(Phenylalkyl)palladium Complexes Containing β-Hydrogen Atoms: Synthesis and Characterization of [PdR_2(dppe)], [PdR(SPh)(dppe)] (R = CH_2CH_2Ph, $CH_2CH_2CH_2Ph$, $CH_2CHMePh$), and [Pd($CH_2CH_2CH_2Ph$)X(dppe)] (X = I, Br, Cl)

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Reactions of HgR_2 (R = CH_2CH_2Ph, **1a**; $CH_2CH_2CH_2Ph$, **1b**; $CH_2CHMePh$, **1c**) (prepared from $HgCl_2$ and the requisite Grignard compounds) with lithium in toluene afforded (phenylalkyl)lithium compounds LiR (**2a**–**c**) in yields of between 64 and 81%. At –30 °C, they react with [$PdCl_2$(dppe)] [dppe = 1,2-bis(diphenylphosphanyl)ethane] yielding bis(phenylalkyl)palladium(II) complexes [PdR_2(dppe)] (**3a**–**c**) which were isolated (T_{dec} = 159 °C, **3a**; 80 °C, **3b**; 145 °C, **3c**) and fully characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. Single-crystal X-ray diffraction of [Pd(CH_2CH_2Ph)$_2$(dppe)] (**3a**) showed that the palladium atom is square-planar coordinated by two 2-phenylethyl ligands and the dppe ligand. The two CH_2CH_2Ph ligands exhibite nearly a fully staggered conformation. Overall, a good approximation for the complex is that it has C_2 symmetry with the C_2 axis defined by the Pd atom and the midpoint of the central C–C bond of the dppe ligand. Bis(phenylalkyl)palladium complexes **3a** and **3b** reacted with PhSH in a 1:1 ratio yielding [PdR(SPh)(dppe)] (R = CH_2CH_2Ph, **5a**; $CH_2CH_2CH_2Ph$, **5b**), whereas in the case of complex **3c**, besides [Pd($CH_2CHMePh$)(SPh)(dppe)] (**5c**), a considerable amount of [Pd(SPh)$_2$(dppe)] (**6a**) was formed. Reactions of **3b** with the less acidic alkanethiols *i*PrSH and *t*BuSH resulted in the formation of [Pd($CH_2CH_2CH_2Ph$)(SR′)(dppe)] (R′ = *i*Pr, **5d**; *t*Bu, **5e**) along with smaller amounts of [Pd(SR′)$_2$(dppe)] (**6**) and [Pd(dppe)$_2$] (**7**). Furthermore, complex **3b** was found to react in THF with disulfides R′SSR′ (R′ = Ph, Bz, Me), yielding [Pd($CH_2CH_2CH_2Ph$)(SR′)(dppe)] (R′ = Ph, **5b**; Bz, **5f**, Me, **5g**) with small amounts (3–13%) of [Pd(SR′)$_2$(dppe)] (**6**) as side products. The corresponding reaction with MeSeSeMe afforded [Pd($CH_2CH_2CH_2Ph$)(SeMe)(dppe)] (**8a**) and 3% of [Pd(SeMe)$_2$(dppe)] (**9a**) and [Pd(dppe)$_2$] (**7**). Reactions of complex **5b** with MeI and H_2C=$CHCH_2Br$ in tetrahydrofuran and with neat H_2C=$CHCH_2Cl$ readily proceeded at –30 °C to give halo(3-phenylpropyl)palladium complexes [Pd($CH_2CH_2CH_2Ph$)X(dppe)] (X = I, **10a**; Br, **10b**; Cl, **10c**). They were isolated as pale yellow powdery/microcrystalline substances and fully characterized by ^{13}C and ^{31}P NMR spectroscopy. Solutions of complexes **10** in THF decompose rapidly above –30 °C.

1. Introduction

The Heck reaction has been proven to be a powerful method for the arylation and vinylation of olefins (Scheme 1).[1] Despite the continuous debate on its mechanism,[2] oxidative addition of RX (R = aryl, vinyl, heteroaryl, ...; X = halide, tosylate, triflate, ...) to the Pd catalyst complex yielding an $L_xPd(R)X$ complex (**I**, Scheme 1) followed by olefin insertion (**II**, Scheme 1) are crucial reaction steps in the classic Heck cycle. The reactions of ethene with phenyl and benzyl halides yielding styrene and allylbenzene, respectively, can be considered as the most simple prototypic model reactions for Heck reactions. Complexes of type **I** in Scheme 1 (R = Ph, Bz) are well known.[3] Contrary to type **I**, those of type **II**, (2-phenylethyl)- and (3-phenylpropyl)palladium complexes, have not yet been described. Due to β-hydrogen atoms in the phenylalkyl ligands the thermal stability of these complexes can be expected to be low. Facile β-hydride elimination reactions, in Heck-type catalysts, are discussed as a reason for the alkylation of olefins being restricted to special cases. Alkyl halides R′CH−CH_2X react to form intermediates **I** [$L_xPd(CH_2-CHR')X$], which undergo β-hydride elimination more easily than insertion of the olefin, giving intermediate **II** and opening the reaction channel to the desired products.

Several mononuclear palladium complexes with β-hydrogen-containing acyclic alkyl ligands have been isolated as solids and characterized. These include: (i) dialkyl− and alkyl/aryl−Pd^{II} complexes [PdR_2L_2] [R = Et, *n*Pr, *n*Bu; L_2 = (PR′$_3$)$_2$, dppe, bpy, ...; R_2 = Et/Ar, *n*Bu/Ar, Ar = Aryl],[4] (ii) monoalkyl−Pd^{II} complexes with an anionic

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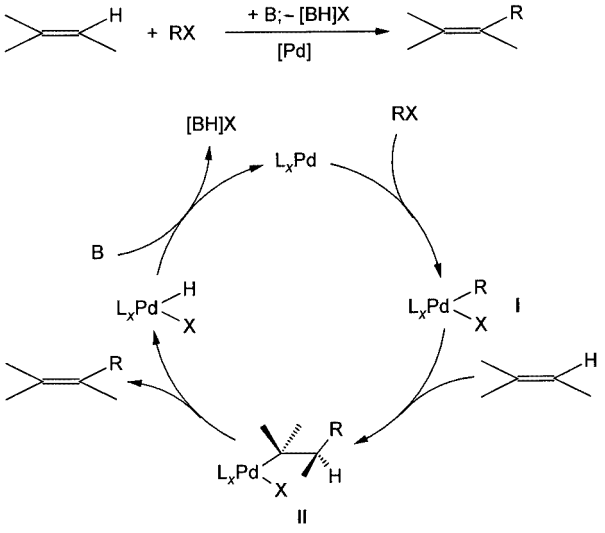


Scheme 1

ligand *trans*-[PdEt(X)(PR′$_3$)$_2$] (X = Cl, Br, I, SPh, OPh, O$_2$CR′),[5] [Pd(CH$_2$CH$_2$CH=CH$_2$)Cl(dppe)],[6] and [PdR(S$_2$CNR′$_2$)(PR′$_3$)] (R = *n*Pr, *i*Pr, *n*Bu, *s*Bu, ...),[7] and (iii) cationic Pd^{II} complexes [PdR{N(CH$_2$CH$_2$PPh$_2$)$_3$}]X (R = Et, *n*Pr, *n*Bu; X = I, BPh$_4$)[8] and [PdEt(η^2-C$_2$H$_4$)(phen)][B{C$_6$H$_3$(CF$_3$)$_2$}$_4$];[9] furthermore, (iv) alkyl-(Et, *n*Pr)–Pd^{IV} complexes with tripodal N-donor and bipyridine co-ligands have been synthesized.[10] Only a few of these complexes could be structurally characterized, namely *trans*-[PdEt(X)(PMe$_3$)$_2$] (X = Br,[5b] SPh[5c]), [PdR{S$_2$CN-(CH$_2$)$_4$}(PEt$_3$)] (R = *n*Pr, *i*Pr),[7b] and [PdEtMe$_2$-{(pz)$_3$BH}].[10d]

Palladium complexes with acyclic β-hydrogen-containing alkyl ligands cover a wide range of stability: PdEtI without supporting ligands already decompose at −100 °C[11] whereas toluene solutions of complexes with dithiocarbamato[7] and tris(pyrazolyl)borate[10d] co-ligands were found to be stable to 60 °C and to at least 80 °C, respectively. On the other hand, many of the above-mentioned complexes are unstable in solution even at room temperature. Preferred decomposition pathways are β-hydrogen elimination and/or reductive elimination in the case of dialkyl complexes. For stereoelectronic reasons organopalladium complexes with β-hydrogen-containing cycloalkyl ligands are thermally more stable.[4b,4c,4f,6,12]

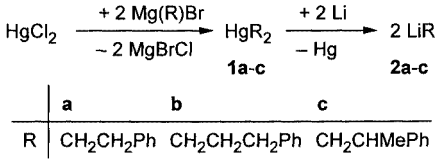
(Phenylalkyl)palladium complexes containing the structural unit Pd–[CH$_2$]$_n$Ph with $n > 1$ [benzyl complexes (n = 1), for which β-hydrogen elimination is lacking, will not be considered here] have not yet been synthesized. Pd(CH$_2$CH$_2$Ph)Cl was proposed as an intermediate in reactions of PdCl$_2$/HgPhCl with ethene and [PdCl$_4$]$^{2-}$ with Hg(CH$_2$CH$_2$Ph)Cl followed by cleavage of the Pd–C bond with CuCl$_2$/LiCl.[13] Furthermore, complexes with CH$_2$–CH$_2$Ph and CHPh–CH$_2$Ph ligands were detected by NMR spectroscopy as intermediates in reactions of phenylpalladium complexes with ethene and styrene, respectively.[14]

Here we report on the synthesis and characterization of (2-phenylethyl)- as well as (2- and 3-phenylpropyl)palladium complexes with bis(diphenylphosphanyl)ethane (dppe) as a stabilizing co-ligand. Reactions of [PdCl$_2$(dppe)] with LiR (R = CH$_2$CH$_2$Ph, CH$_2$CH$_2$CH$_2$Ph, CH$_2$CHMePh) afforded the diorgano complexes [PdR$_2$(dppe)]. Partial protolysis with phenylthiol resulted in formation of mono(phenylalkyl) complexes [PdR(SPh)-(dppe)], whose reactions with organo halides, disulfides and diselenides are described. Furthermore, the molecular structure of the first palladium complex with two β-hydrogen-containing alkyl ligands, [Pd(CH$_2$CH$_2$Ph)$_2$(dppe)], is presented.

2. Results and Discussion

2.1. Synthesis and Characterization of (Phenylalkyl)lithium and -mercury Compounds

The synthesis of (2-phenylethyl)lithium was described in the literature by either a direct synthesis (PhCH$_2$CH$_2$Br + Li),[15] or a lithium/iodide exchange reaction (PhCH$_2$CH$_2$I + *t*BuLi)[16] in diethyl ether. We and others[16b] failed to obtain LiCH$_2$CH$_2$Ph by direct synthesis. By a lithium/iodide exchange reaction we succeeded to obtain LiCH$_2$CH$_2$Ph, although severe impurities due to ether cleavage prevented its use as starting material for the synthesis of organopalladium complexes. Thus, we prepared (phenylalkyl)lithium compounds by transmetalation according to Scheme 2.



Scheme 2

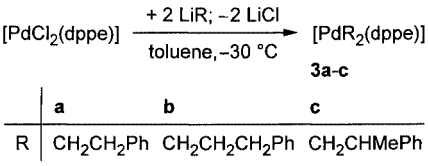
The bis(phenylalkyl)mercury compounds **1a–c** were obtained (Scheme 2) by reaction of the Grignard compounds with mercury chloride in THF/diethyl ether as colorless liquids in moderate to good yields (66–84%). They were characterized by ^{1}H and ^{13}C NMR spectroscopy; all chemical shifts and couplings ($^nJ_{Hg,H}$ and $^nJ_{Hg,C}$, see Exp. Sect.) are in full agreement with expectations. Due to its two equivalent substituted stereogenic centers, the ^{13}C NMR spectrum of Hg(CH$_2$*C*HMePh)$_2$ (**1c**) shows two sets of signals of equal intensity corresponding to *rac* and *meso* forms. Comparison of the $^1J_{Hg,C}$ coupling constants (706 Hz, **1a**; 692 Hz, **1b**; 720 Hz, **1c**) with those of the corresponding non-phenyl-substituted compounds HgEt$_2$ (647 Hz)[17] and Hg(*n*Pr)$_2$ (660 Hz),[17] shows that phenyl substitution in the 2- (**1a**/**1c**) and 3-position (**1b**) gives rise to an increase of the $^1J_{Hg,C}$ coupling constants by 59/60 Hz and 32 Hz, respectively. In terms of Bent's model[18] this indicates a higher electronegativity of phenylalkyl ligands compared with their pure alkyl analogues.

Reactions of bis(phenylalkyl)mercury compounds **1a−c** with lithium in toluene resulted in the formation of (phenylalkyl)lithium compounds **2a−c** in moderate to good yields (64−81%) (Scheme 2). The compounds are stable in toluene at room temperature for days. Despite the use of highly toxic organomercury compounds these transmetalation reactions are superior to all other methods[15,16] because they essentially proceed without side reactions and can be performed in a solvent (toluene) in which the organolithium reagents **2a−c** are stable.

Instead of toluene as a solvent, *n*-pentane can be used for the synthesis of (3-phenylpropyl)lithium (**2b**). This is due to the excellent solubility of **2b** in aliphatic hydrocarbons at room temperature. Without obvious reason the homologous compounds **2a** and **2c** are insoluble in aliphatic hydrocarbons and the transmetalation in these solvents failed. The ^{13}C NMR spectrum of **2b** in perdeuterated *n*-hexane gave evidence for its identity. The signal of the carbon atom attached to the lithium atom is broadened ($b_{1/2} \approx 75$ Hz) due to dynamic processes and/or the quadrupole moment of Li (^{7}Li: $I = 3/2$, 92.6% rel. abund.). Its chemical shift ($\delta = 10.1$ ppm) is in the expected range as compared with other alkyllithium compounds [$\delta(^{13}C_\alpha)$, median: 12.5 ppm; lower/upper quartile: 10.2/17.0 ppm; 17 observations[19]]. The lithium-induced shift in **2b** [$\delta(^{13}C_\alpha)$ in LiR − $\delta(^{13}C_\alpha)$ in HR] amounts to $\delta = 10.1-14.6$ ppm[20] $= -4.5$ ppm, and is somewhat larger than expected for the correlation given in ref.[19] The $^1J_{C,H}$ coupling constant (ca. 94 Hz) is in the range expected for alkyllithium compounds ($^1J_{C,H}$ in $LiCH_3$: 98 Hz[21]).

2.2. Synthesis and Characterization of Bis(phenylalkyl)palladium Complexes

The (phenylalkyl)lithium compounds **2a−c** reacted with [$PdCl_2$(dppe)] in toluene at −30 °C to give bis(phenylalkyl){bis(diphenylphosphanyl)ethane}palladium complexes **3a−c** (Scheme 3). Addition of *n*-pentane resulted in the precipitation of complexes **3a−c**. Note that the choice of solvent determins the success of the synthesis: Despite its low vapor pressure at −30 °C, resulting in a long-lasting procedure to remove it in vacuo at that temperature, toluene is the most preferable one. The (phenylalkyl)lithium compounds **2** are freely soluble in toluene even at −78 °C and they are indefinitely stable in toluene, which is not the case for ethereal solvents.



Scheme 3

Complexes **3a−c** were isolated in yields between 68 and 84% as colorless (**3a/b**) and yellowish (**3c**) microcrystalline substances that are moderately air-sensitive. Heating by a rate of about 4 K/min resulted in decomposition at about 159 °C (**3a**), 80 °C (**3b**) and 145 °C (**3c**). Solutions of these complexes in toluene are stable at −30 °C for several days although decomposition occurs at room temperature within several hours.

The identities of complexes **3** were unambiguously confirmed by ^1H, ^{13}C and ^{31}P NMR spectroscopy and also by X-ray crystallography for **3a**. Selected NMR spectroscopic data are shown in Table 1 along with the data of the dimethyl complex [$PdMe_2$(dppe)] (**4**) for comparison. As for the mercury compound **1c**, ^1H, ^{13}C, and ^{31}P NMR spectra of the 2-phenylpropyl complex [$Pd(CH_2CHMePh)_2$(dppe)] (**3c**) show two sets of signals in a 1:1 ratio due to the existence of *rac* and *meso* forms. Furthermore, in the ^{13}C NMR spectrum of **3c** a further signal splitting for the phenyl carbon atoms of the dppe ligand (e.g. four different C_o signals with coupling to the phosphorus atom, see Exp. Sect.) was observed indicating a pairwise inequivalence of the phenyl groups of the dppe ligand. This was expected as the two asymmetric carbon atoms reduce the symmetry (C_{2v} in terms of the NMR time scale) of simple [PdR_2(dppe)] complexes to C_2 in the *rac* form and C_s in the *meso* form.

Coupling with the magnetically inequivalent P atoms resulted in higher order multiplets of AA′X or − taking into account the isotopic shift of ^{13}C − ABX spin systems (A, B = ^{31}P; X = ^{13}C) for the ^{13}C resonances. For the dimethyl compound [$PdMe_2$(dppe)] (**4**) a complete set of $^nJ(^{31}P,^{13}C)$ coupling constants was obtained by spectral analysis using the program package PERCH[22] (cf. Table 1 and Exp. Sect.). For the methyl carbon atoms (signal pattern 'dd', pseudo-doublet of doublet with roof effect) and the methylene carbon atoms (signal pattern 't', pseudo-triplet) the results obtained by computer analysis are very similar to the results obtained when the signals are handled as first-order multiplets: CH_3: $^2J(P,C_{trans}) = 107.3$ Hz vs. 107.5 Hz, $^2J(P,C_{cis}) = 10.1$ Hz vs. 9.7 Hz; CH_2: $^{1+4}J_{P,C}/^{2+3}J_{P,C} = 19.7/21.9$ Hz (with opposite sign, assignment tentative) vs. 21.5 Hz. Thus, it seems to be justified to obtain approximate coupling constants by a "first-order treatment" as was done for complexes **3** (cf. Table 1).

The α-carbon signals in (phenylalkyl)palladium complexes **3a−c** are strongly lowfield-shifted compared with that in [$PdMe_2$(dppe)] (**4**) ($\delta = 24.9-33.6$ ppm vs. 1.9 ppm). In the couplings of α-carbon atoms to phosphorus atoms ($^2J_{P,C}$) only smaller differences between **3a−c** (*trans* coupling 100−101 Hz; *cis* coupling 9 Hz) and the dimethyl complex **4** (*trans* coupling 107.3 Hz; *cis* coupling 10.1 Hz) were found. The phosphorus chemical shifts are in the order 2-phenyl-substituted alkyl (**3a/c**: $\delta = 38.6-40.3$ ppm) < 3-phenyl-substituted alkyl (**3b**: $\delta = 43.6$ ppm) < Me (**4**: $\delta = 45.6$ ppm).

Single crystals of the 2-phenylethyl complex **3a**, which were suitable for X-ray diffraction analysis were grown from THF/pentane. The molecular structure of complex **3a** is shown in Figure 1, and selected bond lengths and angles are compiled in Table 2. Complex **3a** crystallizes as separate molecules without unusual intermolecular interactions; the shortest ones between non-hydrogen atoms are C···C distances of more than 3.5 Å. The palladium atom, to a good

Table 1. Selected NMR spectroscopic data (δ in ppm, *J* in Hz) for complexes $[PdR_2(dppe)]$ (**3**); data of $[PdMe_2(dppe)]$ (**4**) are given for comparison

R	Me (**4**)[a]	CH_2CH_2Ph (**3a**)	$CH_2CH_2CH_2Ph$ (**3b**)	$CH_2CHMePh$ (**3c**)
C1, δ(^{13}C)	1.9	28.6	24.9	33.5/33.6
$^2J_{P,C}$ *trans*	107.3	101	101	100/101
$^2J_{P,C}$ *cis*	10.1	9	9	9/9
C2, δ(^{13}C)		39.7	35.9	42.4/42.5
C3, δ(^{13}C)			44.0	25.9/26.6
$^4J_{P,C}$ *trans*			11	
PdCH_2, δ(^{1}H)	0.41 (m)	1.62 (m)	1.44 (m)	1.22−2.49 (m)[b]
δ(^{31}P)	45.6	40.3	43.6	38.6/39.7

[a] Coupling constants of complex **4** were calculated by spectral analysis. Couplings given for complexes **3** are only approximate values because they were derived from line distances, see text. [b] Superimposed by other signals.

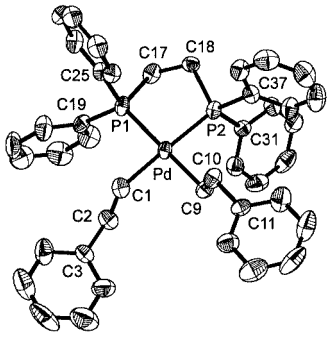


Figure 1. Molecular structure in the solid state with atomic labelling scheme for $[Pd(CH_2CH_2Ph)_2(dppe)]$ (**3a**); hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn with 50% probability

Table 2. Selected bond lengths [Å], bond angles [°] and dihedral angles [°] of complex **3a**

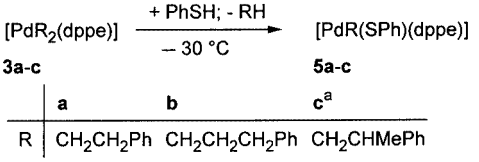
Pd−C1	2.096(5)	C1−C2	1.526(6)
Pd−C9	2.107(6)	C2−C3	1.515(7)
Pd−P1	2.288(3)	C9−C10	1.524(8)
Pd−P2	2.291(1)	C10−C11	1.511(8)
C1−Pd−C9	85.8(2)	C9−Pd−P1	178.7(1)
P1−Pd−P2	85.53(8)	Pd−C1−C2	112.6(4)
C1−Pd−P1	93.1(2)	Pd−C9−C10	111.2(3)
C9−Pd−P2	95.5(2)	C1−C2−C3	112.6(5)
C1−Pd−P2	177.8(2)	C9−C10−C11	114.8(4)
Pd−C1−C2−C3	178.0(4)	Pd−C9−C10−C11	165.0(3)

approximation, is square-planar coordinated by two carbon atoms and two phosphorus atoms [greatest deviation of the least-squares plane: Pd 0.018(1) Å]. The five-membered PdP_2C_2 ring is twisted about C17−C18. The phenyl rings of the dppe ligand are arranged in a typical "face-to-edge"[23] position (face: Ph37/Ph19; edge: Ph31, Ph25; phenyl groups are designated by Ph*x*, where *x* is the number of the *ipso*-carbon atom). The bite of the dppe ligand [P1−Pd−P2 85.53(8)°] is as expected (median: 85.0°; lower/higher quartile: 84.3/85.6°; number of values: 52[24]). The opposite C1−Pd−C9 angle [85.8(2)°] is also markedly smaller than 90°.

As shown by the torsion angles Pd−C1−C2−C3 [178.0(4)°] and Pd−C9−C10−C11 [165.0(4)°] the two 2-phenylethyl ligands exhibit a nearly fully staggered conformation. The Pd−C1−C2/Pd−C9−C10 [112.6(4)/111.2(3)°] and C1−C2−C3/C9−C10−C11 [112.6(5)/114.8(4)°] angles are nearly tetrahedral. The phenyl groups of the 2-phenylethyl ligands are nearly parallel to the complex plane [Ph3/PdP_2C_2 10.8(2)°; Ph11/PdP_2C_2 14.2(3)°] and nearly perpendicular to the face-positioned phenyl groups of the dppe ligand [Ph3/Ph19 80.7(3)°; Ph11/Ph37 89.8(3)°]. Thus, the complex, to a good approximation, is C_2-symmetric with the C_2 axis defined by the Pd atom and the midpoint of the central C17−C18 bond of the dppe ligand.

2.3. Synthesis and Characterization of (Phenylalkyl)(thiolato)palladium Complexes

Yamamoto[5b,25] showed that *trans*-$[PdEt_2(PMe_3)_2]$ and $[PdMe_2(dppe)]$ react selectively with equimolar amounts of PhSH with protolytic cleavage of one of the two Pd−C bonds yielding *trans*-$[PdEt(SPh)(PMe_3)_2]$ and [PdMe(SPh)(dppe)], respectively. The analogous reaction of bis(phenylalkyl)palladium complexes **3a−c** proceeded according to Scheme 4. In the case of the 2-phenylethyl (**3a**) and 3-phenylpropyl (**3b**) complexes the protolytic cleavage of the first Pd−C bond proceeded faster than that of the second one. Thus, at −30 °C using a 1:1 ratio of **3a/3b** and PhSH the desired (phenylalkyl)(thiolato) complexes **5a** and **5b** were obtained. On the other hand, under the same reaction conditions the 2-phenylpropyl complex **3c** reacted with PhSH (1:1) to yield both the mixed complex **5c** (15%) and $[Pd(SPh)_2(dppe)]$ (**6a**) to a remarkable extent (16%) as shown by ^{31}P NMR spectroscopy. Successive additions of further quantities of PhSH (calculated 1:1 in relation to the amount of unchanged starting complex **3c** detected in the



Scheme 4. [a] $[Pd(SPh)_2(dppe)]$ (**6a**) was also formed

^{31}P NMR spectrum) until **3c** had been completely consumed resulted in a mixture of **5c** and **6a** of about 3:1.

The less acidic alkanethiols *i*PrSH and *t*BuSH reacted slower with the 3-phenylpropyl complex **3b** than with PhSH (Scheme 5): At −30 °C the reaction was incomplete even after six days of reaction time. Increasing the temperature to −15 °C for one day and to 0 °C for eight days, resulted in the formation of [Pd($CH_2CH_2CH_2Ph$)(SR′)(dppe)] in 77% (R′ = *i*Pr, **5d**) and 82% yield (R′ = *t*Bu, **5e**). Side products were the bis(thiolato) complexes **6b** (R′ = *i*Pr; 13%) and **6c** (R′ = *t*Bu; 8%), and [Pd(dppe)$_2$] (**7**; 2% for R′ = *i*Pr; 7% for R′ = *t*Bu) as the reduction product. Comparing *i*PrSH and *t*BuSH, the protolytic cleavage of the second Pd−C bond yielding **6c** is less favoured, although the reduction yielding **7** is more favoured with *t*BuSH, which might be explained because of its lower acidity *and* its greater bulkiness.

[PdR$_2$(dppe)] + R′SH → [PdR(SR′)(dppe)] + [Pd(SR′)$_2$(dppe)] + [Pd(dppe)$_2$]

t, *T* [a]	**3b**	**5d/5e**	**6b/6c**	**7**
6 d, -30 °C	38/41[b]	56/55	5/1	1/3
1 d, -15 °C	29/35	62/60	8/2	1/3
8 d, 0 °C	8/3	77/82	13/8	2/7

Scheme 5. R = $CH_2CH_2CH_2Ph$; [a] temperature regime, see text; [b] composition of reaction mixture in % for R′ = *i*Pr/*t*Bu

The (phenylalkyl)(thiolato) complexes **5a** and **5b** were isolated as colorless (**5a**) and pale pink (**5b**) slightly air-sensitive, microcrystalline substances. The solids decomposed at 145 °C (**5a**) and 90 °C (**5b**). Solutions in tetrahydrofuran were stable at −30 °C; at room temperature they decomposed slowly. The identities of (phenylalkyl)(thiolato) complexes **5a** and **5b** were confirmed by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. The bis(thiolato) complexes **6** were characterized by ^{31}P NMR spectroscopy and by comparison with authentic samples prepared by reaction of [PdCl$_2$(dppe)] with LiSR′. Substitution of a phenylalkyl ligand by PhS (**3a/b** → **5a/b**) gives rise to a slight (δ = 1.5/4.1 ppm) lowfield shift of the C1 signal of the remaining phenylalkyl ligand. In complexes **5a/b** the signals of the P atoms *trans* to the carbon atoms are shifted to higher field [**5a/b**: δ($^{31}P_{trans\ to\ C}$) = 34.5/34.0 ppm] relative to those in the analogous bis(phenylalkyl) complexes [**3a/b**: δ(^{31}P) = 40.3/43.6 ppm] and those *trans* to sulfur atoms are lowfield-shifted [**5a/b**: δ($^{31}P_{trans\ to\ S}$) = 53.2/53.1 ppm]. Very similar to the latter one is the phosphorus shift in the bis(thiolato) complex [Pd(SPh)$_2$(dppe)] (**6a**) (δ = 55.4 ppm).

Apart from protolytic cleavage of the Pd−C bonds with alkanethiols (vide supra), reactions of bis(phenylalkyl)palladium complexes **3** with diorgano disulfides are another access to (phenylalkyl)(thiolato)palladium complexes **5**. Thus, reactions of R′SSR′ (R′ = Ph, Bz, Me) with the (3-phenylpropyl)palladium complex **3b** were performed (Scheme 6). PhSSPh exhibited the highest reactivity. It reacted already at −30 °C (to a small extent even at −50 °C) whereas for reactions of BzSSBz and MeSSMe, the temperature had to be increased to 0 °C and 15 °C, respectively. Side products were the bis(thiolato) complexes [Pd(SR′)$_2$(dppe)] (**6**) in all cases.

[PdR$_2$(dppe)] (**3b**) + R′SSR′ → [PdR(SR′)(dppe)] (**5b, 5f, 5g**) + [Pd(SR′)$_2$(dppe)] (**6a, 6d, 6e**)

R′	*t*, *T*	**3b**	**5**	**6**
Ph	5 d, -30 °C	7[a]	90 (**5b**)	3 (**6a**)
Bz	19 d, 0 °C	75	17 (**5f**)	8 (**6d**)
Me	6 d, 15 °C	64	22 (**5g**)	13 (**6e**)[b]

Scheme 6. R = $CH_2CH_2CH_2Ph$; [a] composition of reaction mixture in %; [b] small amounts of [Pd(dppe)$_2$] (**7**) were formed

In analogous reactions diorgano diselenides exhibited a higher reactivity than diorgano disulfides. Thus, at −30 °C, in tetrahydrofuran, reactions of MeSeSeMe with [Pd($CH_2CH_2CH_2Ph$)$_2$(dppe)] (**3b**) afforded the formation of [Pd($CH_2CH_2CH_2Ph$)(SeMe)(dppe)] (**8a**) (73%) and [Pd(SeMe)$_2$(dppe)] (**9a**) (3%), within one day. Formation of 3% [Pd(dppe)$_2$] (**7**) after a further day of reaction indicated a relatively low stability of **8a**. [PdMe$_2$(dppe)] (**4**) reacted with PhSeSePh at −30 °C completely, yielding 91% [PdMe(SePh)(dppe)] (**8b**) and 9% [Pd(SePh)$_2$(dppe)] (**9b**), within one day. No indication for the formation of organopalladium(IV) complexes as intermediates was found in any of the reactions. Analogous reactions between [PdMe$_2$L$_2$] (L$_2$ = bpy, phen) and PhEEPh (E = S, Se) afforded complexes [PdMe$_2$(EPh)$_2$L$_2$] that are unstable for E = S and moderately stable for E = Se.[26] This is further support for the far greater versatility of nitrogen-donor ligands in stabilizing palladium(IV) than that of phosphane ligands.[27]

2.4. Synthesis and Characterization of Halo(3-phenylpropyl)palladium Complexes

The (3-phenylpropyl)(phenylthiolato) complex **5b** reacted with organo halides RX with substitution of the phenylthiolato ligand by the halide yielding halo(3-phenylpropyl)palladium complexes **10a−c** (Scheme 7). Due to the low thermal stability of the products, reactions were performed at −30 °C in tetrahydrofuran as solvent or in neat RX. The reactivity of RX followed the expected order of X (I > Br > Cl) and R (allyl > alkyl). To obtain a complete degree

[Pd($CH_2CH_2CH_2Ph$)(SPh)(dppe)] (**5b**) + RX; − RSPh (thf; −30 °C) → [Pd($CH_2CH_2CH_2Ph$)X(dppe)] (**10a-c**)

	a	**b**	**c**
X	I	Br	Cl
R	Me	$H_2C{=}CHCH_2$	$H_2C{=}CHCH_2$

Scheme 7

of conversion, a threefold excess of methyl iodide was necessary; ethyl bromide did not react at all. Allyl bromide reacted quantitatively when a 50-fold excess was used. In neat allyl chloride complex **10c** was obtained with a 94% degree of conversion whereas allyl fluoride did not react at all. *trans*-[PdEt(SPh)(PMe_3)$_2$] proved to be more reactive than complex **5b** and reacted with MeI, $PhCH_2Br$ and $H_2C{=}CHCH_2Cl$ in a 1:1 ratio yielding *trans*-[PdEt(X)(PMe_3)$_2$] (X = I, Br, Cl) in > 80% yields.[5b]

The iodo (**10a**), bromo (**10b**) and chloro (**10c**) complexes were isolated as yellow (**10a**) and pale yellow (**10b**, **c**) powdery/microcrystalline substances that are moderately air-sensitive. Heating by about 4 K/min results in a decomposition at about 80 °C (**10b**) and 140 °C (**10c**). Solids can be handled at room temperature without noticeable decomposition for a short period of time. Solutions in tetrahydrofuran decompose rapidly above −30 °C, turning intensively violet.

The identities of complexes **10** were confirmed by ^{13}C and ^{31}P NMR spectroscopy. Selected values are shown in Table 3. Substitution of the 3-phenylpropyl ligand by bromide and chloride (**3b** → **10b/c**) gives rise to a lowfield shift of C1 by 4.1 and 6.1 ppm, respectively, whereas substitution by iodide (**3b** → **10a**) leaves the C1 chemical shift practically unchanged. Analogous to mono(phenylalkyl)(thiolato) complexes **5**, P atoms *trans* to the carbon atom resonate at higher fields than those *trans* to the halide ligand (δ = 27.7−30.2 vs. 56.1−59.5 ppm).

Table 3. Selected NMR spectroscopic data (δ in ppm, *J* in Hz) for complexes [Pd($CH_2CH_2CH_2Ph$)X(dppe)] (**10**)

X	I (**10a**)	Br (**10b**)	Cl (**10c**)
C1, δ(^{13}C)	24.3	29.0	31.0
$^2J_{P,C}$ *trans*	100.6	100.4	101.2
C2, δ(^{13}C)	35.8	34.6	34.0
$^3J_{P,C}$ *trans*			4.5
C3, δ(^{13}C)	42.9	42.4	42.2
$^4J_{P,C}$ *trans*	13.9	15.3	15.3
$^4J_{P,C}$ *cis*			3.2
P *trans* to C, δ(^{31}P)	30.2	28.9	27.7
P *trans* to X, δ(^{31}P)	56.1	59.5	59.4
$^{2+3}J_{P,P}$	29.3	29.5	29.5

In the present investigation (2- and 3-phenylalkyl)palladium complexes have been prepared and fully characterized for the first time. All of them contain β-hydrogen atoms and proved to be − at least in solution − of low thermal stability. This is especially pronounced in the *cis*-halo(3-phenylpropyl)palladium complexes [Pd($CH_2CH_2CH_2Ph$)X(dppe)] (**10a**−**c**; X = I, Br, Cl) that are − most likely − intermediates in the catalytic Heck cycle.[1b]

Experimental Section

1. General Comments: All reactions were performed under argon using standard Schlenk techniques. Solvents were dried prior to use: Et_2O, THF, and toluene with Na/benzophenone, *n*-hexane, *n*-pentane and [D_8]THF with $LiAlH_4$. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded with Gemini 200, VXR 400 and Unity 500 NMR spectrometers (Varian). For ^1H and ^{13}C NMR spectra the protio impurities of the deuterated solvent or the solvent signals were used as internal references. For ^{31}P NMR spectra H_3PO_4 (85%) was used as the external reference. In higher order multiplets *N* gives the distance between the two most intense lines. In pseudo-triplets ('t') and pseudo-doublets of doublets ('dd') *N* was derived like couplings in first-order triplets and doublets of doublets, respectively. A CP9000 chromatograph (Chrompack) was used for chromatographic analyses. GC/MS investigations were carried out with an HP 5890 Series II/HP 5972 (Hewlett−Packard). [$PdCl_2$(dppe)] and [Pd(dppe)$_2$] were prepared according to literature methods.[28,29] Reactions of LiSR (R = Ph, *i*Pr, *t*Bu, Bz, Me) [obtained from RSSR and (*n*BuLi)] with [$PdCl_2$(dppe)] afforded complexes [Pd(SR)$_2$(dppe)] (**6a**−**e**) in yields between 40 and 85%. ^{31}P NMR (81 MHz, [D_8]THF): δ = 55.4 (in $CDCl_3$; R = Ph, **6a**), 56.7 (R = *i*Pr, **6b**), 54.3 (R = *t*Bu, **6c**), 58.2 (R = Bz, **6d**), 57.6 (R = Me, **6e**) ppm. Other chemicals were commercially available.

2. HgR_2 (R = CH_2CH_2Ph, 1a; $CH_2CH_2CH_2Ph$, 1b; $CH_2CHMePh$, 1c): Solutions of Grignard compounds RMgBr in diethyl ether (0.7−0.9 M) were prepared following a standard procedure[30] from Mg and RBr. Yields (93−97%) were determined by acidimetric titration. Only solutions of Grignard compounds free from unchanged RBr (checked by GC/MS) were used. These solutions of RMgBr (40.5 mmol) were added dropwise to a solution of $HgCl_2$ (5.0 g, 18.4 mmol) in THF (20 mL) at −78 °C. The reaction mixture was slowly warmed to room temperature and stirred for 2 days. At −78 °C, water (20 mL) was added dropwise. The organic phase was separated, washed with water and dried with Na_2SO_4. The solvent was removed in vacuo. Finally, the temperature was raised to 50 °C (0.1 Torr) to remove all volatile substances. ***Warning!*** All manipulations with the highly toxic organomercurials were done in a separate fume hood using appropriate safety requirements, above all, a special combination of gloves.[31] All glassware used in these syntheses was treated with a solution of bromine in methanol to convert highly toxic organomercurials into less toxic $HgBr_2$.

Compound 1a (R = CH_2CH_2Ph): Colorless oil. Yield: 5.3 g (70%). ^1H NMR (200 MHz, $CDCl_3$): δ = 1.29 ('t' + dt, *N* = 7.7, $^2J_{Hg,H}$ = 96.7 Hz, 4 H, $HgCH_2$), 3.05 ('t' + dt, *N* = 7.7, $^3J_{Hg,H}$ = 112.3 Hz, 4 H, $HgCH_2CH_2$), 7.12−7.33 (m, 10 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.8 (s, $HgCH_2CH_2$), 45.0 (s + d, $^1J_{Hg,C}$ = 706.5 Hz, $HgCH_2$), 125.4 (s, *m*-*C*),[32] 127.9 (s, *p*-*C*), 128.4 (s, *o*-*C*), 147.3 (s, *i*-*C*).

Compound 1b (R = $CH_2CH_2CH_2Ph$): Colorless oil. Yield: 5.3 g (66%). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.77 ('t' + dt, *N* = 7.2, $^2J_{Hg,H}$ = 100.0 Hz, 4 H, $HgCH_2$), 2.13 ('quint' + dt, *N* = 7.2, $^3J_{Hg,H}$ = 112.3 Hz, 4 H, $HgCH_2CH_2$), 2.58 ('t', *N* = 7.2 Hz, 4 H, $HgCH_2CH_2CH_2$), 7.13−7.19 (m, 6 H, Ph), 7.27−7.30 (m, 4 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.5 (s + d, $^2J_{Hg,C}$ = 33.2 Hz, $HgCH_2CH_2$), 40.2 (s + d, $^3J_{Hg,C}$ = 83.8 Hz, $HgCH_2CH_2CH_2$), 41.7 (s + d, $^1J_{Hg,C}$ = 692.0 Hz, $HgCH_2$), 125.7 (s, *p*-*C*), 128.3/128.6 (s/s, *o*-, *m*-*C*), 142.9 (s, *i*-*C*) ppm.

Compound 1c (R = $CH_2CHMePh$, 1:1 Mixture of Two Diastereomers): Colorless oil. Yield: 6.8 g (84%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.22 (d, $^3J_{H,H}$ = 7.0 Hz, 2 × 6 H, CH_3), 1.28 (centered, m, 2 × 4 H, $HgCH_2$), 3.41−3.52 (m, 2 × 2 H, $HgCH_2CH$), 7.11−7.18, 7.22−7.28 (m, 2 × 10 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.50/26.51 (s/s, CH_3), 39.46/39.49 (s/s, $HgCH_2CH$), 54.46/54.49 (s + d/s + d, $^1J_{Hg,C}$ = 720.2/720.2, $HgCH_2$), 2 × 125.6 (s, *p*-*C*), 2 × 126.3/128.3/128.4 (s/s/s, *o*-, *m*-*C*), 151.66/151.68 (s/s, *i*-*C*) ppm.

3. Synthesis of LiR (R = CH_2CH_2Ph, 2a; $CH_2CH_2CH_2Ph$, 2b; $CH_2CHMePh$, 2c): A solution of HgR_2 (**1**) (ca. 7 mmol) in toluene (ca. 15 mL) was stirred for 2 days with freshly cut lithium chips (ca. 75 mmol) at room temperature. The lithium amalgam formed was allowed to settle and the supernatant was filtered [yield (acidimetric): 64%, **2a**; 81%, **2b**; 80%, **2c**]. For isolation of compound **2b**, the reaction was performed in *n*-pentane. Removal of solvent in vacuo resulted in an orange oil that was dissolved in $[D_{14}]$*n*-hexane for NMR spectroscopic investigations.

Compound 2b (R = $CH_2CH_2CH_2Ph$): ^{13}C NMR (100 MHz, $[D_{14}]$*n*-hexane): δ = 10.1 (br., t, $^1J_{C,H} \approx 94$ Hz, Li*C*H_2), 31.0 (t, $^1J_{C,H}$ = 121.8 Hz, LiCH$_2$*C*H_2), 44.2 (t, $^1J_{C,H}$ = 126.6 Hz, LiCH$_2$CH$_2$*C*H_2), 125.7 (dt, $^1J_{C,H}$ = 159.9, $^2J_{C,H}$ = 7.4 Hz, *p*-*C*), 128.3 (dd, $^1J_{C,H}$ = 158.9, $^2J_{C,H}$ = 7.6 Hz, *o*-*C*), 128.7 (dt, $^1J_{C,H}$ = 156.3, $^2J_{C,H}$ = 5.9 Hz, *m*-*C*), 142.6 (s, *i*-*C*). Couplings refer to H-coupled spectrum.

4. [PdR$_2$(dppe)] (R = CH_2CH_2Ph, 3a; $CH_2CHMePh$, 3c): At −78 °C, 1.9 equiv. of LiCH_2CH_2Ph (**2a**) or Li$CH_2CHMePh$ (**2c**) in toluene (20−25 mL) was added to [PdCl$_2$(dppe)] (ca. 3 mmol). The reaction mixture was slowly warmed to −30 °C and stirred overnight. The filtered solution was concentrated to about 5 mL in vacuo at −30 °C. Cooling to −78 °C and addition of *n*-pentane (ca. 25 mL) resulted in precipitation of **3a** or **3c**, respectively, that were filtered off, washed with *n*-pentane (2 × 5 mL) and dried in vacuo at −30 °C.

Complex 3a (R = CH_2CH_2Ph): Colorless microcrystalline powder. Yield: 68%. ^1H NMR (400 MHz, $[D_8]$THF): δ = 1.62 (m, 4 H, PdCH_2), 2.25 (m, *N* = 17.8 Hz, 4 H, PCH_2), 2.65 (m, 4 H, PdCH$_2$CH_2), 6.87 (m, 6 H, Ph), 7.01 (m, 4 H, Ph), 7.43 (m, 12 H, Ph), 7.65 (m, 8 H, Ph) ppm. ^{13}C NMR (125 MHz, −30 °C, $[D_8]$THF): 27.9 ('t', *N* = 21.2 Hz, P*C*H$_2$), 28.6 ('dd', *N* = 101.4/9.3 Hz, Pd*C*H$_2$), 39.7 (s, PdCH$_2$*C*H$_2$), 124.7 (s, *p*-C_{Ph}), 128.4/128.6 (s/s, *o*-C_{Ph}/*m*-C_{Ph}), 129.5 (m, *N* = 8.7 Hz, *m*-C_{dppe}), 130.9 (s, *p*-C_{dppe}), 134.3 (m, *N* = 12.6 Hz, *o*-C_{dppe}), 134.4 (m, superposed, *N* = 29.4 Hz, *i*-C_{dppe}), 150.3 (m, *N* = 10.7 Hz, *i*-C_{Ph}) ppm. ^{31}P NMR (202 MHz, −30 °C, $[D_8]$THF): δ = 40.3 (s) ppm.

Complex 3c (R = $CH_2CHMePh$; 1:1 Mixture of Two Diastereomers): Yellow microcrystalline powder. Yield: 69%. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.92/0.99 (m/m, *N*/*N* = 6.8/6.8 Hz, 6/6 H, CHCH_3), 1.22−2.49 (m, 2 × 8 H, PCH_2 + PdCH_2), 3.05 (m, 2 × 2 H, C*H*Me), 6.9−7.2, 7.3−7.7 (m, 2 × 30 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.9/26.6 (s/s, CH*C*H$_3$), 26.9/26.9 ('t', *N* = 20.9 Hz, P*C*H$_2$), 33.5/33.6 ('dd'/'dd', *N* = 99.7/9.0 Hz/100.8/8.9 Hz, Pd*C*H$_2$), 42.4/42.5 (s/s, PdCH$_2$*C*H), 124.1/124.2 (s/s, *p*-*C*), 126.5/126.6/127.6/127.7 (s/s/s/s, *o*-*C*, *m*-*C*), 128.4/128.5/128.6/128.7 (m/m/m/m, *N* = 9.0/9.0/9.0/9.0 Hz, *m*-C_{dppe}), 129.5/2 × 129.9/130.4 (s/s/s, *p*-C_{dppe}), 132.5/133.3/133.5/134.3 (m/m/m/m, *N* = 10.9/11.9/13.9/13.9 Hz, *o*-C_{dppe}), 132.7/133.9 (m, *N* = 29.0/30.0 Hz, *i*-C_{dppe}, 2 × *i*-C_{dppe} not found due to superposition), 154.0/154.2 (m/m, *N* = 8.0/9.0 Hz, *i*-*C*) ppm. ^{31}P NMR (81 MHz, $CDCl_3$): δ = 38.6/39.7 (s/s) ppm.

5. [Pd(CH$_2$CH$_2$CH$_2$Ph)$_2$(dppe)] (3b): At −78 °C, a solution of Li$CH_2CH_2CH_2Ph$ (**2b**) (34.2 mmol) in toluene (50 mL) was added to [PdCl$_2$(dppe)] (3.30 g, 5.73 mmol). The reaction mixture was slowly warmed to −30 °C and stirred overnight. The colorless precipitate was filtered off and washed at room temperature with *n*-pentane as long as the filtrate remained colorless (ca. 20 mL). The precipitate was dissolved in toluene (100 mL) at room temperature and immediately filtered. At −30 °C, the solution was concentrated in vacuo to about 10 mL. Cooling to −78 °C and addition of *n*-pentane (ca. 50 mL) resulted in the formation of **3b** as a colorless microcrystalline precipitate that was filtered off, washed with *n*-pentane (2 × 5 mL) and dried in vacuo at −30 °C. Yield: 3.56 g (84%). ^1H NMR (400 MHz, $[D_8]$THF): δ = 1.44 (m, 4 H, PdCH_2), 1.67 (m, 4 H, PdCH$_2$CH_2), 2.20 (m, *N* = 17.8 Hz, 4 H, PCH_2), 2.31 ('t', *N* = 7.8 Hz, 4 H, PdCH$_2$CH$_2$CH_2), 6.87−7.60 (m, 30 H, Ph) ppm. ^{13}C NMR (125 MHz, $[D_8]$THF, −30 °C): δ = 24.9 ('dd', *N* = 100.7/9.1 Hz, Pd*C*H$_2$), 28.2 ('t', *N* = 20.9 Hz, P*C*H$_2$), 35.9 (s, PdCH$_2$*C*H$_2$), 44.0 (m, *N* = 10.9 Hz, PdCH$_2$CH$_2$*C*H$_2$), 125.3 (s, *p*-C_{Ph}), 128.3/129.1 (s/s, *o*-C_{Ph}, *m*-C_{Ph}), 129.3 (m, *N* = 9.9 Hz, *m*-C_{dppe}), 130.6 (s, *p*-C_{dppe}), 134.1 (m, *N* = 12.9 Hz, *o*-C_{dppe}), 134.9 (m, *N* = 26.9 Hz, *i*-C_{dppe}), 145.1 (s, *i*-C_{Ph}) ppm. ^{31}P NMR (81 MHz, $[D_8]$THF): δ = 43.6 (s) ppm.

6. [PdMe$_2$(dppe)] (4): In a modified synthesis to that described in ref.[33], a solution of MeLi (6.25 mmol) in diethyl ether (24 mL) was added to [PdCl$_2$(dppe)] (2.00 g, 3.47 mmol) at −78 °C. The reaction mixture was slowly warmed to −30 °C, stirred overnight and filtered. At −30 °C the solvent was distilled off in vacuo and toluene (20 mL) was added to the residue. The precipitated LiCl was filtered off and the solution was concentrated to about 5 mL in vacuo at −30 °C. At −78 °C the addition of *n*-pentane (ca. 30 mL) resulted in the formation of **4** as a colourless precipitate that was filtered off, washed with *n*-pentane (2 × 10 mL) and dried in vacuo at −30 °C. Yield: 0.95 g (51%). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.41 (m, *N* = 0.8 Hz, *N*′ = 14.1 Hz, 6 H, PdCH_3; *N*′: distance of the two outer lines lower in intensity), 2.22 (m, *N* = 18.2 Hz, 4 H, PCH_2), 7.32−7.42 (m, 12 H, Ph), 7.57−7.83 (m, 8 H, Ph) ppm. ^{13}C NMR (100 MHz, $[D_8]$THF), for analysis PERCH[22] program package was used: δ = 1.95 (m, *trans*-$^2J_{P,C}$ = 107.3 Hz, *cis*-$^2J_{P,C}$ = 10.1 Hz, Pd*C*H$_3$), 28.5 (m, $^{1+4}J_{P,C}$/$^{2+3}J_{P,C}$ = 19.7/21.9 Hz, P*C*H$_2$; with opposite signs, assignment tentative), 129.5 (m, $^3J_{P,C}$ = 8.6, $^5J_{P,C}$ = 0.5 Hz, *m*-*C*), 130.9 (s, *p*-*C*), 134.2 (m, $^2J_{P,C}$ = 13.6, $^4J_{P,C}$ = −1.1 Hz, *o*-*C*), 135.0 (m, $^1J_{P,C}$ = 28.8 Hz, $^{3+4}J_{P,C}$ = 1.9 Hz, *i*-*C*) ppm. ^{31}P NMR (81 MHz, $[D_8]$THF): δ = 45.6 (s) ppm.

7. [Pd(CH$_2$CH$_2$Ph)(SPh)(dppe)] (5a): At −78 °C, PhSH (77 mg, 0.70 mmol) in THF (15 mL) was added to a solution of [Pd(CH$_2$CH$_2$Ph)$_2$(dppe)] (**3a**) (500 mg, 0.70 mmol) in THF (15 mL). After warming to −30 °C, the reaction mixture was stirred overnight. At −30 °C, the precipitate formed was filtered off, washed with pentane (2 × 10 mL) and dried in vacuo. Yield: 251 mg (50%). ^1H NMR (200 MHz, $CDCl_3$): δ = 1.53 (m, 2 H, PdCH_2), 2.00−2.48 (m, 4 H, PCH_2), 2.22 (m, 2 H, PdCH$_2$CH_2), 6.0−6.2, 6.8−7.0, 7.2−7.8 (m, 30 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.1 (dd, $^{1+4}J_{P,C}$ = 24.7 Hz, $^{2+3}J_{P,C}$ = 14.7 Hz, P*C*H$_2$), 29.4 (dd, $^{1+4}J_{P,C}$ = 28.2 Hz, $^{2+3}J_{P,C}$ = 22.0 Hz, P*C*H$_2$), 30.1 (d, $^2J_{Ptrans,C}$ = 91.6 Hz, Pd*C*H$_2$), 37.0 (d, $^3J_{Ptrans,C}$ = 4.2 Hz, PdCH$_2$*C*H$_2$), 122.9 (s, *p*-C_{SPh}), 124.2 (s, *p*-C_{Ph}), 127.3/127.4/128.0 (s/s/s, *o*-C_{Ph}, *m*-C_{Ph}, *m*-C_{SPh}), 128.8 (d, $^3J_{P,C}$ = 9.6 Hz, *m*-C_{dppe}), 129.0 (d, $^3J_{P,C}$ = 10.4 Hz, *m*-C_{dppe}), 130.3 (d, $^1J_{P,C}$ = 43.1 Hz, *i*-C_{dppe}), 130.4 (d, $^4J_{P,C}$ = 2.5 Hz, *p*-C_{dppe}), 131.0 (d, $^4J_{P,C}$ = 2.5 Hz, *p*-C_{dppe}), 132.1 (d, $^1J_{P,C}$ = 28.6 Hz, *i*-C_{dppe}), 133.3 (d, $^2J_{P,C}$ = 12.5 Hz, *o*-C_{dppe}), 133.7 (d, $^2J_{P,C}$ = 12.0 Hz, *o*-C_{dppe}), 135.7 (d, $^4J_{Ptrans,C}$ = 1.6 Hz, *o*-C_{SPh}), 144.5 (m, *i*-C_{Ph}), 147.0 (dd, $^3J_{Ptrans,C}$ = 13.1, $^3J_{Pcis,C}$ = 3.1 Hz, *i*-C_{SPh}) ppm. ^{31}P NMR (81 MHz, $CDCl_3$): δ = 34.5 (d, $^{2+3}J_{P,P}$ = 26.9 Hz, P_{trans} to CH_2CH_2Ph), 53.2 (d, $^{2+3}J_{P,P}$ = 26.9 Hz, P_{trans} to SPh) ppm.

8. [Pd(CH$_2$CH$_2$CH$_2$Ph)(SPh)(dppe)] (5b): At −78 °C, PhSH (244 mg, 2.21 mmol) in THF (90 mL) was slowly added to a solution of [Pd(CH$_2$CH$_2$CH$_2$Ph)$_2$(dppe)] (**3b**) (1.644 g, 2.21 mmol) in THF (90 mL). After warming to −30 °C, the reaction mixture was stirred overnight. At −30 °C the solution was concentrated in vacuo to 5 mL and at −78 °C pentane (25 mL) was added. At −30

°C the pale pink precipitate that formed was filtered off, washed with pentane (2 × 10 mL) and dried in vacuo. Yield: 1.54 g (95%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.12 (m, 2 H, PdCH_2), 1.37 (m, 2 H, PdCH$_2$CH_2), 1.71 (m, 2 H, PdCH$_2$CH$_2$CH_2), 1.94−2.43 (m, 4 H, PCH_2), 6.6−6.7, 6.9−7.2, 7.4−7.8 (m, 30 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.9 (dd, $^{1+4}J_{P,C}$ = 25.0 Hz, $^{2+3}J_{P,C}$ = 15.0 Hz, P*C*H$_2$), 28.9 (dd, $^{1+4}J_{P,C}$ = 27.9 Hz, $^{2+3}J_{P,C}$ = 22.0 Hz, P*C*H$_2$), 29.0 (d, $^{2}J_{Ptrans,C}$ = 90.8 Hz, Pd*C*H$_2$), 33.3 (d, $^{3}J_{Ptrans,C}$ = 4.0 Hz, PdCH$_2$*C*H$_2$), 41.3 (dd, $^{4}J_{Ptrans,C}$ = 14.9, $^{4}J_{Pcis,C}$ = 3.0 Hz, PdCH$_2$CH$_2$*C*H$_2$), 122.6 (s, *p*-C_{SPh}), 124.5 (s, *p*-C_{Ph}), 126.8 (s, *m*-C_{SPh}), 127.5/128.2 (s/s, *o*-C_{Ph}, *m*-C_{Ph}), 128.5 (d, $^{3}J_{P,C}$ = 9.0 Hz, *m*-C_{dppe}), 128.7 (d, $^{3}J_{P,C}$ = 11.0 Hz, *m*-C_{dppe}), 130.1 (s, *p*-C_{dppe}), 130.3 (d, $^{1}J_{P,C}$ = 42.9 Hz, *i*-C_{dppe}), 130.7 (s, *p*-C_{dppe}), 132.0 (d, $^{1}J_{P,C}$ = 27.9 Hz, *i*-C_{dppe}), 133.1 (d, $^{2}J_{P,C}$ = 12.0 Hz, *o*-C_{dppe}), 133.3 (d, $^{2}J_{P,C}$ = 12.1 Hz, *o*-C_{dppe}), 135.4 (s, *o*-C_{SPh}), 143.2 (s, *i*-C_{Ph}), 144.6 (d, $^{3}J_{Ptrans,C}$ = 9.9 Hz, *i*-C_{SPh}) ppm. ^{31}P NMR (81 MHz, $CDCl_3$): δ = 34.0 (d, $^{2+3}J_{P,P}$ = 26.8 Hz, P_{trans} to CH$_2$CH$_2$CH$_2$Ph), 53.1 (d, $^{2+3}J_{P,P}$ = 25.6 Hz, P_{trans} to SPh) ppm.

9. [Pd(CH$_2$CHMePh)(SPh)(dppe)] (5c)/[Pd(SPh)$_2$(dppe)] (6a): At −78 °C, PhSH (115 mg, 1.04 mmol) was added to a solution of [Pd(CH$_2$CHMePh)$_2$(dppe)] (**3c**) (770 mg, 1.04 mmol) in THF (50 mL). After stirring overnight at −30 °C, the degree of conversion was determined by ^{31}P NMR spectroscopy. Then, PhSH was added in a quantity that corresponded to the unchanged amount of **3c** and stirring (−30 °C) was continued. This procedure was repeated until all of **3c** had been consumed (final ratio **3c**/PhSH = 1:6). At −30 °C, THF was removed in vacuo. The residue was taken up in toluene (10 mL). Addition of pentane (50 mL) at −78 °C resulted in the precipitation of a mixture of **5c/6a** (74/26%) that was filtered, washed with pentane and dried in vacuo at −30 °C.

Complex 5c: ^{31}P NMR (81 MHz, [D$_8$]THF): δ = 35.6 (d, $^{2+3}J_{P,P}$ = 25.7 Hz, P_{trans} to CH$_2$CHMePh), 51.3 (d, $^{2+3}J_{P,P}$ = 25.7 Hz, P_{trans} to SPh) ppm.

Complex 6a: ^{31}P NMR (81 MHz, $CDCl_3$): δ = 55.4 ppm.

10. [Pd(CH$_2$CH$_2$CH$_2$Ph)X(dppe)] (X = I, 10a; Br, 10b; Cl, 10c): At −78 °C, MeI (290 mg, 2.04 mmol), H$_2$C=CHCH$_2$Br (4.12 g, 34.1 mmol), or H$_2$C=CHCH$_2$Cl (10 mL, without THF) was added to [Pd(CH$_2$CH$_2$CH$_2$Ph)(SPh)(dppe)] **5b** (500 mg, 0.68 mmol) in THF (10 mL). After stirring overnight at −30 °C, solvent and unchanged RX compound were removed in vacuo. The residue was taken up in toluene (10 mL) and cooled to −78 °C. Addition of pentane (ca. 30 mL) resulted in precipitation of complexes **10** that were filtered off, washed with pentane (2 × 5 mL) and dried in vacuo. All manipulations were performed at a maximum temperature of −30 °C.

Complex 10a (X = I): Yellow solid. Yield: 500 mg (98%). ^{13}C NMR (125 MHz, −30 °C, [D$_8$]THF): δ = 24.3 (d, $^{2}J_{Ptrans,C}$ = 100.6 Hz, Pd*C*H$_2$), 30.2 (dd, $^{1+4}J_{P,C}$ = 30.0 Hz, $^{2+3}J_{P,C}$ = 22.6 Hz, P*C*H$_2$; other P*C*H$_2$ not found, probably beneath solvent signal), 35.8 (s, PdCH$_2$*C*H$_2$), 42.9 (d, $^{4}J_{Ptrans,C}$ = 13.9 Hz, PdCH$_2$CH$_2$*C*H$_2$), 125.6 (s, *p*-C_{Ph}), 128.5/128.9 (s/s, *o*-C_{Ph}, *m*-C_{Ph}), 129.2 (d, $^{3}J_{P,C}$ = 9.2 Hz, *m*-C_{dppe}), 129.9 (d, $^{3}J_{P,C}$ = 10.3 Hz, *m*-C_{dppe}), 130.2 (d, $^{1}J_{P,C}$ = 47.4 Hz, *i*-C_{dppe}), 131.1 (s, *p*-C_{dppe}), 132.1 (s, *p*-C_{dppe}), 133.6 (d, $^{1}J_{P,C}$ = 28.9 Hz, *i*-C_{dppe}), 134.5 (d, $^{2}J_{P,C}$ = 11.8 Hz, *o*-C_{dppe}), 134.7 (d, $^{2}J_{P,C}$ = 11.7 Hz, *o*-C_{dppe}), 143.8 (s, *i*-C_{Ph}) ppm. ^{31}P NMR (202 MHz, −30 °C, [D$_8$]THF): δ = 30.2 (d, $^{2+3}J_{P,P}$ = 29.3 Hz, P_{trans} to CH$_2$CH$_2$CH$_2$Ph), 56.1 (d, $^{2+3}J_{P,P}$ = 29.3 Hz, P_{trans} to I) ppm.

Complex 10b (X = Br): Pale yellow solid. Yield: 456 mg (95%). ^{13}C NMR (125 MHz, −30 °C, [D$_8$]THF): δ = 24.0 (dd, $^{1+4}J_{P,C}$ = 25.6 Hz, $^{2+3}J_{P,C}$ = 11.9 Hz, P*C*H$_2$), 29.0 (d, $^{2}J_{Ptrans,C}$ = 100.4 Hz, Pd*C*H$_2$), 30.4 (dd, $^{1+4}J_{P,C}$ = 31.3 Hz, $^{2+3}J_{P,C}$ = 24.1 Hz, P*C*H$_2$), 34.6 (s, PdCH$_2$*C*H$_2$), 42.4 (d, $^{4}J_{Ptrans,C}$ = 15.3 Hz, PdCH$_2$CH$_2$*C*H$_2$), 125.5 (s, *p*-C_{Ph}), 128.5/129.0 (s/s, *o*-C_{Ph}, *m*-C_{Ph}), 129.3 (d, $^{3}J_{P,C}$ = 9.7 Hz, *m*-C_{dppe}), 129.8 (d, $^{3}J_{P,C}$ = 9.7 Hz, *m*-C_{dppe}), 130.6 (d, $^{1}J_{P,C}$ = 49.0 Hz, *i*-C_{dppe}), 131.0 (s, *p*-C_{dppe}), 132.0 (s, *p*-C_{dppe}), 134.0 (d, $^{1}J_{P,C}$ = 27.3 Hz, *i*-C_{dppe}), 134.5 (d, $^{2}J_{P,C}$ = 9.7 Hz, *o*-C_{dppe}), 144.1 (s, *i*-C_{Ph}) ppm. ^{31}P NMR (202 MHz, −30 °C, [D$_8$]THF): δ = 28.9 (d, $^{2+3}J_{P,P}$ = 29.5 Hz, P_{trans} to CH$_2$CH$_2$CH$_2$Ph), 59.5 (d, $^{2+3}J_{P,P}$ = 29.5 Hz, P_{trans} to Br) ppm.

Complex 10c (X = Cl): Pale yellow solid. Yield: 420 mg (94%). ^{13}C NMR (125 MHz, −30 °C, [D$_8$]THF): δ = 23.2 (dd, $^{1+4}J_{P,C}$ = 26.3 Hz, $^{2+3}J_{P,C}$ = 11.0 Hz, P*C*H$_2$), 30.3 (dd, $^{1+4}J_{P,C}$ = 32.7 Hz, $^{2+3}J_{P,C}$ = 23.9 Hz, P*C*H$_2$), 31.0 (d, $^{2}J_{Ptrans,C}$ = 101.2 Hz, Pd*C*H$_2$), 34.0 (d, $^{3}J_{P,C}$ = 4.5 Hz, PdCH$_2$*C*H$_2$), 42.2 (dd, $^{4}J_{Ptrans,C}$ = 15.3, $^{4}J_{Pcis,C}$ = 3.2 Hz, PdCH$_2$CH$_2$*C*H$_2$), 125.5 (s, *p*-C_{Ph}), 128.5/129.0 (s/s, *o*-C_{Ph}, *m*-C_{Ph}), 129.4 (d, $^{3}J_{P,C}$ = 8.8 Hz, *m*-C_{dppe}), 129.7 (d, $^{3}J_{P,C}$ = 10.1 Hz, *m*-C_{dppe}), 130.7 (d, $^{1}J_{P,C}$ = 49.0 Hz, *i*-C_{dppe}), 131.0 (s, *p*-C_{dppe}), 131.9 (s, *p*-C_{dppe}), 134.1 (one line of d, other one superposed, *i*-C_{dppe}), 134.3 (d, $^{2}J_{P,C}$ = 11.3 Hz, *o*-C_{dppe}), 134.5 (d, $^{2}J_{P,C}$ = 11.3 Hz, *o*-C_{dppe}), 144.2 (s, *i*-C_{Ph}) ppm. ^{31}P NMR (202 MHz, −30 °C, [D$_8$]THF): δ = 27.7 (d, $^{2+3}J_{P,P}$ = 29.5 Hz, P_{trans} to CH$_2$CH$_2$CH$_2$Ph), 59.4 (d, $^{2+3}J_{P,P}$ = 29.5 Hz, P_{trans} to Cl) ppm.

11. Experiments Monitored by ^{31}P NMR Spectroscopy: The corresponding amounts of sulfur or selenium compounds were added with a syringe to solutions of the palladium complex in THF/[D$_8$]THF (ca. 4:1). The reaction mixtures were transferred to NMR tubes that were then sealed. The reactions were monitored by ^{31}P{^{1}H} NMR spectroscopy.

[Pd(CH$_2$CH$_2$CH$_2$Ph)(SPh)(dppe)] (5b) from 3b and PhSSPh: ^{31}P NMR (81 MHz): δ = 34.0 (d, $^{2+3}J_{P,P}$ = 25.6 Hz, P_{trans} to CH$_2$CH$_2$CH$_2$Ph), 53.1 (d, $^{2+3}J_{P,P}$ = 25.6 Hz, P_{trans} to SPh) ppm.

[Pd(CH$_2$CH$_2$CH$_2$Ph){S(*i*Pr)}(dppe)] (5d) from 3b and *i*PrSH: ^{31}P NMR (81 MHz): δ = 40.7 (d, $^{2+3}J_{P,P}$ = 22.0 Hz, P_{trans} to CH$_2$CH$_2$CH$_2$Ph), 55.9 [d, $^{2+3}J_{P,P}$ = 22.0 Hz, P_{trans} to S(*i*Pr)] ppm.

[Pd(CH$_2$CH$_2$CH$_2$Ph){S(tBu)}(dppe)] (5e) from 3b and tBuSH: ^{31}P NMR (81 MHz): δ = 35.3 (d, $^{2+3}J_{P,P}$ = 23.2 Hz, P_{trans} to CH$_2$CH$_2$CH$_2$Ph), 56.9 [d, $^{2+3}J_{P,P}$ = 22.0 Hz, P_{trans} to S(*t*Bu)] ppm.

[Pd(CH$_2$CH$_2$CH$_2$Ph)(SBz)(dppe)] (5f) from 3b and BzSSBz: ^{31}P NMR (81 MHz): δ = 41.9 (d, $^{2+3}J_{P,P}$ = 23.2 Hz, P_{trans} to CH$_2$CH$_2$CH$_2$Ph), 56.6 (d, $^{2+3}J_{P,P}$ = 23.2 Hz, P_{trans} to SBz) ppm.

[Pd(CH$_2$CH$_2$CH$_2$Ph)(SMe)(dppe)] (5g) from 3b and MeSSMe: ^{31}P NMR (81 MHz): δ = 41.3 (d, $^{2+3}J_{P,P}$ = 23.2 Hz, P_{trans} to CH$_2$CH$_2$CH$_2$Ph), 55.6 (d, $^{2+3}J_{P,P}$ = 23.2 Hz, P_{trans} to SMe) ppm.

[Pd(CH$_2$CH$_2$CH$_2$Ph)(SeMe)(dppe)] (9a) from 3b and MeSeSeMe: ^{31}P NMR (81 MHz): δ = 46.1 (d, $^{2+3}J_{P,P}$ = 23.2 Hz, P_{trans} to CH$_2$CH$_2$CH$_2$Ph), 52.4 (d, $^{2+3}J_{P,P}$ = 23.2 Hz, P_{trans} to SeMe) ppm.

[PdMe(SePh)(dppe)] (9b) from 4 and PhSeSePh: ^{31}P NMR (81 MHz): δ = 45.0 (d, $^{2+3}J_{P,P}$ = 23.2 Hz, P_{trans} to Me), 56.8 (d, $^{2+3}J_{P,P}$ = 23.2 Hz, P_{trans} to SePh) ppm.

12. X-ray Structure of [Pd(CH$_2$CH$_2$Ph)$_2$(dppe)] (3a): Single crystals of complex **3a** suitable for X-ray diffraction analysis were grown at −30 °C by slow diffusion of *n*-pentane into a solution of **3a** in THF. Intensity data for complex **3a** were collected at 200(2) K with a Stoe STADI4 diffractometer with Mo-K_α radiation (0.71073 Å, graphite monochromator). A summary of crystallographic data, data collection parameters, and refinement parameters is given in

Table 4. The structure was solved by direct methods with SHELXS-86[34] and refined using full-matrix least-squares routines against F^2 with SHELXL-93.[34] Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were found in the difference Fourier map and were refined isotropically. CCDC-184402 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 4. Crystal data and details of the structure determination for complex **3a**

Empirical formula	$C_{42}H_{42}P_2Pd$
Formula mass	715.10
Crystal system	orthorhombic
Space group	*Pbca*
a [Å]	12.97(2)
b [Å]	22.000(5)
c [Å]	25.545(6)
Z	8
V [Å^3]	7290(12)
$D_{calcd.}$[g cm^{-3}]	1.303
F(000)	2960
μ(Mo-K_α) [cm^{-1}]	6.24
2θ range [°]	1.59−26.04
Recip. latt. segment (*h*, *k*, *l*)	0 → 8, 0 → 27, 0 → 31
Measured reflections	7659
Independent reflections [$R_{int.}$]	4775 [0.0387]
Observed reflections	3590
Parameters	575
*R*1, *wR*2 [$I > 2\sigma(I)$]	0.0387, 0.0794
*R*1, *wR*2 (all data)	0.0647, 0.0930
Goodness-of-fit on F^2	1.108
Min. and max. resd. electron density [e·Å^{-3}]	−0.558 and 0.333

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