C═CHSiMe_2)$_2$O}]$_2$ (3). The reaction was performed as for **1** by treating a suspension of (cod)-$PdCl_2$ (2.86 g, 10.0 mmol) in dvds (10 mL) with a 0.2 M ethereal solution of Li_2(cot) (50 mL, 10.0 mmol) at 20 °C. Ether was evaporated under vacuum to afford an ocher suspension. After D4-filtration (removal of LiCl) the light yellow solution was concentrated under high vacuum to give a sticky oil, to which some pentane (5 mL) was added. Between −30 and −78 °C an almost colorless mirocrystalline precipitate was obtained, from which the mother liquor was removed by filtration. The product was washed with a small portion of cold pentane and dried under vacumm (−30 °C): yield 2.90 g (75%); mp 55 °C dec. ^{1}H NMR (300 MHz, −80 °C): δ 4.3−3.4 (18 overlapping multiplets, each 2H; H_ZH$_E$C═ and ═CH−), 0.25, 0.25, 0.23, 0.23, 0.11, 0.10, −0.05, −0.05, −0.22, −0.23, −0.32, −0.32 (each s, 6H, SiMe). ^{13}C NMR (75.5 MHz, −80 °C): δ 75.85, 75.8, 75.1, 75.1, 74.4, 74.4, 73.7, 73.7, 73.4, 73.4, 72.8, 72.8 (vinyl), 3.14, 3.14, 1.60, 1.60, 1.52, 1.52, 1.45, 1.41, −0.92, −0.94, −1.17, −1.17 (SiMe); all signals have the same intensity (2C). The signals and intensities refer to the diastereomeric mixture of **3**. Anal. Calcd for $C_{24}H_{54}O_3Pd_2Si_6$ (772.0): C, 37.34; H, 7.05; O, 6.22; Pd, 27.57; Si, 21.83. Found: C, 37.26; H, 7.12; Pd, 27.48; Si, 21.89.

(μ-η^2,η^2-C_7H_{12}){Pt(η^2,η^2-C_7H_{12})}$_2$ (4). A suspension of (cod)$PtCl_2$ (1.496 g, 4.00 mmol) in hepta-1,6-diene (12 mL) was combined with a 0.2 M ethereal solution of Li_2(cot) (20 mL, 4.00 mmol) at −78 °C. The stirred brown mixture was slowly (2 h) warmed to ambient temperature, ether was evaporated, and the concentrated suspension was stirred for a further 15 h. LiCl was removed by D4-filtration and washed twice with pentane (10 mL). After addition of further pentane (20 mL) to the brown solution a yellow beige solid precipitated at −78 °C which was separated by filtration, washed with cold pentane, and dried under vacuum (20 °C): yield 510 mg (38%); mp 110 °C dec. EI-MS (90 °C): *m*/*e* (%) 582 ([Pt_2(C_7H_{12})$_2$]$^+$, 0.1), 387 ([Pt(C_7H_{12})$_2$]$^+$, 5), 291 ([Pt(C_7H_{12})]$^+$, 15); M$^+$ was not detected. Anal. Calcd for $C_{21}H_{36}$-Pt_2 (678.7): C, 37.17; H, 5.35; Pt, 57.49. Found: C, 37.10; H, 5.37; Pt, 57.62.

Pd(η^2,η^2-C_7H_{12})(η^2-C_7H_{12}) (5). Complex **1** (ca. 80 mg) was dissolved in hepta-1,6-diene (0.2 mL) and THF-d_8 (0.7 mL). ^{13}C NMR (75.5 MHz, −80 °C): δ 139.6 (═CH−$_{uncoord}$), 115.1 (H_2C═$_{uncoord}$), 84.4, 84.2, 84.0 (═CH−), 62.8, 62.4, 61.6 (H_2C═), 35.6, 34.7, 32.9, 32.6, 32.5, 32.4 (═CHCH_2− and −CH_2−); all signals of equal intensity. $C_{14}H_{24}Pd$ (298.8).

Pd(η^2,η^2-$C_6H_{10}O$)(η^2-$C_6H_{10}O$) (6). Preparation was performed as for **5** by dissolving **2** (ca 80 mg) in diallyl ether (0.2 mL) and THF-d_8. ^{13}C NMR (75.5 MHz, −80 °C): δ 136.4 (═CH−$_{uncoord}$), 115.7 (H_2C═$_{uncoord}$), 85.6, 85.4, 77.3 (═CH−), 73.4, 70.5, 69.9, 69.6 (−CH_2O−), 63.9, 59.6, 59.4 (H_2C═); all signals were of equal intensity. $C_{12}H_{20}O_2$-Pd (302.7).

Pd(η^2,η^2-dvds)(η^2-dvds) (7). Preparation was as for **5** by dissolving **3** (ca 80 mg) in dvds (0.2 mL) and THF-d_8. ^{13}C NMR (75.5 MHz, −80 °C): δ 140 (═CH−$_{uncoord}$), 133 (H_2C═$_{uncood}$), 75.6, 75.0, 74.6 (═CH−), 73.5, 73.2, 73.0 (H_2C═), each 1C, vinyl; 3.1 (1C), 1.5 (2C), 1.2 (1C), 0.7 (2C), −0.9 (1C), −1.1 (1C), $SiMe_aMe_b$; all signals are broad. $C_{16}H_{36}O_2PdSi_4$ (479.2).

Pt(η^2,η^2-C_7H_{12})(η^2-C_7H_{12}) (8). Preparation was as for **5** by dissolving **4** (ca 80 mg) in hepta-1,6-diene (0.2 mL) and THF-d_8. ^{13}C NMR (75.5 MHz, −30 °C): δ 139.7 (═CH−$_{uncoord}$, C13), 114.8 (H_2C═$_{uncoord}$, C14), 70.0, 69.8 (each J(^{195}PtC) = 108 Hz, C2 and C6), 65.6 (137 Hz, C9), 48.5 (137 Hz, C1/7), 48.1 (133 Hz, C1/7), 46.8 (121 Hz, C8), 35.3 (24 Hz, C11), 34.7 (13 Hz, C12), 33.6 (37 Hz, C4), 33.3 (55 Hz, C10), 31.4, 31.3 (each 28 Hz, C3 and C5); all signals were of equal intensity. At 27 °C the resonances are broad but still resolved. $C_{14}H_{24}$-Pt (387.4).

(C_2H_4)Pd(η^2,η^2-C_7H_{12}) (9). A colorless suspension of **1** (ca 80 mg) in 1 mL of THF-d_8 was saturated with ethene at −78 °C. When the mixture was warmed to −30 °C, the solid dissolved (10 min) to give a yellow solution. ^{1}H NMR (200 MHz, −30 °C) (for C_7H_{12} see Table 1): δ 3.39 (4H, C_2H_4). ^{13}C NMR (75.5 MHz, −30 °C) (for C_7H_{12} see Table 1): δ 61.9 (2C, C_2H_4). The spectra displayed additional signals for 1 half-equiv of the displaced 1,6-diene (Table 1) and for uncoordinated ethene (δ(H) 5.39, δ(C) 123.7). $C_9H_{16}Pd$ (230.7).

(C_2H_4)Pd(η^2,η^2-$C_6H_{10}O$) (10). The synthesis was performed as for **9** by reacting **2** (ca. 80 mg) with ethene in THF-d_8 at −30 °C. ^{1}H NMR (300 MHz, −30 °C) (for $C_6H_{10}O$ see Table 1): δ 3.53 (4H, C_2H_4). ^{13}C NMR (75.5 MHz, −30 °C) (for $C_6H_{10}O$ see Table 1): δ 63.0 (2C, C_2H_4). $C_9H_{14}OPd$ (244.6).

(C_2H_4)Pd{(η^2-H_2C═CHSiMe_2)$_2$O} (11). The synthesis was performed as for **9** by reacting **3** (ca. 80 mg) with ethene in THF-d_8 at −30 °C. ^{1}H NMR (300 MHz, −30 °C) (for dvds see Table 1): δ 3.79 (4H, C_2H_4). ^{13}C NMR (75.5 MHz, −30 °C) (for dvds see Table 1): δ 73.3 (2C, C_2H_4). $C_{10}H_{22}OPdSi_2$ (320.9).

(C_2H_4)Pt(η^2,η^2-C_7H_{12}) (12). A suspension of **4** (204 mg, 0.30 mmol) in pentane (5 mL) was saturated with ethene (−78 °C) and stirred at 0 °C to produce a clear yellow solution. The solvent was evaporated in a light vacuum to yield a low-melting, semisolid yellow residue of pure **12**: yield 35−40 mg (40%). Although the reaction appears to be quantitative, the yield of isolated **12** is low due to its high volatility. For subsequent reactions an in situ preparation is recommended. EI-MS: see text. ^{1}H NMR (300 MHz, 27 °C) (for C_7H_{12} see Table 1): δ 2.95 (4H, ^2J(PtH) = 59 Hz, C_2H_4). ^{13}C NMR (75.5 MHz, 27 °C) (for C_7H_{12} see Table 1): δ 44.3 (2C, ^1J(PtC) = 122 Hz, C_2H_4). $C_9H_{16}Pt$ (319.3).

(Me_3P)Pd(η^2,η^2-C_7H_{12}) (13). (a) From 1. A suspension of complex **1** (501 mg, 1.00 mmol) in 2 mL of hepta-1,6-diene (0 °C) was treated with a solution of PMe_3 (152 mg, 2.00 mmol) in 5 mL of pentane at −78 °C. The mixture was slowly warmed to 20 °C, and insoluble impurities were removed by D4-filtration. From the solution colorless thin needles separated between −30 and −78 °C. After removal of the mother liquor by cannulation, the product was washed with a small volume of cold pentane and dried under vacuum at −30 °C: yield 400 mg (72%). **(b) From (η^5-C_5H_5)Pd(η^3-C_3H_5).** Addition of PMe_3 (0.20 mL, 152 mg, 2.00 mmol) to a red suspension of (η^5-C_5H_5)Pd(η^3-C_3H_5) (425 mg, 2.00 mmol) in 3 mL of hepta-1,6-diene at −30 °C immediately afforded a light yellow precipitate. Heating the mixture to 80 °C for 5 h resulted in a clear yellow solution from which thin colorless needles crystallized at −78 °C. Isolation was as described above: yield 290 mg (52%); mp ca. 27 °C. EI-MS (0 °C): *m*/*e* (%) 278 (M$^+$, 31), 182 ([(Me_3P)Pd]$^+$, 81). ^{1}H NMR (200 MHz, 27 °C) (for C_7H_{12} see Table 1): δ 1.22 (d, 9H), PMe_3. ^{13}C NMR (50.3 MHz, 27 °C) (for C_7H_{12} see Table 1): δ 19.2 (3C), PMe_3. ^{31}P NMR (81 MHz, 27 °C): see Table

1. Anal. Calcd for $C_{10}H_{21}PPd$ (278.7): C, 43.10; H, 7.60; P, 11.11; Pd, 38.19. Found: C, 42.95; H, 7.66; P, 11.03; Pd, 38.42.

(^{i}Pr$_3$P)Pd(η^2,η^2-C$_7$H$_{12}$) (14). (a) From 1. Synthesis was as for **13**, route a, by using P^iPr_3 (320 mg, 2.00 mmol) in 5 mL of pentane (20 °C). Between −30 and −78 °C colorless crystals separated which were washed twice with cold pentane and dried under vacuum at 20 °C: yield 610 mg (84%). **(b) From (tmeda)PdMe$_2$.** To (tmeda)$PdMe_2$ (1.263 g, 5.00 mmol) was added a solution of P^iPr_3 (801 mg, 5.00 mmol) in 5 mL of hepta-1,6-diene at −30 °C. The stirred colorless suspension was slowly heated to 25−30 °C, whereupon ethane evolved and an orange solution was formed. Between −30 and −78 °C a microcrystalline precipitate was obtained which was isolated as described (route a): yield 1.69 g (93%). **(c) From Pd(η^3-C$_3$H$_5$)$_2$.** P^iPr_3 (801 mg, 5.00 mmol) was added to a solution of Pd(η^3-C_3H_5)$_2$ (943 mg, 5.00 mmol) in 5 mL of hepta-1,6-diene. The yellow mixture was heated to 80 °C for 2 h, whereupon the solution decolorized. After evaporation of the excess of hepta-1,6-diene the residue was dissolved in pentane (20 mL) and some deposited Pd was removed by filtration. Between −30 and −78 °C colorless crystals separated which were isolated as described (route a): yield 1.54 g (85%). **(d) From {(^{i}Pr$_3$P)Pd}$_2$(μ-C$_3$H$_5$)$_2$.** The yellow suspension of {(^{i}Pr$_3$P)Pd}$_2$(μ-C_3H_5)$_2$ (615 mg, 1.00 mmol) in 5 mL of hepta-1,6-diene was heated to 80 °C for 2 h, whereupon the solution decolorized. After evaporation of the excess of hepta-1,6-diene and addition of pentane (10 mL) the solution was treated further as described (routes a and c): yield 630 mg (87%). **(e) From (tmeda)PdMe$_2$ and Pd(P^{i}Pr$_3$)$_2$.** A suspension of (tmeda)$PdMe_2$ (253 mg, 1.00 mmol) in 1 mL of hepta-1,6-diene was combined at −30 °C with a solution of Pd(P^iPr_3)$_2$ (427 mg, 1.00 mmol) in 2 mL of hepta-1,6-diene. When the mixture was heated to 30 °C ethane evolved and an orange-yellow solution was obtained. After addition of pentane (10 mL) the colorless product crystallized between −30 and −78 °C and was isolated as described (route a): yield 545 mg (75%); mp 52 °C. EI-MS (43 °C): *m*/*e* (%) 362 (M^+, 28), 266 ([(^{i}Pr$_3$P)Pd]$^+$, 88). ^{1}H NMR (200 MHz, 27 °C) (for C_7H_{12} see Table 1): δ 2.18 (m, 3H, PCH), 1.16 (dd, 18H, Me), P^iPr_3. ^{13}C NMR (100.6 MHz, 27 °C) (for C_7H_{12} see Table 1): δ 26.9 (3C, PCH), 20.9 (6C, Me), P^iPr_3. ^{31}P NMR (81 MHz, 27 °C): see Table 1. Anal. Calcd for $C_{16}H_{33}PPd$ (362.8): C, 52.97; H, 9.17; P, 8.54; Pd, 29.33. Found: C, 52.84; H, 9.25; P, 8.60; Pd, 29.54.

(Cy$_3$P)Pd(η^2,η^2-C$_7$H$_{12}$) (15). The synthesis was carried out as for **14**, route b, by reacting (tmeda)$PdMe_2$ (506 mg, 2.00 mmol) with Cy_3P (561 mg, 2.00 mmol) in 5 mL of hepta-1,6-diene. At 30 °C a green-yellow solution formed from which a colorless solid precipitated. The excess of hepta-1,6-diene was siphoned off (20 °C), and the solid was recrystallized from diethyl ether (50 mL) to yield colorless cubes (−30 °C) which were isolated as described for **14**, route a: yield 735 mg (76%); mp 131 °C. EI-MS (80 °C): *m*/*e* 482 (M^+, 1), 386 ([(Cy_3P)Pd]$^+$, 4), 304 ([(Cy_2PH)Pd]$^+$, 2). ^{1}H NMR (200 MHz, 27 °C) (for C_7H_{12} see Table 1): δ 2.1−1.6 (18H), 1.5−1.2 (15H), (*c*-C_6H_{11})$_3$P. ^{13}C NMR (50.3 MHz, 27 °C) (for C_7H_{12} see Table 1): δ 37.4 (3C, ^1J(PC) = 9.6 Hz, PC_α), 31.8 (6C, $PCHC_\beta$), 28.8 (6C, C_γ), 27.8 (3C, C_δ), P(*c*-C_6H_{11})$_3$. ^{31}P NMR (81 MHz, 27 °C): see Table 1. Anal. Calcd for $C_{25}H_{45}PPd$ (483.0): C, 62.17; H, 9.39; Pd, 22.03; P, 6.41. Found: C, 62.34; H, 9.29; Pd, 22.10; P, 6.63.

(^{t}Bu$_3$P)Pd(η^2,η^2-C$_7$H$_{12}$) (16). A suspension of complex **1** (501 mg, 1.00 mmol) in 10 mL of pentane is reacted with ethene at −30 °C to give a yellow solution of **9**. After filtration to remove some insoluble impurities the mixture is combined with a solution of $^tBu_3P$ (404 mg, 2.00 mmol) in 5 mL of pentane at −78 °C. From such a solution only small amounts of product crystallized (up to 30%) in the course of serveral days. Therefore, the solvent was evaporated under high vacuum (−78 °C) to give a beige residue that was about 90% pure (NMR). Isolated **16** contained some Pd(P^tBu_3)$_2$ and **5** as impurities (each about 5%). The product was stable only below −30 °C; at this temperature it slowly converted into Pd(P^tBu_3)$_2$. EI-MS: the complex decomposed and only Pd(P^tBu_3)$_2$ was detected. ^{1}H NMR (200 MHz, −80 °C) (for C_7H_{12} see Table 1): δ 1.34 (d, 27H, ^3J(PH) = 12 Hz, Me), P^tBu_3. ^{31}P NMR (81 MHz, −80 °C): see Table 1. $C_{19}H_{39}PPd$ (404.9). No elemental analysis was performed.

(Ph$_3$P)Pd(η^2,η^2-C$_7$H$_{12}$) (17). (a) From 1. A suspension of **1** (250 mg, 0.50 mmol) in 1 mL of hepta-1,6-diene (0 °C) was treated with a solution of PPh_3 (262 mg, 1.00 mmol) in 5 mL of diethyl ether at −78 °C. The mixture was slowly warmed to 20 °C, and insoluble impurities were removed by D4-filtration. From the colorless solution pale yellow intergrown crystals separated at −78 °C, which were isolated as described for **13**: yield 350 mg (75%). **(b) From (tmeda)PdMe$_2$.** A mixture of (tmeda)$PdMe_2$ (758 mg, 3.00 mmol) and PPh_3 (786 mg, 3.00 mmol) in hepta-1,6-diene (5 mL) was heated to 80 °C for 15 min. After cooling all volatiles were evaporated in a vacuum and the residue was dissolved in a small volume of diethyl ether. The product crystallized at −78 °C and was isolated as described for route a: yield 1.18 g (85%); mp 87 °C dec. Crystalline **17** is stable at ambient temperature for at least several days but slowly decomposes in solution. EI-MS: the compound decomposed and the spectra of C_7H_{12} (*m*/*e* 96) and PPh_3 (*m*/*e* 262) were observed. ^{1}H NMR (400 MHz, 27 °C) (for C_7H_{12} see Table 1): δ 7.40 (3H, Ph), 7.32 (12H, Ph), PPh_3. ^{13}C NMR (50.3 MHz, 27 °C) (for C_7H_{12} see Table 1): δ 138.7 (3C), 134.3 (6C), 129.6 (3C), 128.7 (6C), PPh_3. ^{31}P NMR (81 MHz, 27 °C): see Table 1. Anal. Calcd for $C_{25}H_{27}PPd$ (464.9): C, 64.59; H, 5.40; P, 6.66; Pd, 22.89. Found: C, 64.46; H, 5.55; P, 6.77; Pd, 23.08.

{(4-MeC$_6$H$_4$)$_3$P}Pd(η^2,η^2-C$_7$H$_{12}$) (18). The reaction was carried out similarly as described for **17** by reacting a suspension of **1** (501 mg, 1.00 mmol) in hepta-1,6-diene (2 mL) with a solution of (4-MeC_6H_4)$_3$P (609 mg, 2.00 mmol) in 5 mL of diethyl ether. After warming the mixture from −78 to 20 °C the solvent was evaporated under vacuum to give a beige residue. Recrystallization from diethyl ether, including D4-filtration, afforded small red brown cubes (−30 °C) which were isolated as described: yield 710 mg (70%); mp 114 °C. EI-MS: the complex decomposed. ^{1}H NMR (200 MHz, 27 °C) (for C_7H_{12} see Table 1): δ 7.20 (12H, C_6H_4), 2.31 (9H, Me), (4-MeC_6H_4)$_3$P. ^{13}C NMR (50.3 MHz, 27 °C) (for C_7H_{12} see Table 1): δ 139.7 (s, 3C, C_δ), 136.0 (3C, PC_α), 134.6 (6C, C_β), 129.6 (6C, C_γ), 21.5 (3C, Me), (4-MeC_6H_4)$_3$P. ^{31}P NMR (81 MHz, 27 °C): see Table 1. Anal. Calcd for $C_{28}H_{33}PPd$ (507.0): C, 66.34; H, 6.56; P, 6.11; Pd, 20.99. Found: C, 66.45; H, 6.49; P, 6.02; Pd, 21.11.

{(2-MeC$_6$H$_4$)$_3$P}Pd(η^2,η^2-C$_7$H$_{12}$) (19). A solution of **1** (251 mg, 0.50 mmol) in hepta-1,6-diene (3 mL) was added to solid P(*o*-tolyl)$_3$ (304 mg, 1.00 mol). The solvent was evaporated from the resulting yellow solution under vacuum to obtain a yellow-greenish residue, which was washed with ether and dried under vacuum at −30 °C: yield 500 mg. Isolated **19** contained about 10% of Pd{P(*o*-tolyl)$_3$}$_2$ (δ(P) −6.9) as an impurity. The complex slowly decomposed at ambient temperature. ^{1}H NMR (200 MHz, 27 °C) (for C_7H_{12} see Table 1): δ 7.46 (3H), 7.20 (9H), 2.10 (9H), (2-MeC_6H_4)$_3$P. ^{13}C NMR (50.3 MHz, 27 °C) (for C_7H_{12} see Table 1):[50] δ 142.8, 134.9, 134.5, 132.1, 129.9, 126.2, 22.9 (each 3C), (2-MeC_6H_4)$_3$P. ^{31}P NMR (81 MHz, 27 °C): see Table 1. $C_{28}H_{33}PPd$ (507.0). No elemental analysis was performed.

{(PhO)$_3$P}Pd(η^2,η^2-C$_7$H$_{12}$) (20). The reaction was carried out as described for **13** by reacting a suspension of **1** (501 mg, 1.00 mmol) in hepta-1,6-diene (2 mL) with a solution of P(OPh)$_3$ (620 mg, 2.00 mmol) in 5 mL of pentane. From the colorless solution obtained by D4-filtration (20 °C) small intergrown crystals separated at −78 °C. Isolation was as described: yield 760 mg (74%). Crystalline **20** is stable at ambient temperature for at least several days but slowly decomposes in solution. ^{1}H NMR (200 MHz, −30 °C) (for C_7H_{12} see Table 1): δ 7.30 (12H), 7.12 (3H), P(OC_6H_5)$_3$. ^{31}P NMR (81 MHz, −30 °C): See Table 1. Anal. Calcd for $C_{25}H_{27}O_3PPd$ (512.9): C, 58.55; H, 5.31; O, 9.36; P, 6.04; Pd, 20.75. Found: C, 58.95; H, 5.45; P, 5.91; Pd, 20.77.

{(2,6-Me$_2$C$_6$H$_3$O)$_3$P}Pd(η^2,η^2-C$_7$H$_{12}$) (21). The synthesis was carried out as for **14**, route b, by reacting (tmeda)$PdMe_2$ (505 mg, 2.00 mmol) with (2,6-$Me_2C_6H_3O$)$_3$P (791 mg, 2.00 mmol) in 5 mL of hepta-1,6-diene at 80 °C (evolution of ethane starts at about 70 °C). From the resulting solution small colorless needles crystallized between 0 and −78 °C, which were isolated as described (**14**): yield 1.09 g (91%); mp 131 °C dec. EI-MS: the compound decomposed and the spectra of C_7H_{12} (*m*/*e* 96) and P($OC_6H_3Me_2$)$_3$ (*m*/*e* 394) were observed. ^{1}H NMR (400 MHz, 27 °C) (for C_7H_{12} see Table 1): δ 6.90 (6H, Ph), 6.80 (3H, Ph), 2.32 (18H, Me), P($OC_6H_3Me_2$)$_3$. ^{13}C NMR (50.3 MHz, 27 °C) (for C_7H_{12} see Table 1): δ 151.1 (3C), 131.7 (3C), 129.5 (6C), 124.9 (6C), 19.1 (6C), P($OC_6H_3Me_2$)$_3$. ^{31}P NMR (81 MHz, 27 °C):

see Table 1. Anal. Calcd for $C_{31}H_{39}O_3PPd$ (597.0): C, 62.36; H, 6.58; O, 8.04; P, 5.19; Pd, 17.82. Found: C, 62.53; H, 6.72; P, 5.28; Pd, 17.69.

{(2,6-^{i}Pr$_2$C$_6$H$_3$O)$_3$P}Pd(η^2,η^2-C$_7$H$_{12}$) (22). (a) From 1. The reaction was carried out as described for **13** by reacting a suspension of **1** (501 mg, 1.00 mmol) in hepta-1,6-diene (2 mL) with a solution of (2,6-^{i}Pr$_2$C$_6$H$_3$O)$_3$P (1.12 g, 2.00 mmol) in 10 mL of pentane. Warming the mixture from −78 to 0 °C gave a clear yellow solution from which a colorless solid precipitated at 20 °C. The mother liquor was siphoned off and the product was recrystallized from 5 mL of diethyl ether (−30 °C) to afford colorless intergrown needles which were washed twice with pentane (20 °C) and dried under vacuum: yield 460 mg (30%). **(b) From (tmeda)PdMe$_2$.** The synthesis was according to that of **14**, route b, and **21** by reacting (tmeda)PdMe$_2$ (758 mg, 3.00 mmol) with (2,6-^{i}Pr$_2$C$_6$H$_3$O)$_3$P (1.69 g, 3.00 mmol) in 5 mL of hepta-1,6-diene at 80 °C. A colorless solid precipitated (80 °C) from which the mother liquor was siphoned off (20 °C). The product was recrystallized and isolated as described above: yield 1.62 g (71%); mp 142 °C. EI-MS: the complex decomposed and upon fractional vaporization (50−90 °C) the ions $[Pd(C_7H_{12})]^+$ (*m*/*e* 222) and $[(2,6\text{-}^i Pr_2C_6H_3O)_3P]^+$ (*m*/*e* 562) were detected. ^{1}H NMR (400 MHz, 27 °C) (for C_7H_{12} see Table 1): δ 7.09 (9H, C_6H_3), 3.65 (sept, 6H, C*H*Me$_2$), 0.98 (d, 36H, ^3J(HH) = 6.8 Hz, Me), (2,6-^{i}Pr$_2$C$_6$H$_3$O)$_3$P. ^{13}C NMR (50.3 MHz, 27 °C) (for C_7H_{12} see Table 1): δ 148.8 (3C, POC$_\alpha$), 142.7 (6C, C$_\beta$), 126.2 (3C, C$_\delta$), 125.2 (6C, C$_\gamma$), 28.8 (6C, *C*HMe$_2$), 25.0 (12C, Me), (2,6-^{i}Pr$_2$C$_6$H$_3$O)$_3$P. ^{31}P NMR (81 MHz, 27 °C): see Table 1. Anal. Calcd for $C_{43}H_{63}O_3PPd$ (765.4): C, 67.48; H, 8.30; O, 6.27; P, 4.05; Pd, 13.90. Found: C, 67.38; H, 8.25; P, 4.11; Pd, 14.06.

(μ-^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$){Pd(η^2,η^2-C$_7$H$_{12}$)}$_2$ (23). Synthesis was as for **13**, route a, by using d^{i}ppe (262 mg, 1.00 mmol) dissolved in 5 mL of pentane. After filtration (20 °C) beige needles separated from the light brown solution at −78 °C. Isolation was as described: yield 535 mg (80%); mp 92 °C dec. ^{1}H NMR (400 MHz, −30 °C) (for C_7H_{12} see Table 1): δ 2.07 (m, 4H, PCH), 1.87 ("s", 4H, PCH$_2$), 1.11, 1.09 (each q, 12H, diastereotopic Me), d^{i}ppe. ^{31}P NMR (81 MHz, −30 °C): see Table 1. Anal. Calcd for $C_{28}H_{56}P_2Pd_2$ (667.5): C, 50.38; H, 8.46; P, 9.28; Pd, 31.88. Found: C, 50.42; H, 8.54; P, 9.29; Pd, 31.72.

(Me$_3$P)Pd(η^2,η^2-C$_6$H$_{10}$O) (24). Addition of PMe$_3$ (0.20 mL, 152 mg, 2.00 mmol) to a red suspension of (η^5-C$_5$H$_5$)Pd(η^3-C$_3$H$_5$) (425 mg, 2.00 mmol) in 3 mL of diallyl ether at −78 °C afforded a light yellow precipitate. When the mixture was warmed to 20 °C a clear solution was obtained from which colorless cuboids crystallized between −30 and −78 °C. The crystals were freed from the mother liquor, washed twice with cold pentane, and dried under vacuum at 20 °C: yield 505 mg (90%); mp 79 °C dec. EI-MS (20 °C): *m*/*e* (%) 280 (M^+, 27), 223 ($[(Me_3P)Pd(C_3H_5)]^+$, 64), 182 ($[(Me_3P)Pd]^+$, 64). ^{1}H NMR (200 MHz, 27 °C) (for $C_6H_{10}O$ see Table 1): δ 1.36 (d, 9H, Me), PMe$_3$. ^{13}C NMR (50.3 MHz, 27 °C) (for $C_6H_{10}O$ see Table 1): δ 19.2 (3C), PMe$_3$. ^{31}P NMR (81 MHz, 27 °C): see Table 1. Anal. Calcd for $C_9H_{19}OPPd$ (280.6): C, 38.52; H, 6.82; O, 5.70; P, 11.04; Pd, 37.92. Found: C, 38.28; H, 6.82; P, 11.09; Pd, 38.03.

(i Pr$_3$P)Pd(η^2,η^2-C$_6$H$_{10}$O) (25). (a) From (tmeda)PdMe$_2$. The synthesis was performed as for **14**, route b, by reacting (tmeda)PdMe$_2$ (1.263 g, 5.00 mmol) with P^{i}Pr$_3$ (801 mg, 5.00 mmol) in diallyl ether (5 mL). The stirred suspension was slowly warmed from −30 to 25−30 °C, whereupon ethane evolved and an orange solution was formed. Between −30 and −78 °C a colorless precipitate was obtained that was isolated as described: yield 1.73 g (93%). **(b) From Pd(η^3-C$_3$H$_5$)$_2$.** The synthesis followed that of **14**, route c, by heating a mixture of Pd(η^3-C$_3$H$_5$)$_2$ (943 mg, 5.00 mmol) and P^{i}Pr$_3$ (801 mg, 5.00 mmol) in 5 mL of diallyl ether to 80 °C for 2 h. Between −30 and −78 °C colorless crystals were obtained which were isolated as described: yield 1.55 g (85%). **(c) From 14.** A colorless solution of **14** (363 mg, 1.00 mmol) in diethyl ether (5 mL) was combined with diallyl ether (98 mg, 1.00 mmol) dissolved in ether (2 mL). After standing at ambient temperature for 1 h the mixture was cooled to −78 °C, whereupon colorless crystals separated which were isolated as described above: yield 347 mg (95%); mp 63 °C. EI-MS (70 °C): *m*/*e* (%) 364 (M^+, 1), 266 ($[(^iPr_3P)Pd]^+$, 4). ^{1}H NMR (200 MHz, 27 °C) (for $C_6H_{10}O$ see Table 1): δ 2.18 (m, 3H, PCH), 1.15 (dd, 18H, Me), P^{i}Pr$_3$. ^{13}C NMR (50.3 MHz, 27 °C) (for $C_6H_{10}O$ see Table 1): δ 26.9 (3C, PC), 20.8 (6C, Me), P^{i}Pr$_3$. ^{31}P NMR (81 MHz, 27 °C): see Table 1. Anal. Calcd for $C_{15}H_{31}OPPd$ (364.8): C, 49.39; H, 8.57; O, 4.39; P, 8.49; Pd, 29.17. Found: C, 49.25; H, 8.68; P, 8.60; Pd, 29.31.

(Cy$_3$P)Pd(η^2,η^2-C$_6$H$_{10}$O) (26). The synthesis was performed as for **14**, route b, by reacting (tmeda)PdMe$_2$ (505 mg, 2.00 mmol) with Cy$_3$P (561 mg, 2.00 mmol) in diallyl ether (5 mL). The stirred suspension was slowly warmed from −30 to 25−30 °C, whereupon ethane evolved and a colorless solution was formed from which the product precipitated in the course of 30 min. After cooling to −78 °C the solid was isolated as described: yield 790 mg (81%); dec 145 °C. EI-MS (115 °C): *m*/*e* (%) 484 (M^+, 2), 386 ($[(Cy_3P)Pd]^+$, 7), 304 ($[(Cy_2PH)Pd]^+$, 3), 280 ($[Cy_3P]^+$, 5). ^{1}H NMR (300 MHz, 27 °C) (for $C_6H_{10}O$ see Table 1): δ 2.0 (3H), 1.90 (6H), 1.85−1.7 (9H), 1.5−1.2 (15H), P(*c*-C$_6$H$_{11}$)$_3$. ^{13}C NMR (75.5 MHz, 27 °C) (for $C_6H_{10}O$ see Table 1): δ 37.1 (3C, PC$_\alpha$H), 31.6 (6C, C$_\beta$H$_2$), 28.5 (6C, C$_\gamma$H$_2$), 27.5 (3C, C$_\delta$H$_2$), P(*c*-C$_6$H$_{11}$)$_3$. ^{31}P NMR (121.5 MHz, 27 °C): see Table 1. Anal. Calcd for $C_{24}H_{43}OPPd$ (485.0): C, 59.44; H, 8.94; Pd, 21.94; P, 6.39; O, 3.30. Found: C, 59.24; H, 9.00; Pd, 22.10; P, 6.55.

(^{t}Bu$_3$P)Pd(η^2,η^2-C$_6$H$_{10}$O) (27). A suspension of **2′** (303 mg, 0.50 mmol) in 2 mL of diethyl ether was combined at −30 °C with an ethereal solution (5 mL) of ^{t}Bu$_3$P (202 mg, 1.00 mmol). After stirring the mixture for 1 h (−30 °C), colorless cubes crystallized at −78 °C. These were freed from the mother liquor and dried under vacuum: yield 220 mg (55%). The product contained about 10% of Pd(P^{t}Bu$_3$)$_2$. Solid **27** decomposes at ambient temperature in the course of 1 day. EI-MS: only the spectrum of Pd(P^{t}Bu$_3$)$_2$ was observed. ^{1}H NMR (300 MHz, −80 °C) (for $C_6H_{10}O$ see Table 1): δ 1.65−1.25 (broad, ^{t}Bu); at −30 °C: 1.43 (d, 27H, ^3J(PH) = 11 Hz, ^{t}Bu). ^{13}C NMR (75.5 MHz, −80 °C) (for $C_6H_{10}O$ see Table 1): δ 39.3 (s, 3C, PC), 35.3 (6C, Me), 28.2 (3C, Me′), P^{t}Bu$_3$. ^{31}P NMR (121.5 MHz, −80 °C): see Table 1. $C_{18}H_{37}OPPd$ (406.9). No elemental analysis was performed.

(Ph$_3$P)Pd(η^2,η^2-C$_6$H$_{10}$O) (28). (a) From (tmeda)PdMe$_2$. The synthesis was performed as for **14**, route b, by reacting (tmeda)PdMe$_2$ (505 mg, 2.00 mmol) with PPh$_3$ (525 mg, 2.00 mmol) in diallyl ether (5 mL). The stirred suspension was heated to 80 °C (15 min), whereupon ethane evolved (70 °C), and a light yellow solution was formed. After filtration, cooling from 0 to −78 °C gave small colorless needles which were isolated as described: yield 820 mg (88%). **(b) From (tmeda)PdMe$_2$ and (Ph$_3$P)$_2$PdMe$_2$.** A stirred suspension of (Ph$_3$P)$_2$PdMe$_2$ (330 mg, 0.50 mmol) and (tmeda)PdMe$_2$ (126 mg, 0.50 mmol) in diallyl ether (5 mL) was heated to 80 °C (15 min) to afford a colorless solution. After evaporation of all volatiles the pure product was obtained: yield 450 mg (96%). **(c) From (tmeda)PdMe$_2$ and Pd(PPh$_3$)$_4$.** Heating a stirred suspension of Pd(PPh$_3$)$_4$ (231 mg, 0.20 mmol) and (tmeda)PdMe$_2$ (151 mg, 0.60 mmol) in diallyl ether (3 mL) to 80 °C (15 min) afforded a yellow solution that was treated further as described for route a: yield 300 mg (82%). **(d) From Pd(η^3-C$_3$H$_5$)$_2$.** The synthesis followed that of **14**, route c, by heating a yellow solution of Pd(η^3-C$_3$H$_5$)$_2$ (377 mg, 2.00 mmol) and PPh$_3$ (525 mg, 2.00 mmol) in 5 mL of diallyl ether to 90 °C for a few minutes until the yellow color of the initially precipitated (Ph$_3$P)$_2$Pd$_2$(μ-C$_3$H$_5$)$_2$ disappeared (some metallic Pd deposited thereby). The mixture was cooled to 20 °C and filtered to afford a colorless solution, from which the product crystallized below 0 °C; isolation was as described: yield 800 mg (86%); mp 112 °C dec. ^{1}H NMR (200 MHz, 27 °C) (for $C_6H_{10}O$ see Table 1): δ 7.75 (3H), 7.65 (12H), PPh$_3$. ^{13}C NMR (50.3 MHz, 27 °C) (for $C_6H_{10}O$ see Table 1): δ 138.3 (3C), 134.4 (6C), 129.9 (3C), 128.9 (6C), PPh$_3$. ^{31}P NMR (81 MHz, 27 °C): see Table 1. Anal. Calcd for $C_{24}H_{25}OPPd$ (466.9): C, 61.75; H, 5.40; O, 3.43; P, 6.63; Pd, 22.80. Found: C, 61.93; H, 5.32; P, 6.65; Pd, 22.57.

{(2-MeC$_6$H$_4$)$_3$P}Pd(η^2,η^2-C$_6$H$_{10}$O) (29). A solution of (tmeda)-PdMe$_2$ (126 mg, 0.50 mmol) and P(*o*-tolyl)$_3$ (152 mg, 0.50 mmol) in 5 mL of diallyl ether was stirred at 20 °C for 48 h. The solvent was evaporated under vacuum and the product was washed with diethyl ether to remove small quantities of unreacted reagents: yield 200 mg (80%). ^{1}H NMR (300 MHz, 27 °C) (for $C_6H_{10}O$ see Table 1): δ 7.46, 7.31, 7.22, 7.15 (each 3H), 2.10 (9H), (2-MeC$_6$H$_4$)$_3$P. ^{13}C NMR (75.5 MHz, 27 °C) (for $C_6H_{10}O$ see Table 1): δ 142.9, 134.9, 134.0, 132.2, 130.3, 126.4, 22.9, each 3C, (2-MeC$_6$H$_4$)$_3$P. ^{31}P NMR (121.5 MHz, 27 °C): see Table 1. $C_{27}H_{31}OPPd$ (508.9). No elemental analysis was performed.

{(PhO)$_3$P}Pd(η^2,η^2-C$_6$H$_{10}$O) (30). The synthesis was performed as for **14**, route b, by reacting (tmeda)PdMe$_2$ (505 mg, 2.00 mmol) with P(OPh)$_3$ (621 mg, 2.00 mmol) in diallyl ether (5 mL). The stirred colorless suspension was slowly heated to 80 °C, whereupon ethane evolved (70 °C), and the solid dissolved. Cooling from 0 to −78 °C gave colorless crystals which were isolated as described: yield 980 mg (95%); mp 92 °C dec. ^{1}H NMR (200 MHz, 27 °C) (for C$_6$H$_{10}$O see Table 1): δ 7.2 (15H), P(OPh)$_3$. ^{31}P NMR (81 MHz, 27 °C): see Table 1. Anal. Calcd for C$_{24}$H$_{25}$O$_4$PPd (514.9): C, 55.99; H, 4.89; O, 12.43; P, 6.02; Pd, 20.67. Found: C, 56.14; H, 5.07; P, 6.15; Pd, 20.59.

(^{t}BuNC)Pd(η^2,η^2-C$_6$H$_{10}$O) (31). ^{t}BuNC (0.56 mL, 415 mg, 5.00 mmol) was added to a suspension of Pd(η^3-2-MeC$_3$H$_4$)$_2$ (1.083 g, 5.00 mmol) in 3 mL of diallyl ether at −78 °C. When the mixture was warmed to 20 °C an intensive yellow solution was obtained. In the course of 12 h the color changed to dark brown and light brown leaflets precipitated. These were freed from the mother liquor, washed with cold pentane, and dried under vacuum at −30 °C: yield 1.12 g (78%). EI-MS: the compound decomposed. ^{1}H NMR (200 MHz, −30 °C) (for C$_6$H$_{10}$O see Table 1): δ 1.51 (s, 9H), CN^{t}Bu. ^{13}C NMR (50.3 MHz, −30 °C) (for C$_6$H$_{10}$O see Table 1): δ 149.2 (1C, C≡N), 57.1 (1C, *C*Me$_3$), 30.6 (3C, Me), CN^{t}Bu. Anal. Calcd for C$_{11}$H$_{19}$NOPd (287.7): C, 45.92; H, 6.66; N, 4.87; O, 5.56; Pd, 36.99. Found: C, 45.82; H, 6.70; N, 4.80; Pd, 36.83. In THF, diethyl ether, or pentane the compound decomposes above −30 °C.

(^{i}Pr$_3$P)Pd(η^2,η^2-C$_6$H$_{10}$NH) (32). The synthesis was performed as for **14**, route b, by reacting (tmeda)PdMe$_2$ (505 mg, 2.00 mmol) with ^{i}Pr$_3$P (320 mg, 2.00 mmol) in diallylamine (5 mL). When the suspension was warmed to 20 °C (2 h), ethane evolved and a light green solution was obtained. The excess of diallylamine was evaporated under vacuum and the oily residue was dissolved in diethyl ether. After D4-filtration colorless cubes crystallized at −30 °C which were isolated as described: yield 520 mg (72%); mp 92 °C. EI-MS (35 °C): *m*/*e* (%) 363 (M$^+$, 28), 266 ([(^{i}Pr$_3$P)Pd]$^+$, 43), 224 ([(^{i}Pr$_2$PH)Pd]$^+$, 43). ^{1}H NMR (400 MHz, 27 °C) (for allylic groups of C$_6$H$_{10}$NH, see Table 1): δ 1.97 (br, 1H, NH), amine; 2.15 (m, 3H, PCH), 1.17 (dd, 18H, Me), ^{i}Pr$_3$P. ^{13}C NMR (75.5 MHz, 27 °C) (for C$_6$H$_{10}$NH see Table 1): δ 26.9 (3C, PCH), 20.8 (6C, Me), ^{i}Pr$_3$P. ^{31}P NMR (121.5 MHz, 27 °C): see Table 1. Anal. Calcd for C$_{15}$H$_{32}$NPPd (363.8): C, 49.52; H, 8.87; N, 3.85; P, 8.51; Pd, 29.25. Found: C, 49.58; H, 8.81; N, 3.78; P, 8.42; Pd, 29.20.

(Ph$_3$P)Pd(η^2,η^2-C$_6$H$_{10}$NH) (33). (a) From (tmeda)PdMe$_2$. The synthesis was performed as for **14**, route b, by reacting (tmeda)PdMe$_2$ (505 mg, 2.00 mmol) with PPh$_3$ (524 mg, 2.00 mmol) in diallylamine (5 mL). When the suspension was heated to 80 °C (5 min), ethane evolved and a light green solution resulted. The solution was worked-up as for **32** to afford an almost colorless microcrystalline precipitate at −78 °C: yield 720 mg (77%). **(b) From 17.** The synthesis followed that of **25**, route c, by reacting **17** (233 mg, 0.50 mmol) with diallylamine (200 mg, excess) in diethyl ether (5 mL) at 20 °C (2 h). All volatiles were evaporated in a vacuum and the residue was recrystallized from diethyl ether (−30 °C) to give light ocher cubes: yield 150 mg (64%); 77 °C dec. EI-MS: the compound decomposed and the spectra of C$_6$H$_{10}$NH (*m*/*e* 97) and PPh$_3$ (*m*/*e* 262) were observed. ^{1}H NMR (300 MHz, 27 °C) (for allylic groups of C$_6$H$_{10}$NH, see Table 1): δ 2.10 (br, 1H, NH), amine; 7.5−7.3 (15H), PPh$_3$. ^{13}C NMR (50.3 MHz, 27 °C) (for C$_6$H$_{10}$NH see Table 1): δ 138.7 (3C, PC$_\alpha$), 134.5 (6C, C$_\beta$), 129.7 (s, 3C, C$_\delta$), 128.8 (6C, C$_\gamma$), PPh$_3$. ^{31}P NMR (81 MHz, 27 °C): see Table 1. Anal. Calcd for C$_{24}$H$_{26}$NPPd (465.9): C, 61.88; H, 5.63; N, 3.01; P, 6.65; Pd, 22.84. Found: C, 62.10; H, 5.70; N, 2.90; P, 6.44; Pd, 22.74.

(Me$_3$P)Pd{(η^2-H$_2$C═CHSiMe$_2$)$_2$O} (34). A solution of **24** (281 mg, 1.00 mmol) in 5 mL of diethyl ether was treated with dvds (1 mL) at 20 °C. All volatiles were evaporated in a vacuum and the oily residue was recrystallized from pentane at −78 °C to give colorless cubes, which were isolated and dried under vacuum (20 °C): yield 300 mg (81%); mp 34 °C. EI-MS (15 °C): *m*/*e* (%) 368 (M$^+$, 19), 182 ([(Me$_3$P)-Pd]$^+$, 42), 171 ([C$_4$H$_6$Me$_3$Si$_2$O]$^+$, 100). ^{1}H NMR (200 MHz, 27 °C) (for dvds see Table 1): δ 1.38 (d, 9H), PMe$_3$. ^{13}C NMR (50.3 MHz, 27 °C) (for dvds see Table 1): δ 18.1 (d, 3C), PMe$_3$. Anal. Calcd for C$_{11}$H$_{27}$OPPdSi$_2$ (368.9): C, 35.81; H, 7.38; O, 4.34; P, 8.40; Pd, 28.85; Si, 15.23. Found: C, 35.63; H, 7.43; P, 8.28; Pd, 28.80.

(^{i}Pr$_3$P)Pd{(η^2-H$_2$C═CHSiMe$_2$)$_2$O} (35). (a) From (tmeda)PdMe$_2$. P^{i}Pr$_3$ (320 mg, 2.00 mmol) was added to a suspension of (tmeda)-PdMe$_2$ (505 mg, 2.00 mmol) in 5 mL of dvds at −30 °C. When the mixture was warmed to 20 °C a colorless solution resulted from which the product crystallized between 0 and −78 °C. The crystals were freed from the mother liquor, washed twice with cold pentane, and dried under vacuum (20 °C): yield 810 mg (89%). **(b) From Pd(P^{i}Pr$_3$)$_2$.** Pd(P^{i}Pr$_3$)$_2$ (223 mg, 0.50 mmol) was dissolved in dvds (3 mL). In the course of 2 h some Pd(P^{i}Pr$_3$)$_3$ precipitated, which was removed by filtration. Cooling the solution to −78 °C afforded colorless crystals, which were isolated as described: yield 150 mg (66%); mp 75 °C dec. EI-MS (55 °C): *m*/*e* (%) 452 (M$^+$, 16), 266 ([(^{i}Pr$_3$P)Pd]$^+$, 24), 171 ([C$_4$H$_6$Me$_3$Si$_2$O]$^+$, 100). ^{1}H NMR (200 MHz, 27 °C) (for dvds see Table 1): δ 2.32 (m, 3H, PCH), 1.20 (dd, 18H, Me), ^{i}Pr$_3$P. ^{13}C NMR (50.3 MHz, 27 °C) (for dvds see Table 1): δ 27.1 (3C, PC), 20.5 (6C, Me), P^{i}Pr$_3$. ^{31}P NMR (81 MHz, 27 °C): see Table 1. Anal. Calcd for C$_{17}$H$_{39}$-OPPdSi$_2$ (453.1): C, 45.07; H, 8.68; O, 3.53; P, 6.84; Pd, 23.49; Si, 12.40. Found: C, 45.25; H, 8.75; P, 6.94; Pd, 23.42; Si, 12.28.

(^{t}Bu$_3$P)Pd{(η^2-H$_2$C═CHSiMe$_2$)$_2$O} (36). To the yellow suspension of **3** (772 mg, 1.00 mmol) in 5 mL of dvds was added at −30 °C a solution of ^{t}Bu$_3$P (404 mg, 2.00 mmol) in 10 mL of diethyl ether. In the course of 1 h a colorless suspension was obtained that was left at −78 °C (12 h) for complete crystallization. The solid was freed from the mother liquor, washed twice with cold pentane, and dried under vacuum at −30 °C: yield 650 mg (66%); mp >100 °C dec. EI-MS (50 °C): *m*/*e* (%) 494 (M$^+$, <1), 308 ([(^{t}Bu$_3$P)Pd]$^+$, <1), 171 ([C$_4$H$_6$-Me$_3$Si$_2$O]$^+$, 100). ^{1}H NMR (300 MHz, −80 °C) (for dvds see Table 1): δ 1.58 (9H), 1.37 (18H), ^{t}Bu$_3$P. ^{13}C NMR (75.5 MHz, −80 °C) (for dvds see Table 1): δ 39.7 (3C, PC), 35.4 (6C, Me), 28.7 (3C, Me), ^{t}Bu$_3$P. ^{31}P NMR (81 MHz, −30 °C): see Table 1. Anal. Calcd for C$_{20}$H$_{45}$OPPdSi$_2$ (495.1): C, 48.52; H, 9.16; O, 3.23; P, 6.26; Pd, 21.49; Si, 11.34. Found: C, 48.78; H, 9.10; P, 6.17; Pd, 21.29; Si, 11.43.

(Ph$_3$P)Pd{(η^2-H$_2$C═CHSiMe$_2$)$_2$O} (37). A solution of **17** (232 mg, 0.50 mmol) in diethyl ether (5 mL) was treated with 0.5 mL of dvds. After 1 h the volatiles were evaporated in a vacuum and the residue was recrystallized (−78 °C) from a small volume of ether to give colorless intergrown cubes: yield 210 mg (80%). EI-MS: the compound decomposed and the spectra of dvds (*m*/*e* 186) and PPh$_3$ (*m*/*e* 262) were observed. ^{1}H NMR (300 MHz, 27 °C) (for dvds see Table 1): δ 7.43 (3H), 7.37 (12H), PPh$_3$. ^{13}C NMR (75.5 MHz, 27 °C) (for dvds see Table 1): δ 137.6 (3C, ^1J(PC) = 29 Hz, PC$_\alpha$), 134.3 (6C, C$_\beta$), 130.1 (3C, C$_\delta$), 129.0 (6C, C$_\gamma$), PPh$_3$. ^{31}P NMR (121.5 MHz, 27 °C): see Table 1. C$_{26}$H$_{33}$OPPdSi$_2$ (555.1). No elemental analysis was performed.

{(2-MeC$_6$H$_4$)$_3$P}Pd(dvds) (38). The synthesis followed that of **29** by reacting (tmeda)PdMe$_2$ (126 mg, 0.50 mmol) with P(*o*-tolyl)$_3$ (152 mg, 0.50 mmol) in 5 mL of dvds (20 °C). The complex was isolated by evaporating the solvent: yield 280 mg. ^{1}H NMR (300 MHz, 27 °C) (for dvds see Table 1): δ 7.46, 7.25, 7.17, 7.13 (each 3H), 2.00 (9H), (2-MeC$_6$H$_4$)$_3$P. ^{13}C NMR (75.5 MHz, 27 °C) (for dvds see Table 1): δ 142.9, 135.0, 133.4, 132.3, 130.4, 126.3, 23.0, each 3C, (2-MeC$_6$H$_4$)$_3$P. ^{31}P NMR (121.5 MHz, 27 °C): see Table 1. C$_{29}$H$_{39}$-OPPdSi$_2$ (597.2). No elemental analysis was performed. In an inert solvent the compound slowly decomposes at 20 °C.

(Me$_3$P)Pt(η^2,η^2-C$_7$H$_{12}$) (39). A solution of **12** in pentane (5 mL), obtained from **4** (204 mg, 0.30 mmol) and ethene at 0 °C, was combined with a solution of PMe$_3$ (46 mg, 0.60 mmol) in 2 mL of pentane at −78 °C. In the course of several hours yellow brownish crystals separated, which were isolated by filtration and dried under high vacuum at −30 °C: yield 70 mg (32%); mp 42 °C. EI-MS (10 °C): *m*/*e* (%) 367 (M$^+$, 63), 365 ([M − 2H]$^+$, 50), 363 ([M − 4H]$^+$, 81), 271 ([(Me$_3$P)Pt]$^+$, 100). ^{1}H NMR (300 MHz, 27 °C) (for C$_7$H$_{12}$ see Table 1): δ 1.51 (d, 9H, PMe$_3$). ^{13}C NMR (75.5 MHz, 27 °C) (for C$_7$H$_{12}$ see Table 1): δ 19.3 (3C, ^2J(^{195}PtC) = 52 Hz, PMe$_3$). ^{31}P NMR (121.5 MHz, 27 °C): see Table 1. Anal. Calcd for C$_{10}$H$_{21}$PPt (367.3): C, 32.70; H, 5.76; P, 8.43; Pt, 53.11. Found: P, 8.96; Pt, 53.65.

(^{i}Pr$_3$P)Pt(η^2,η^2-C$_7$H$_{12}$) (40). A suspension of **4** (339 mg, 0.50 mmol) in diethyl ether (5 mL) was treated with a solution of ^{i}Pr$_3$P (262 mg, 1.00 mmol) in diethyl ether (5 mL) at 20 °C. When the mixture was stirred for 10 min an orange solution was obtained which was filtered through a D4 glas fritt. At −78 °C orange crystals separated. The mother liquor was cannulated away from the crystals and the product was washed with some cold pentane and dried under vacuum at 20 °C: yield 360 mg (80%); mp 75 °C. EI-MS (43 °C): *m*/*e* (%) 451 (M^+, 55), 408 ([M − C_3H_7]$^+$, 69), 355 ([(^{i}Pr$_3$P)Pt]$^+$, 11). ^{1}H NMR (400 MHz, 27 °C) (for C_7H_{12} see Table 1): δ 2.42 (m, 3H, PCH), 1.17 (dd, 18H, Me), P^{i}Pr$_3$. ^{13}C NMR (50.3 MHz, 27 °C) (for C_7H_{12} see Table 1): δ 28.0 (3C, PCH), 20.3 (6C, Me), P^{i}Pr$_3$. ^{31}P NMR (81 MHz, 27 °C): see Table 1. Anal. Calcd for $C_{16}H_{33}PPt$ (451.5): C, 42.56; H, 7.37; P, 6.86; Pt, 43.21. Found: C, 42.44; H, 7.38; P, 6.87; Pt, 43.28.

(Ph$_3$P)Pt(η^2,η^2-C$_7$H$_{12}$) (41). The synthesis was carried out as for **40** by starting from **4** (339 mg, 0.50 mmol) and PPh_3 (262 mg, 1.00 mmol). Yellow intergrown crystals were obtained: yield 470 mg (85%); mp 110 °C dec. EI-MS (120 °C): *m*/*e* (%) 553 (M^+, 10), 457 ([(Ph$_3$P)Pt]$^+$, 3), 378 ([($C_{12}H_8$P)Pt]$^+$, 6), 154 (Ph_2, 81), 78 (C_6H_6, 100). ^{1}H NMR (400 MHz, 27 °C) (for C_7H_{12} see Table 1): δ 7.40 (6H), 7.30 (9H), PPh_3. ^{13}C NMR (50.3 MHz, 27 °C) (for C_7H_{12} see Table 1): δ 137.8 (3C, PC_α), 134.4 (6C, C_β), 130.2 (3C, C_δ), 128.7 (6C, C_γ), PPh_3. ^{31}P NMR (81 MHz, 27 °C): see Table 1. Anal. Calcd for $C_{25}H_{27}PPt$ (553.5): C, 54.23; H, 4.92; P, 5.60; Pt, 35.25. Found: C, 54.36; H, 4.97; P, 5.56; Pt, 35.19.

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