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Trimethylstannyl (diphenylphosphino)acetate: a source of (diphenylphosphino)acetate ligand in the synthesis of coordination compounds

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Abstract

Trimethylstannyl (diphenylphosphino)acetate (**1**), which is readily accessible from potassium (diphenylphosphino)acetate and trimethylstannyl chloride, may serve as the source of (diphenylphosphino)acetate anion in the preparation of coordination compounds.Thus, the reactions between [M(cod)Cl_2] (M = Pd and Pt; cod = η^2:η^2-cycloocta-1,5-diene) and two equivalents of **1** give [M($Ph_2PCH_2CO_2$-κ^2O,P)$_2$] (**2** and **3**), while the reaction of [{Pd(μ-Cl)Cl($PFur_3$)}$_2$] (**4**; Fur = 2-furyl) with one equivalent of **1** yields [*SP*-4-3]-[PdCl($Ph_2PCH_2CO_2$-κ^2O,P)($PFur_3$)] (**5**).The reactions of **1** with the dimers [{Rh(η^5-C_5Me_5)Cl(μ-Cl)}$_2$] and [{Ru(η^6-1,4-$MeC_6H_4(CHMe_2)$)Cl(μ-Cl)}$_2$] (at **1**-to-metal ratio 1:1) produce *O*,*P*-chelated complexes as well, albeit as stable adducts with the liberated Me_3SnCl: [RhCl(η^5-C_5Me_5)($Ph_2PCH_2CO_2$-κ^2O,P)] · Me_3SnCl (**6**) and[RuCl(η^6-1,4-$MeC_6H_4(CHMe_2)$)($Ph_2PCH_2CO_2$-κ^2O,P)] · Me_3SnCl (**8**). The related complexes with *P*-monodentate (diphenylphosphino)acetic acid, [$RhCl_2$(η^5-C_5Me_5)($Ph_2PCH_2CO_2H$-κ,*P*)] (**7**) and [$RuCl_2$(η^6-1,4-$MeC_6H_4(CHMe_2)$)($Ph_2PCH_2CO_2H$-κ*P*)] (**9**), were obtained by bridge splitting in the dimers with the phosphinocarboxylic ligand. All new compounds were characterized by spectral methods and combustion analyses, and the structures of **2** · **3CH_2Cl_2**, **3**, **4**, **5**, **6** and **8** were determined by X-ray crystallography.

Keywords: Tin; Phosphines; Phosphinocarboxylic ligands; Palladium; Platinum; Rhodium; Ruthenium; X-ray diffraction

1. Introduction

Organotin monophosphines, e.g. $Ph_2P(CH_2)_nSnR_3$, usually coordinate to transition metals as monodentate *P*-donors [1]. In specific cases, they also provide an access to metalacycles involving a tin atom and a *P*-coordinated transition metal through oxidative addition of the C–Sn bond across a suitable, low-valent transition metal precursor compound [2]. Recently, it has been shown that trichlorostannylphosphine $Ph_2P(CH_2)_2SnCl_3$ reacts with palladium and platinum complexes [ML_2Cl_2] (M = Pd(II) and Pt(II); L_2 = η^2:η^2-cycloocta-1,5-diene (cod) or $(SEt_2)_2$) to give zwitterionic compounds [$M^+L_2(Cl)(Ph_2P(CH_2)_2Sn^-Cl_4)$] at 1:1 molar metal-to-phosphine ratio, and diphosphine complexes resulting from the replacement of both labile ligands L when two equivalents of the phosphine per metal atom are used. With [PdMe(cod)Cl], the reaction at 1:1 molar ratio gave a product resulting from transmetallation from tin to palladium, [Pd^+(cod)(Cl) ($Ph_2P(CH_2)_2Sn^-MeCl_3$)] [3]. These findings initiated our interest in the reactivity of phosphinocarboxylic stannyl esters. First, we focused our interest on the very basic

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representative, trimethylstannyl (diphenylphosphino)acetate (**1**). The organotin moiety and the carboxyphosphine moieties in **1** are connected by a reactive Sn–O bond and, hence, the compound may open new synthetic possibilities for the preparation of novel complexes involving this versatile phosphinocarboxylic ligand [4].

2. Results and discussion

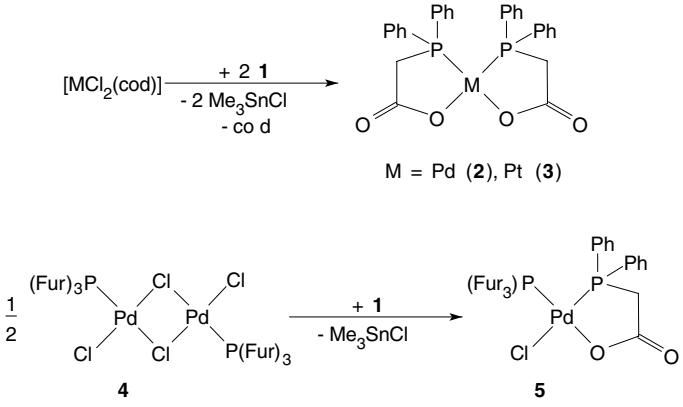
2.1. Syntheses and spectra

Trimethylstannyl (diphenylphosphino)acetate (**1**) was obtained as a white solid from salt metathesis between trimethylstannyl chloride and potassium (diphenylphosphino)acetate, which was generated only in situ by reacting (diphenylphosphino)acetic acid with one molar equivalent of potassium *tert*-butoxide. The compound exhibits typical strong carboxylate bands in the IR spectra at 1574 and 1554 cm^{-1}, which are shifted to lower energies than for the parent acid (1700 cm^{-1} [5]), sodium (diphenylphosphino)acetate (1595 cm^{-1} [5]), and even for ethyl (diphenylphosphino)acetate (1728 cm^{-1} [6]). In ^{1}H and ^{13}C NMR spectra, **1** shows typical $^{117/119}Sn$ satellites ($SnMe_3$) and splittings due to the phosphorus atom. The ^{31}P and ^{119}Sn NMR spectra rule out any tin-phosphorus interaction by showing, respectively, a single resonance close to the parent acid (δ_P **1**, −16.3; the acid, −15.1 [7]) and a signal at δ_{Sn} 140.1, which is similar to organic trimethylstannyl carboxylates (cf. δ_{Sn} 129 for $MeCO_2SnMe_3$ and 150 for HCO_2SnMe_3 [8,9]).

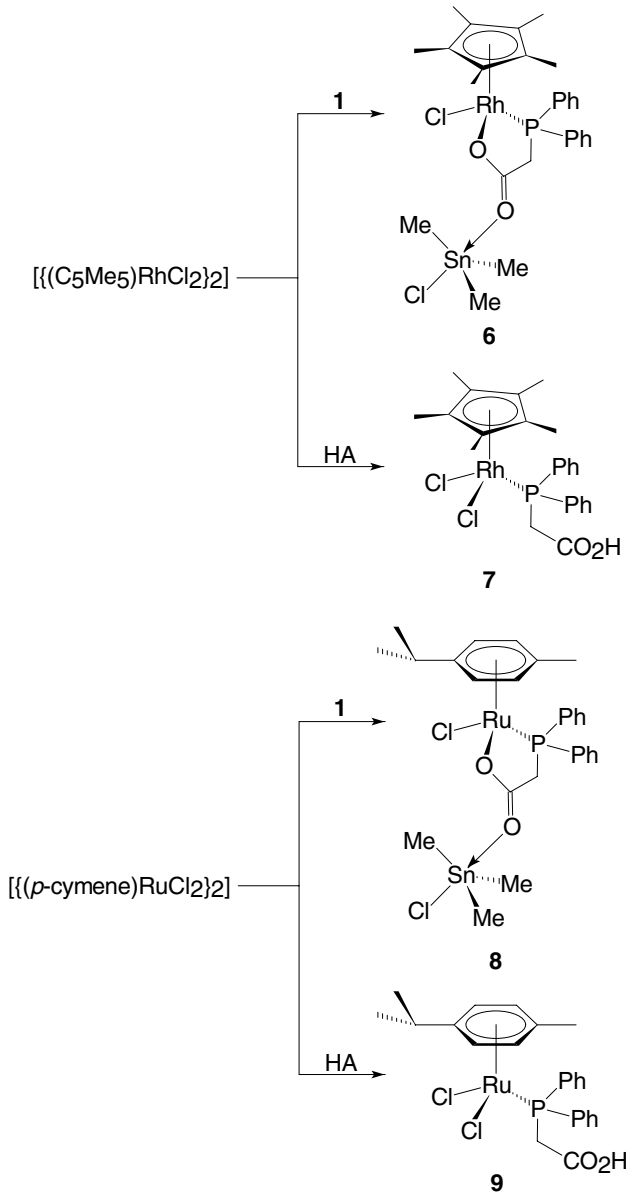
The stannyl ester **1** reacts with a half molar equivalent of $[M(cod)Cl_2]$ (M = Pd and Pt) under substitution of the diene ligand with a concurrent chloride transfer from palladium to tin (a formal transmetallation) to give Me_3SnCl and chelated complexes *cis*-$[M(Ph_2PCH_2CO_2\text{-}\kappa^2O,P)_2]$, M = Pd (**2**), and Pt (**3**) (Scheme 1), which have been previously synthesized from $K_2[MCl_4]$ and sodium (diphenylphosphino)acetate [10]. Likewise, the reaction of dipalladium(II) complex **4** in dichloromethane with two equivalents of **1** gave a yellow solid, which was characterized as an *O*,*P*-chelated complex with *cis*-disposed phosphine donors, **5**, and Me_3SnCl as the side product. Complex **5** apparently results from a bridge splitting with the carboxyphosphine and chloride transfer to tin, similarly to the previous cases. The starting bridged, *trans*-diphosphine complex **4** was obtained as a bright orange solid from the reaction of the stoichiometric amounts of tri(2-furyl)phosphine and $Na_2[PdCl_4]$ according to a general procedure in ref. [11].

Similar transfer of (diphenylphosphino)acetate from **1** to a transition metal occurs also with chloride bridged dimers $[\{Rh(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ and $[\{Ru(\eta^6\text{-}1,4\text{-}MeC_6H_4(CHMe_2))Cl(\mu\text{-}Cl)\}_2]$. However, unlike the above cases, these reactions produce adducts of the *O*,*P*-chelated products with the liberated Me_3SnCl: $[RhCl(\eta^5\text{-}C_5Me_5)(Ph_2PCH_2CO_2\text{-}\kappa^2O,P)]\cdot Me_3SnCl$ (**6**) and $[RuCl(\eta^6\text{-}1,4\text{-}MeC_6H_4(CHMe_2))(Ph_2PCH_2CO_2\text{-}\kappa^2O,P)]\cdot Me_3SnCl$ (**8**) (Scheme 2). The tin atom in the adducts is coordinated with the carbonyl oxygen of the chelating carboxylate and thus acquires a coordination number of five and the regular trigonal-bipyramidal geometry.

Adduct formation is best reflected by ^{119}Sn NMR spectra: the tin resonances of **6** and **8** are shifted from the region expected for tetracoordinated organotin compounds (Me_3SnCl: δ_{Sn} ca. 164 in $CDCl_3$ [12]) to higher fields, i.e. towards values typical for pentacoordinated tin compounds (cf. $Me_3SnCl\cdot L$, δ_{Sn}: L = dmso, +3 (in dmso-d_6) [12], and δ_{Sn} 110–137 for 2–72 mol% Me_3SnCl in acetone [8]). A different extent of this high-field shift in **6** (δ_{Sn} 85.7) and **8** (δ_{Sn} 127.2) most likely corresponds with the strength of the C = $O \rightarrow$ Sn donation and, consequently, with the nature of the bonding between the carboxylate and the central atom. The donation from the carboxylate carbonyl group is reflected also by a lowering of the frequency due to the carboxylate bands in IR spectra, the magnitude of the



Scheme 1.



Scheme 2.

shift being in agreement with the trend in δ_{Sn} values (**6**, 1569; **8**, 1580 cm^{-1}). Notably, the adducts are firmly bonded; for instance, compound **8** was recovered unchanged even after treating its dichloromethane solution with a large excess of pyridine.

Complexes **6** and **8** are chiral at the metal atoms, possessing the expected three-legged piano stool structures with the stereogenic metal atoms surrounded by the π-ligand, the *O*,*P*-coordinated phosphinocarboxylate, and the terminal chloride ligand, and result as racemic mixtures. The presence of the chiral center renders the protons of the PCH_2 group in **6** and **8** as well as the CH resonances of the arene ligand in **8** diastereotopic and anisochronic in the NMR spectra. This is not observed for analogous achiral complexes with *P*-bonded (diphenylphosphino)acetic acid: $[RhCl_2(\eta^5\text{-}C_5Me_5)(Ph_2PCH_2CO_2H\text{-}\kappa P)]$ (**7**) and $[RuCl_2(\eta^6\text{-}1,4\text{-}MeC_6H_4\text{-}(CHMe_2))(Ph_2PCH_2CO_2H\text{-}\kappa P)]$ (**9**), which were synthesized by bridge splitting reactions from the above mentioned dimeric precursors (Scheme 2; HA = $Ph_2PCH_2CO_2H$). Due to a poor solubility in halogenated solvents, the NMR spectra of complexes **7** and **8** were recorded in dmso-d_6, which prevents a direct comparison of NMR spectral data in the pairs **6**–**7** and **8**–**9**. Nevertheless, when neglecting a possible solvent effect on the ^{31}P NMR resonance of the metal bonded phosphine group, there is a shift to lower field on going from *P*-bonded acid to *O*,*P*-bonded carboxylated, much smaller for the rhodium(I) complexes than for their ruthenium(II) analogues. In IR spectra of **7** and **9**, the bands of the carboxyl group (both 1690 cm^{-1}) are observed at nearly the same position as for the free phosphinocarboxylic acid (see above), indicating that the carboxyl groups do not participate in coordination.

2.2. The molecular structures of palladium and platinum complexes

The structures of phosphinoacetate complexes **2** · $3CH_2Cl_2$ (Fig. 1, Table 1), **3** (Fig. 2, Table 1), and **5** (Fig. 3, Table 2) as determined by X-ray crystallography are rather unexceptional, corroborating the *cis*-P–P, square-planar coordination geometries in all cases. The solvated complex **2** · $3CH_2Cl_2$ crystallizes in a centrosymmetric triclinic unit cell, different from the monoclinic cell of unsolvated **2**; however, the molecular geometries of both solvatomorphs do not differ noticeably [13]. Likewise, the arrangements of the

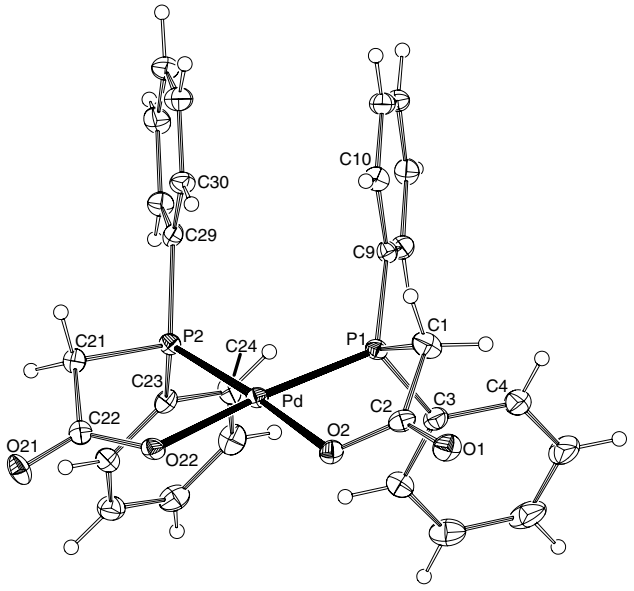


Fig. 1. A view of the molecular structure of complex **2** · $3CH_2Cl_2$. Thermal motion ellipsoids are drawn with 30% probability. The solvent molecules are omitted for clarity.

Table 1
Selected geometric parameters for **2** · **3CH$_2$Cl$_2$** and **3** (in Å and °)

Compound	**2** · **3CH$_2$Cl$_2$**	**3**
M	Pd	Pt
M–P(1)	2.220(1)	2.2142(8)
M–P(2)	2.217(1)	2.2070(9)
M–O(2)	2.081(3)	2.069(2)
M–O(22)	2.073(3)	2.074(2)
P(1)–C(1)	1.826(6)	1.824(3)
P(2)–C(21)	1.825(5)	1.818(3)
C(1)–C(2)	1.530(8)	1.533(4)
C(2)–O(1)	1.221(7)	1.222(4)
C(2)–O(2)	1.297(7)	1.305(4)
C(21)–C(22)	1.510(7)	1.529(4)
C(22)–O(21)	1.224(6)	1.227(4)
C(22)–O(22)	1.298(6)	1.298(4)
P(1)–M–P(2)	102.82(5)	105.05(3)
P(1)–M–O(2)	81.58(9)	83.03(6)
P(2)–M–O(22)	83.88(8)	82.68(6)
O(2)–M–O(22)	91.7(1)	89.18(8)
P(1)–C(1)–C(2)	108.2(4)	109.0(2)
P(2)–C(21)–C(22)	111.6(3)	108.8(2)
C(1)–C(2)–O(2)	116.0(4)	116.2(2)
C(21)–C(22)–O(22)	115.6(4)	117.0(3)
O(1)–C(2)–O(2)	124.0(5)	123.1(3)
O(21)–C(22)–O(22)	123.2(5)	122.5(3)
P(1)–C(1)–C(2)–O(2)	−27.6(5)	−27.6(3)
P(2)–C(21)–C(22)–O(22)	27.0(5)	−25.1(3)

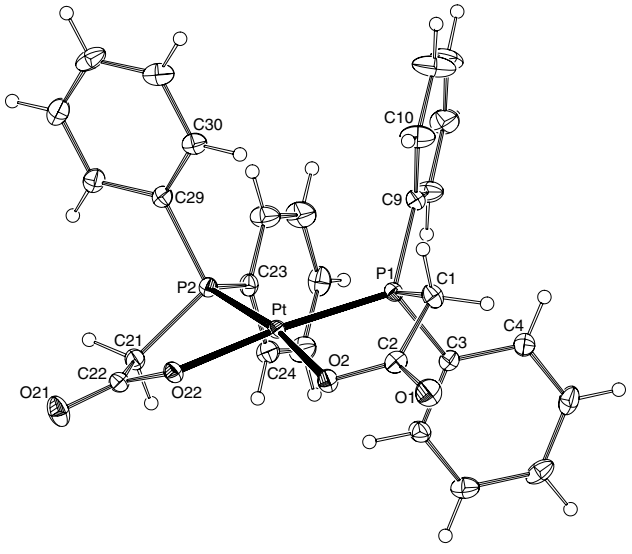


Fig. 2. A view of the molecular structure of complex **3**. Thermal motion ellipsoids are drawn with 30% probability.

M(Ph$_2$PCH$_2$CO$_2$-κ^2*O*,*P*) motifs (M = Pd and Pt), i.e., the respective bond distances and angles, and the conformation at the PC–CO$_2$ bond, in all the *O*,*P*-chelated complexes **2** · **3CH$_2$Cl$_2$**, **3**, and **5** are similar to each other, and to those in unsolvated **2** and [PtBr(Ph$_2$PCH$_2$CO$_2$-κ^2*O*,*P*)(Ph$_2$PCH$_2$CO$_2$H-κ*P*)] · H$_2$O [14]. The *cis*-arrangement of the bulky phosphino groups in **2** · **3CH$_2$Cl$_2$** and **3** results in an opening of

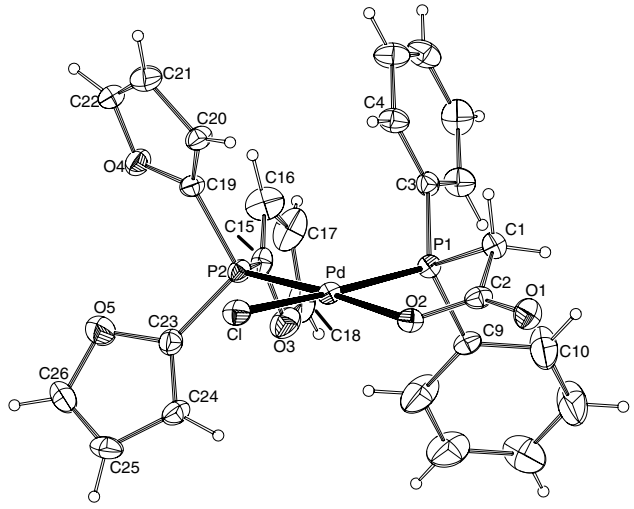


Fig. 3. A view of the molecular structure of complex **5**. Thermal motion ellipsoids are drawn with 30% probability.

Table 2
Selected intratomic distances and angles for **5** (in Å and °)[a]

Pd–Cl	2.334(2)	Cl–Pd–P(2)	88.18(8)
Pd–P(1)	2.235(2)	Cl–Pd–O(2)	90.1(2)
Pd–P(2)	2.234(2)	P(1)–Pd–P(2)	99.85(8)
Pd–O(2)	2.075(6)	P(1)–Pd–O(2)	82.2(2)
P(1)–C(1)	1.824(8)	P(1)–C(1)–C(2)	108.8(5)
C(1)–C(2)	1.53(1)	C(1)–C(2)–O(1)	123.2(5)
C(2)–O(1)	1.215(7)	C(1)–C(2)–O(2)	120.6(5)
C(2)–O(2)	1.298(6)	O(1)–C(2)–O(2)	116.1(4)

[a] Further data: P(1)–C(3) 1.814(4), P(1)–C(9) 1.804(3), P(2)–C(15) 1.80(1), P(2)–C(19) 1.774(8), P(2)–C(23) 1.77(1) Å; P(1)–C(1)–C(2)–O(2) −29.2(6)°.

the coordination polyhedra at the edge accommodating the phosphorus ligands. This is compensated by a closure of the remaining interligand angles, though without an observable tetrahedral deformation. A similar but less pronounced deformation is observed also for **5**.

The compounds exhibit interesting intermolecular interactions: the molecules of **2** are connected via offset π···π interactions of exactly parallel phenyl rings C(3–8): Ph···Ph & (2 − *x*, 1 − *y*, 1 − *z*), at a ring centroid distance of 3.883(4) Å (interplanar separation 3.70 Å). The individual molecules feature similar, though *intramolecular* interactions between the aromatic rings C(9–14) and C(29–34) (Cg···Cg 3.671(3) Å), which are mutually rotated by only ca. 19 °. The molecules of complex **3** also associate predominantly via graphite-like π···π stacking of parallel aromatic rings (Fig. 4). The orientation of the neighbouring phenyl rings C(9–14) and C(23–28), which seems to stabilize the conformation of **2**, is less favourable in **3**: the distance of the ring centroids is as long as 5.057(2) Å and the planes are tilted (the dihedral angle of the ring planes amounts to 25°). In additon to the mentioned π-interactions, the molecules of complex **3**

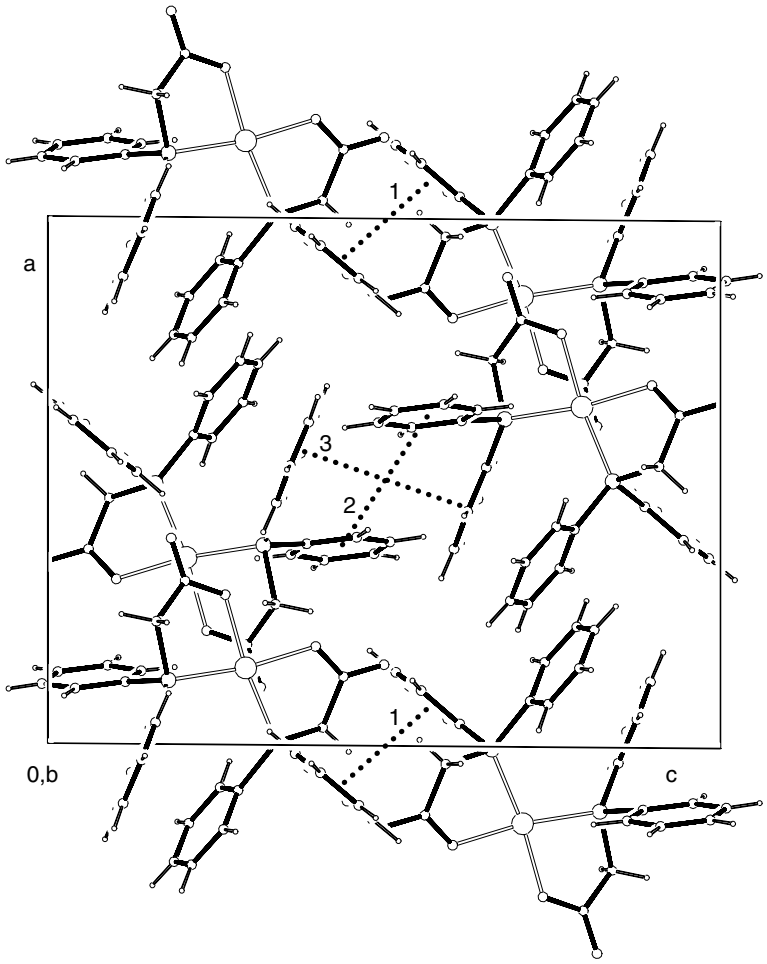


Fig. 4. A view of the crystal packing of **3** along the crystallographic *b* axis. The π···π interactions are indicated as dotted lines. Selected parameters for the interactions:

Code	Phenyl ring	Cg···Cg (Å)	Interplanar distance (Å)
1	C(29–34)···C(29–34)^{i}	3.664(2)	3.41
2	C(3–8)···C(3–8)^{ii}	4.359(2)	3.42
3	C(9–14)···C(9–14)^{iii}	4.995(2)	4.95

The rings are exactly parallel due to the crystallographic symmetry. Symmetry codes: (*i*) $1-x, 1-y, -z$; (*ii*) $1-x, -y, 1-z$; (*iii*) $1-x, 1-y, 1-z$. Cg denotes the ring centroid.

are involved in weak, intermolecular C–H···O hydrogen bonding to carboxylate oxygen atoms.

The solid-state assembly of **5** is analogous to the packings of the bis(chelated) complexes since the molecules of the complex associate to centrosymmetric dimers via π···π stacking of the phenyl rings C(3–8) (Cg···Cg^{i} 3.821(2) Å, interplanar separation 3.63 Å; *i*: $1-x$, $1-y$, $1-z$). The molecular network is further interconnected by intermolecular C–H···O hydrogen bonds to carboxylate [O(1) and O(2)] and furane oxygen [O(4)] atoms (C···O 3.23(1)–3.488(6) Å).

The molecule of the dimer **4** (Fig. 5, Table 3) resides on the crystallographic inversion centre, which renders only the half of the molecule crystallographically independent. The coordination environment around the palladium atoms are almost perfectly planar and the interligand angles do not differ much from the right angle. Distances from palladium to bridging chloride ligands are slightly elongated (significantly with respect to esd) when compared to the bond length to the terminal chloride (relatively by 2 and 6% for Cl(1) and Cl(1)^{ii}, respectively; *ii*: $2-x, 1-y, -z$). The crystal packing of **4** shows no significant intermolecular contacts except for offset π···π stacking of the parallel furane rings involving O(3) oxygen atom, the respective ring centroid and interplanar distances being Cg···Cg^{iii} 3.713(2) Å and ca. 3.45 Å; *iii*: $1-x, -y, -z$. The other furane rings stack as well but at much longer distances, cf. Cg···Cg^{iv}

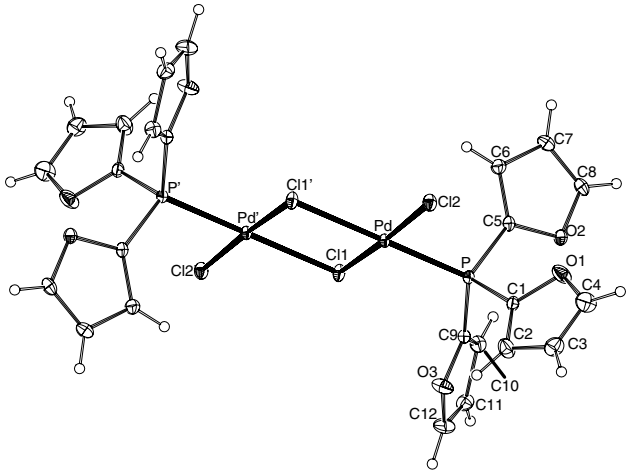


Fig. 5. A view of the molecular structure of complex **4**. Thermal motion ellipsoids are drawn with 30% probability.

4.077(1) Å for the ring involving O(2), and Cg···Cg^{v} 5.832(2) Å for the ring involving O(1) [*iv*: $1-x$, $-y$, $1-z$; *v*: $(2-x, -y, 1-z]$.

2.3. The molecular structures of the adducts *6* and *8*

The views of the molecular structures of **6** and **8** are shown in Figs. 6 and 7, and the selected geometric data are given in Tables 4 and 5. Adduct **8** forms racemic crystals, which accommodate equal numbers of the enantiomeric molecules within the centrosymmetric unit cells (monoclinic $P2_1/n$). In the case of **6**, a chiral crystal with an orthorhombic $P2_12_12_1$ symmetry was selected from the racemic reaction batch. The structure refinement revealed an (*S*)-configuration at the stereogenic rhodium atom.

The compounds possess similar pseudotetrahedral structures as proposed from the spectral data. In both compounds, the steric hindrance between the π-ligand and the bulky diphenylphosphino group causes the Cg–M–P angles (Cg is the centroid of the aromatic ligand, M = Rh or Ru) to be more opened that the other

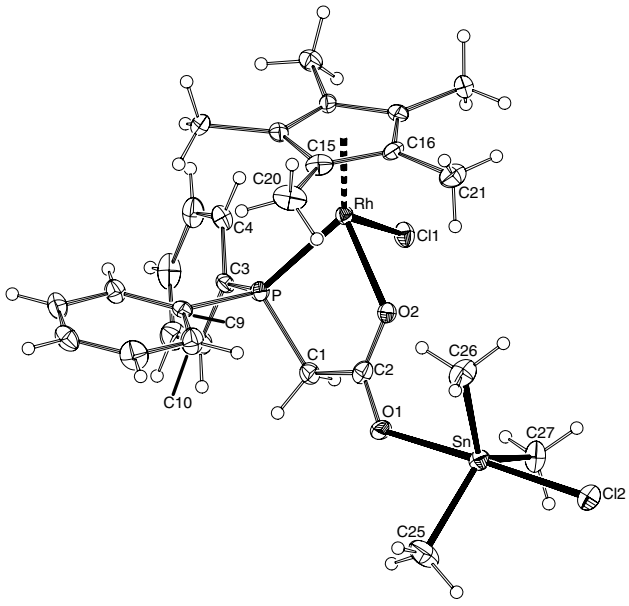


Fig. 6. A view of the molecular structure of adduct **6**. Thermal motion ellipsoids are drawn with 30% probability.

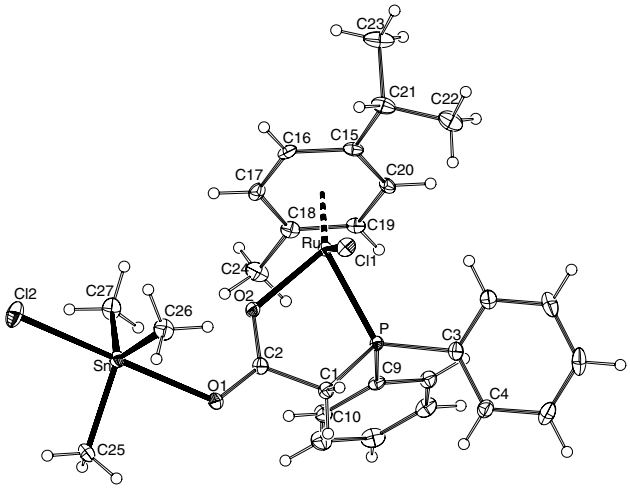


Fig. 7. A view of the molecular structure of adduct **8**. Thermal motion ellipsoids are drawn with 30% probability.

Table 3
Selected intratomic distances and angles for **4** (in Å and °)[a]

Pd–Cl(1)	2.3268(5)	Cl(1)–Pd–P	93.32(2)		
Pd–Cl(2)	2.2793(5)	Cl(1)–Pd–Cl(1)^{i}	85.61(2)		
Pd–Cl(1)^{i}	2.4230(6)	Cl(2)–Pd–P	87.39(2)		
Pd–P	2.2141(6)	Cl(2)–Pd–Cl(1)^{i}	93.64(2)		
Pd···Pd^{i}	3.4853(2)	Pd–Cl(1)–Pd^{i}	94.39(2)		
P–C(1)	1.792(2)	P–C(5)	1.772(2)	P–C(9)	1.785(2)
O(1)–C(1)	1.358(3)	O(2)–C(5)	1.374(3)	O(3)–C(9)	1.374(3)
O(1)–C(4)	1.371(3)	O(2)–C(8)	1.369(3)	O(3)–C(12)	1.371(3)
C(1)–C(2)	1.343(4)	C(5)–C(6)	1.352(3)	C(9)–C(10)	1.347(4)
C(2)–C(3)	1.429(4)	C(6)–C(7)	1.425(4)	C(10)–C(11)	1.424(3)
C(3)–C(4)	1.327(4)	C(7)–C(8)	1.336(4)	C(11)–C(12)	1.337(4)

[a] Symmetry operations: (*i*) $2-x$, $1-y$, $-z$.

Table 4
Selected intratomic distances and angles for **6** (in Å and °)[a]

Rh–Cg	1.807(3)	Cg–Rh–Cl(1)	125.33(9)
Rh–Cl(1)	2.395(2)	Cg–Rh–P	135.2(1)
Rh–P	2.299(2)	Cg–Rh–O(2)	124.89(2)
Rh–O(2)	2.143(3)	Cl(1)–Rh–P	86.04(6)
Rh···Sn	5.7286(6)	Cl(1)–Rh–O(2)	89.2(2)
P–C(1)	1.820(6)	P–Rh–O(2)	80.9(1)
P–C(3)	1.807(6)	P–C(1)–C(2)	110.3(4)
P–C(9)	1.815(6)	O(1)–C(2)–O(2)	124.2(5)
C(1)–C(2)	1.515(8)	O(1)–C(2)–C(1)	118.0(5)
C(2)–O(1)	1.245(6)	O(2)–C(2)–C(1)	117.7(4)
C(2)–O(2)	1.273(7)		
Sn···O(1)	2.357(4)	C(2)–O(1)···Sn	130.9(4)
Sn–Cl(2)	2.561(2)	O(1)–Sn–Cl(2)	176.7(1)
Sn–C(25)	2.106(5)	Cl(2)–Sn–Me[b]	91.2(2)–93.9(2)
Sn–C(26)	2.109(7)	O(1)–Sn–Me[b]	84.4(2)–92.0(2)
Sn–C(27)	2.116(7)	Me–Sn–Me[b]	117.1(3)–125.6(3)

[a] Cg is the centroid of the cyclopentadienyl ring C(15–19).
[b] Me = C(25), C(26), and C(27).

Table 5
Selected intratomic distances and angles for **8** (in Å and °)[a]

Ru–Cg	1.700(1)	Cg–Ru–Cl(1)	129.38(4)
Ru–Cl(1)	2.4063(6)	Cg–Ru–P	132.51(4)
Ru–P	2.3185(8)	Cg–Ru–O(2)	127.12(7)
Ru–O(2)	2.100(2)	Cl(1)–Ru–P	86.45(2)
Ru···Sn	5.3491(3)	Cl(1)–Ru–O(2)	84.65(5)
P–C(1)	1.826(3)	P–Ru-O(2)	79.14(6)
P–C(3)	1.813(3)	P–C(1)–C(2)	108.0(2)
P–C(9)	1.815(3)	O(1)–C(2)–O(2)	122.3(3)
C(1)–C(2)	1.517(4)	O(1)–C(2)–C(1)	119.2(2)
C(2)–O(1)	1.254(3)	O(2)–C(2)–C(1)	118.5(2)
C(2)–O(2)	1.275(3)		
Sn···O(1)	2.372(2)	C(2)–O(1)···Sn	120.5(2)
Sn–Cl(2)	2.5440(9)	O(1)–Sn–Cl(2)	175.52(5)
Sn–C(25)	2.121(3)	Cl(2)–Sn–Me[b]	91.5(1)–95.2(1)
Sn–C(26)	2.133(3)	O(1)–Sn–Me[b]	85.2(1)–92.3(1)
Sn–C(27)	2.130(3)	Me–Sn–Me[b]	115.7(1)–126.0(1)

[a] Cg is the centroid of the η^6-arene ring C(15–20).
[b] Me = C(25), C(26), and C(27).

two Cg–M–donor angles. This deformation is larger in the rhodium(I) complex **6**, bearing the bulky pentamethylcyclopentadienyl ligand. The geometry around the ruthenium atom in **8** does not differ significantly from that in an analogous complex with chelating ferrocenecarboxylate, (R_{Ru},S_p)-chloro-(η^6-*p*-cymene)-{2-(diphenylphosphino)ferrocenecarboxylate-κ^2*O*,*P*}ruthenium(II) [4b].

The arrangements around tin atoms in **6** and **8** are trigonal-bipyramidal with the bond angles deviating only slightly from the theoretical ones. The Sn···O(1) separation in both compounds roughly correspond to the distances observed for solid adducts $Me_3SnCl \cdot O{=}C(Me)CH{=}PPh_3$ (Sn···O 2.332 Å [15]) and $Ph_3SnL \cdot L$, where L = *N*,*N*,*N*′,*N*′-tetramethylurea (2.384 Å [16]), ε-caprolactone (2.399 Å), and diphenylcyclopropenone (2.510 Å [17]). The Sn···O distance in **6** is by ca. 0.015 Å shorter than in **8**, which is in accordance with the spectral data (see above).

3. Experimental

3.1. Materials and methods

All syntheses were carried out under argon blanket. Dichloromethane was dried over anhydrous potassium carbonate. Solvents for crystallizations were used without purification (p.a. quality). (Diphenylphosphino)acetic acid [5], $[Pd(cod)Cl_2]$, $[Pt(cod)Cl_2]$ [18], and $[\{Rh(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ [19] were synthesized according to the literature methods. Other chemicals were commercial products and were used as obtained from the suppliers (Strem, Aldrich, and Fluka).

NMR spectra were recorded on a Varian UNITY Inova 400 spectrometer (^{1}H, 399.95; ^{13}C, 100.58; ^{31}P, 161.9; ^{119}Sn 149.14 MHz) at 298 K. Chemical shifts (δ/ppm) are given relative to internal tetramethylsilane (^{1}H and ^{13}C), external 85% aqueous H_3PO_4 (^{31}P), and external neat $SnMe_4$ (^{119}Sn). IR spectra were recorded on an a Perkin–Elmer 684 FT IR spectrometer in the range of 400–4000 cm^{-1}.

3.2. Preparation of trimethylstannyl (diphenylphosphino)acetate (*1*)

Potassium *tert*-butoxide (0.7322 g, 6.52 mmol) was added into a solution of (diphenylphosphino)acetic acid (1.532 g, 6.27 mmol) in dichloromethane (10 mL). After stirring the resulting suspension for 1 h at room temperature, a solution of Me_3SnCl (1.251 g, 6.27 mmol) in dichloromethane (10 mL) was introduced and stirring was continued overnight (the suspension dissolved quickly upon addition; however, the formation of a white precipitate started simultaneously). Then, the reaction mixture was diluted with equal volume of hexane and, after standing for 1 h, filtered. The filtrate was evaporated and the solid residue dried under vacuum to give **1** as an off-white solid (1.684 g, 66%).

^{1}H NMR ($CDCl_3$): δ 0.43 (s with tin satellites: $^2J_{119SnH}$ = 58.5, $^2J_{117SnH}$ = 56.0 Hz, 9H, $SnMe_3$), 3.14 (s, 2H, CH_2), 7.29–7.49 (m, 10H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ −2.49 (s with tin satellites: $^1J_{119SnC}$ = 396, $^1J_{117SnC}$ = 377 Hz, $SnMe_3$), 35.87 (d, $^1J_{PC}$ = 20 Hz, CH_2), 128.39 (d, J_{PC} = 7 Hz), 128.78 (s), 132.69 (d, J_{PC} = 20 Hz) (3× CH of PPh_2); 137.93 (d, $^1J_{PC}$ = 14 Hz, C_{ipso} of PPh_2), 175.49 (d, $^2J_{PC}$ = 8 Hz, COO). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −16.3 (s). ^{119}Sn{^{1}H} NMR ($CDCl_3$): δ 140.1 (s). IR (Nujol): $\tilde{\nu}$/cm^{-1} 1574 s, 1554 s, 1192 w, 1147 w, 1100 w, 860 m 774 m, 740 s, 696 s, 556 m, 546 m, 507 m, 486 m, 429 m. Anal. Calcd.

for $C_{17}H_{21}O_2PSn$: C, 50.16; H, 5.20%. Found: C, 50.07; H, 5.40%.

3.3. The reaction of **1** with [Pd(cod)Cl$_2$]

[$PdCl_2$(cod)] (57 mg, 0.20 mmol) and **1** (179 mg, 0.44 mmol) were dissolved in dichloromethane (10 mL) and the clear was mixture stirred for 3 days at room temperature, whereupon it deposited a yellowish solid. The mixture was cooled in a refrigerator (−18 °C) overnight, the solid was filtered off, washed well with diethyl ether and dried under vacuum to afford *cis*-bis{(diphenylphosphino)acetate-κ^2P,O}palladium(II) (**2**) as a yellowish microcrystalline solid. Yield: 97 mg (82%).

^{1}H NMR (CD_2Cl_2): δ 3.60 (d, $^2J_{PH}$ = 12.5 Hz, 2H, CH_2), 7.26–7.54 (m, 10 H, PPh_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 13.7 (s). IR (Nujol): $\tilde{\nu}$/cm^{-1} 1652 vs, 1626 vs, 1604 vs, 1300 s, 1100 s, 998 m, 914 m, 904 m, 863 m composite, 745 s, 739 s, 694 s, 532 m, 500 m.

3.4. The reaction of **1** with [Pt(cod)Cl$_2$]

[$PtCl_2$(cod)] (75 mg, 0.20 mmol) and **1** (179 mg, 0.44 mmol) were reacted as described in Sect. 3.3 The isolation as above gave *cis*-bis{(diphenylphosphino)acetate-κ^2P,O}platinum(II) (**3**) as a fine, white solid. Yield: 95 mg (70%).

^{1}H NMR (CD_2Cl_2): δ 3.47 (d, $^2J_{PH}$ = 11.5 Hz, 2H, CH_2), 7.25–7.50 (m, 10H, PPh_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −12.1 (s with ^{195}Pt satellites, $^1J_{PtP}$ = 3404 Hz). IR (Nujol): $\tilde{\nu}$/cm^{-1} 1664 vs, 1628 vs, 1609 vs, 1101 s, 906 m, 862 s, 738 s, 693 m, 501 m.

3.5. Preparation of trans-bis{(μ-chloro)chloro-tri(2-furyl)phosphinepalladium(II)} (**4**)

$Na_2[PdCl_4]$ (294 mg, 1.0 mmol) was dissolved in warm (ca. 50 °C) absolute ethanol (25 mL), the solution was filtered, and the filtrate mixed with a solution of tri(2-furyl)phosphine (233 mg, 1.0 mmol) in chloroform (25 ml). The reaction flask was flushed with argon and the mixture was heated to reflux for 90 min. Then, it was cooled to room temperature, the solvent was removed under reduced pressure, and the solid residue was taken up with little chloroform, transferred on a glass frit, and washed with the same solvent until the filtrate remained colourless (from bright yellow-orange, ca. 30 mL). The product was precipitated from the filtrate by adding hexane (ca. 100 mL), filtered off and dried under vacuum (80 °C/1 Torr/2 h). Yield: 361 mg (88%), rusty orange powder. (*Note*: well-developed, bright orange red microcrystals of **4** can be obtained when the dichloromethane extract is layered with hexane and the mixture allowed to crystallize by diffusion for several days.)

^{1}H NMR ($CDCl_3$): δ 6.55 (br dt, $J \approx 1.9$, 1.3 Hz, 1H), 7.34 (br d, $J \approx 3.3$ Hz, 1H), 7.77 (br s, 1H) (3×CH of Fur). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 111.74 (d, J_{PC} = 9 Hz), 127.50 (d, J_{PC} = 23 Hz) (3× CH of Fur); 138.10 (d, $^1J_{PC}$ = 99 Hz, C_{ipso} of Fur), 149.78 (d, J_{PC} = 5 Hz, CH of Fur). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −25.5 (s). Anal. Calcd. for $C_{24}H_{18}Cl_4O_6P_2Pd_2$: C, 35.20; H, 2.22%. Found: C, 34.96; H, 2.44%.

3.6. The reaction of **1** with **4**

A solution of **1** (82 mg, 0.20 mmol) in dichloromethane (3 mL) was added to a solution of **4** (82 mg, 0.10 mmol) in the same solvent (5 mL), and the reaction mixture was stirred for two days at room temperature. Then, it was evaporated under reduced pressure, and the solid residue was washed thoroughly with diethyl ether and dried under vacuum to give [*SP*-4-3]-chloro-{(diphenylphosphino)acetate-κ^2P,*O*}-tri(2-furyl)phosphinepalladium(II) (**5**) as a yellowish microcrystalline solid (103 mg, 84%). The compound can be further purified by dissolving in dichloromethane and precipitation with hexane.

^{1}H NMR (CD_2Cl_2): δ 3.57 (dd, $^2J_{PH}$ = 11.9, $^4J_{PH}$ = 1.0 Hz, 2H, CH_2), 6.39 (dt, J = 3.6, 1.8 Hz, 3H, Fur), 7.03 (ddd, $J \approx 2.9$, 2.0, 0.4 Hz, 3H, Fur), 7.38–7.64 (m, 13H, PPh_2 and Fur). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 43.22 (dd, $^1J_{PC}$ = 35, $^3J_{PC}$ = 2 Hz, CH_2), 112.03 (d, J_{PC} = 8 Hz, CH of Fur), 125.46 (dd, $^1J_{PC}$ = 57, $^3J_{PC}$ = 2 Hz, C_{ipso} of PPh_2), 126.61 (d, J_{PC} = 21 Hz, CH of Fur), 129.66 (d, J_{PC} = 11 Hz, CH of PPh_2), 132.88 (d, J_{PC} = 3 Hz, CH of PPh_2), 133.60 (d, J_{PC} = 11 Hz, CH of PPh_2), 140.25 (dd, $^1J_{PC}$ = 94, $^3J_{PC}$ = 2 Hz, C_{ipso} of Fur), 149.40 (d, J_{PC} = 6 Hz, CH of Fur), 175.20 (dd, $^2J_{PC}$ = 10, $^3J_{PC}$ = 2 Hz, CO_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −22.2 (d, $^2J_{PP}$ = 6 Hz, $PFur_3$), 18.2 (d, $^2J_{PP}$ = 6 Hz, $Ph_2PCH_2CO_2$). IR (Nujol): $\tilde{\nu}$/cm^{-1} 1645 vs composite, 1553 m, 1290 s, 1133 m, 1122 m, 1106 m, 1016 m, 907 m, 882 m, 856 m, 773 s, 745 s, 695 m, 554 s, 536 s, 522 s, 494 s. Anal. Calcd. for $C_{26}H_{21}ClO_5P_2Pd$: C, 50.59; H, 3.42%. Found: C, 50.37; H, 3.69%.

3.7. The reaction of **1** with [{Rh(η^5-C_5Me_5)Cl(μ-Cl)}$_2$]

[{Rh(η^5-C_5Me_5)Cl(μ-Cl)}$_2$] (54 mg, 0.087 mmol) and **1** (71 mg, 0.174 mmol) were dissolved in dichloromethane (5 mL). The resulting clear solution was stirred overnight and layered with hexane. Crystallization by liquid-phase diffusion over several days afforded chloro-{(diphenylphosphino)acetate-κ^2P,O}(η^5-pentamethylcyclopentadienyl)rhodium(I)-trimethylstannyl chloride (1/1) (**6**) as well-developed red crystals (111 mg, 90%).

^{1}H NMR ($CDCl_3$): δ 0.71 (s with tin satellites, $^2J_{119SnH}$ = 63.7, $^2J_{117SnH}$ = 60.9 Hz, 9H, $SnMe_3$), 1.53 (d, $^3J_{RhH}$ or $^4J_{PH}$ = 3.6 Hz, 15 H, C_5Me_5), 3.31 (ddd,

$^2J_{HH}$ = 16.1, $^2J_{PH}$ = 9.9 Hz, $^3J_{RhH}$ = 0.5 Hz, 1H, CH_2), 3.67 (dd, $^2J_{HH}$ = 16.1, $^2J_{PH}$ = 10.3 Hz, 1H, CH_2), 7.27–7.65 (m, 10 H, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 1.10 ($SnMe_3$), 8.99 (Me of C_5Me_5), 39.77 (d, $^1J_{PC}$ = 34 Hz, CH_2), 98.15 (dd, $^1J_{RhC}/^2J_{PC} \approx 3$ and 8 Hz, C_{ipso} of C_5Me_5), 125.51 (dd, $^1J_{PC}$ = 42 Hz, $^2J_{RhC}$ unresolved, C_{ipso} of PPh_2), 129.00 (d, J_{PC} = 11 Hz), 129.09 (d, J_{PC} = 10 Hz), 131.07 (d, J_{PC} = 9 Hz), 131.32 (d, J_{PC} = 2 Hz), 132.22 (d, J_{PC} = 2 Hz) (5× CH of PPh_2); 132.75 (d, $^1J_{PC}$ = 42 Hz, C_{ipso} of PPh_2), 134.78 (d, J_{PC} = 11 Hz, CH of PPh_2); 178.25 (d, $^2J_{PC}$ = 9 Hz, COO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.7 (d, $^1J_{RhP}$ = 133 Hz). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ 85.7 (s). IR (Nujol): $\tilde{\nu}/cm^{-1}$ 1569 vs, 1139 m, 1108 m, 1028 m, 928 m, 860 m, 789 br m, 758 m, 746 s, 694 s, 553 m, 514 s, 502 m. Anal. Calcd. for $C_{27}H_{36}Cl_2O_2PRhSn$: C, 45.29; H, 5.07%. Found: C, 45.44; H, 4.92%.

3.8. Preparation of dichloro-{(diphenylphosphino)acetic acid-κP}(η⁵-pentamethylcyclopentadienyl)rhodium(I) (7)

A solution of $Ph_2PCH_2CO_2H$ (98 mg, 0.40 mmol) in dichloromethane (2 mL) was added into a solution of $[\{Rh(\eta^5\text{-}C_5Me_5)Cl(\mu\text{-}Cl)\}_2]$ (124 mg, 0.20 mmol) in the same solvent (3 mL). The resulting, clear orange-red solution was stirred for 2 h, filtered, and the filtrate was layered with hexane. The solid deposited after standing for several days was filtered off, washed well with diethyl ether and dried under vacuum to give **7** as an orange-red powdery solid. Yield: 175 mg (79%).

^1H NMR ($(CD_3)_2SO$): δ 1.25 (d, $^3J_{RhH}$ or $^4J_{PH}$ = 3.7 Hz, 15H, C_5Me_5), 3.66 (d, $^2J_{PH}$ = 9.9 Hz, CH_2), 7.49–7.92 (m, 10H, PPh_2). $^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$): δ 8.16 (d, $^2J_{RhC}$ or $^3J_{PC} \approx 1$ Hz, Me of C_5Me_5), 34.05 (d, $^1J_{PC}$ = 22 Hz, CH_2), 98.48 (dd, $^1J_{RhC}/^2J_{PC} \approx 3$ and 7 Hz, C_{ipso} of C_5Me_5), 127.82 (d, J_{PC} = 10 Hz, CH of PPh_2), 127.96 (d, $^1J_{PC}$ = 42 Hz, C_{ipso} of PPh_2), 131.01 (d, J_{PC} = 3 Hz), 133.53 (d, J_{PC} = 10 H) (2× CH of PPh_2); 169.05 (d, $^2J_{PC}$ = 12 Hz, COO). $^{31}P\{^1H\}$ NMR ($(CD_3)_2SO$): δ 28.8 (d, $^1J_{RhP}$ = 244 Hz). IR (Nujol): $\tilde{\nu}/cm^{-1}$ 1690 s, 1271 m, 1136 m, 1105 m, 1098 m, 851 m, 756 m, 746 m, 696 m, 560 m, 513 m, 447 m. Anal. Calcd. for $C_{24}H_{28}Cl_2O_2PRh$: C, 52.10; H, 5.10%. Found: C, 51.88; H, 5.14%.

3.9. The reaction of 1 with [{Ru(η⁶-p-cymene)Cl(μ-Cl)}₂]

$[\{Ru(\eta^6\text{-}1,4\text{-}MeC_6H_4(CHMe_2))Cl(\mu\text{-}Cl)\}_2]$ (61 mg, 0.10 mmol) and **1** (81 mg, 0.20 mmol) were dissolved in dichloromethane (5 mL) and the mixture was stirred for 2 days (precipitate is formed). The mixture was evaporated, the residue was dissolved in chloroform, the solution filtered and layered with hexane. Bright orange-red crystals of chloro-(η⁶-1-methyl-4-(1-methylethyl)benzene){(diphenylphosphino)acetate-κ^2P,O}ruthenium(II)-trimethylstannyl chloride adduct (1/1) (**8**) that formed after standing for several days, were filtered off and dried in air. Yield: 73 mg (51%).

^1H NMR ($CDCl_3$): δ 0.69 (s with tin satellites, $^2J_{119SnH}$ = 61.0, $^2J_{117SnH}$ = 58.3 Hz, 9H, $SnMe_3$), 1.08, 1.22 (2× d, $^3J_{HH}$ = 6.9 Hz, 3H, $CHMe_2$), 1.94 (s, 3H, Me), 2.56 (septuplet, $^3J_{HH}$ = 6.9 Hz, 1H, $CHMe_2$), 3.08 (dd, $^2J_{HH}$ = 16.2, $^2J_{PH}$ = 12.4 Hz, 1H, CH_2), 3.37 (dd, $^2J_{HH}$ = 16.2, $^2J_{PH}$ = 10.5 Hz, 1H, CH_2), 5.12–5.64 (m, 4H, C_6H_4), 7.38–7.72 (m, 10 H, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 0.17 ($SnMe_3$), 18.10, 22.07, 22.19 (Me and $CHMe_2$); 30.49 ($CHMe_2$), 35.77 (d, $^1J_{PC}$ = 34 Hz, CH_2), 84.86 (d, $^2J_{PC}$ = 3 Hz), 85.66 (d, $^2J_{PC}$ = 5 Hz), 86.27 (d, $^2J_{PC}$ = 4 Hz), 89.09 (d, $^2J_{PC}$ = 4 Hz) (CH of C_6H_4); 96.48, 108.76 (d, $^2J_{PC}$ = 2 Hz) (C_{ipso} of C_6H_4); 126.92 (d, $^1J_{PC}$ = 54 Hz, C_{ipso} of PPh_2), 128.83 (d, J_{PC} = 11 Hz), 129.33 (d, J_{PC} = 10 Hz), 130.48 (d, J_{PC} = 9 Hz), 130.95 (d, J_{PC} = 3 Hz), 131.93 (d, J_{PC} = 3 Hz), 134.54 (d, J_{PC} = 11 Hz) (6× CH of PPh_2); 136.54 (d, $^1J_{PC}$ = 47 Hz, C_{ipso} of PPh_2), 179.10 (d, $^2J_{PC}$ = 10 Hz, COO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.5 (s). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ 127.2 (s). IR (Nujol): $\tilde{\nu}/cm^{-1}$ 1639 m, 1580 vs, 1310 m, 1196 m, 1108 s, 930 m, 854 m, 786 m, 749 s, 699 s, 553 m, 521 s, 503 m, 486 m. Anal. Calcd. for $C_{27}H_{35}Cl_2O_2PRuSn$: C, 45.47; H, 4.95%. Found; C, 45.74; H, 4.94%.

3.10. Preparation of dichloro-(η⁶-1-methyl-4-(1- methylethyl)benzene){(diphenylphosphino)aceticacid-κ,P}-ruthenium(II) (9)

A solution of $Ph_2PCH_2CO_2H$ (98 mg, 0.40 mmol) in dichloromethane (2 mL) was added to a solution of $[\{Ru(\eta^6\text{-}1,4\text{-}MeC_6H_4(CHMe_2))Cl(\mu\text{-}Cl)\}_2]$ (122.5 mg, 0.20 mmol) in the same solvent (5 mL). A red precipitate was formed immediately. The mixture was mixed with hexane and, after standing overnight, the precipitate was filtered off, washed with diethyl ether and dried under vacuum to give **9** as an orange-red solid (220 mg, 98%).

^1H NMR ($(CD_3)_2SO$): δ 0.72 (d, $^3J_{HH}$ = 6.9 Hz, 6H, $CHMe_2$), 1.78 (s, 3H, Me), 2.27 (septuplet, $^3J_{HH}$ = 6.9 Hz, 1H, $CHMe_2$), 3.46 (d, $^2J_{PH}$ = 9.8 Hz, 2H, CH_2), 5.26 (d, J = 6.2 Hz, 2H), 5.47 (dd, J = 6.3, 1.5 Hz, 2H) (AA'BB' system of C_6H_4); 7.46–7.90 (m, 10 H, PPh_2). $^{13}C\{^1H\}$ NMR ($(CD_3)_2SO$): δ 16.82 (Me), 20.78 ($CHMe_2$), 29.38 ($CHMe_2$), 30.02 (d, $^1J_{PC}$ = 23 Hz, CH_2), 85.35 (d, $^2J_{PC}$ = 6 Hz), 90.12 (d, $^2J_{PC}$ = 6 Hz) (CH of C_6H_4); 90.37, 106.47 (C_{ipso} of C_6H_4); 127.65 (d, J_{PC} = 10 Hz), 130.52 (d, $^1J_{PC}$ = 2 Hz) (2× CH of PPh_2); 131.76 (d, $^1J_{PC}$ = 45 Hz, CH of PPh_2), 133.12 (d, J_{PC} = 10 Hz, CH of PPh_2), 169.03 (d, $^2J_{PC}$ = 12 Hz, COO). $^{31}P\{^1H\}$ NMR ($(CD_3)_2SO$): δ 25.5 (s). IR (Nujol): $\tilde{\nu}/cm^{-1}$ 1690 vs, 1294 s, 1195 m, 1185 m, 1115 m, 920 m composite, 886 m, 862 w, 842 m, 747 s, 693 m, 583 m, 514 s, 450 m. Anal. Calcd. for $C_{24}H_{27}Cl_2O_2PRu$: C, 52.37; H, 4.94%. Found; C, 52.31; H, 4.86%.

3.11. X-ray crystallography

Single crystals were grown by recrystallization from hexane/dichloromethane: **2 · 3 CH_2Cl_2**: colourless prism, $0.18 \times 0.25 \times 0.43$ mm^3; **3**: colourless plate, $0.03 \times 0.15 \times 0.35$ mm^3; **4**: yellow plate, $0.10 \times 0.20 \times 0.25$ mm^3; **5**: colourless plate, $0.05 \times 0.10 \times 0.20$ mm^3; **6**: orange fragment, $0.13 \times 0.20 \times 0.28$ mm^3; **8**: orange needle, $0.18 \times 0.20 \times 0.85$ mm^3.

The selected specimens were mounted on a glass fibre with was and transfered to a Nonius KappaCCD diffractometer equipped with a Cryostream Cooler

Table 6
Crystallographic data, data collection parameters and structure refinement for **2 · 3CH_2Cl_2**, **3**, **4**, **5**, **6**, and **8**

Compound	**2 · 3CH_2Cl_2**	**3**	**4**
Formula	$C_{31}H_{30}Cl_6O_4P_2Pd$	$C_{28}H_{24}O_4P_2Pt$	$C_{24}H_{18}Cl_4O_6P_2Pd_2$
M (g mol^{-1})	847.59	681.50	818.92
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
T (K)	150(2)	150(2)	150(2)
a (Å)	9.6801(3)	14.342(1)	8.1300(2)
b (Å)	13.2589(5)	9.6896(8)	8.8564(2)
c (Å)	13.8520(4)	18.303(2)	10.1067(2)
α (°)	96.530(1)	90	79.260(1)
β (°)	102.757(2)	90.468(5)	89.723(1)
γ (°)	91.640(2)	90	77.8879(8)
V (Å^3)	1720.1(1)	2543.5(4)	698.60(3)
Z	2	4	1
D_c (g cm^{-3})	1.636	1.780	1.947
θ_{max} (°)	25.07	27.43	27.45
Collected diffractions	28819	11186	11493
Unique/observed[b] diffractions	6100/4914	5794/4928	3183/2946
Data completeness (%)	99.7	99.7	99.4
μ (Mo Kα) (mm^{-1})	1.134	5.675	21.823
T_{min}, T_{max}[a]	0.713–0.831	0.281–0.861	0.776–0.837
No. of parameters	397	316	172
R observed diffractions (%)[c]	4.58	2.37	2.41
R, wR all data (%)[c]	6.45, 11.7	3.36, 5.20	2.76, 5.99
$\Delta\rho$ (e Å^{-3})	0.61, −0.87	2.00, −1.26	0.62, −0.98

Compound	**5**	**6**	**8**
Formula	$C_{26}H_{21}ClO_5P_2Pd$	$C_{27}H_{36}Cl_2O_2PRhSn$	$C_{27}H_{35}Cl_2O_2PRuSn$
M (g mol^{-1})	617.22	716.03	713.18
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1,lc$ (no. 14)	$P2_12_12_1$ (no. 19)[d]	$P2_1/n$ (no. 14)
T (K)	150(2)	150(2)	150(2)
a (Å)	10.6904(4)	9.2556(4)	9.4920(2)
b (Å)	17.088(1)	16.7621(4)	20.9110(3)
c (Å)	16.1850(8)	18.8871(9)	14.7960(3)
α(°)	90	90	90
β (°)	122.328(3)	90	105.2080(9)
γ (°)	90	90	90
V (Å^3)	2498.4(2)	2930.2(2)	2833.97(9)
Z	4	4	4
D_c (g cm^{-3})	1.641	1.623	1.672
θ_{max} (°)	25.99	27.48	27.88
Collected diffractions	21 590	16 612	23 304
Unique/observed[b] diffractions	4854/3179	6574/4660	6742/5941
Data completeness (%)	99.2	99.7	99.2
μ (Mo Kα) (mm^{-1})	1.014	1.674	1.682
T_{min}, T_{max}[a]	–	0.768, 0.812	0.443, 0.796
No. of parameters	280	315	314
R observed diffractions (%)[c]	5.84	4.58	3.42
R, wR all data (%)[c]	10.9, 20.7	7.55, 8.89	4.06, 8.74
$\Delta\rho$ (e Å^{-3})	−0.97, 1.26	−0.86, 0.82	−1.53, 1.15

[a] The range of transmission coefficients.
[b] Diffractions with $I_o > 2\sigma(I_o)$.
[c] $R(F) = \sum||F_o| - s|F_c||/\sum|F_o|$, $wR(F^2) = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum w(F_o^2)^2]^{1/2}$.
[d] Flack's enantiomorph parameter: −0.02(3).

(Oxford Cryosystems). Full-set diffraction data ($\pm h \pm k \pm l$) were collected using graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) and processed with the HKL program package [20] (Table 6). Except for **5**, the data were corrected for absorption anisotropy using either a multiscan routine incorporated in the diffractometer software (**4**; Sortav procedure [21]), an empirical correction (**2** · 3 CH_2Cl_2, **6**, and **8**; Platon [22]) or an analytical correction based on the indexed crystal shape (**3**; Platon, the crystal shape was optimized with Euhedral program [23]). Transmission factor ranges are given in Table 6.

The structures were solved by direct methods (SIR97 [24]) and refined by weighted full-matrix least-squares procedure on F^2 (SHELXL97 [25]). Final geometric calculations were carried out with a recent version of Platon program. All non-hydrogen atoms were refined with anisotropic thermal motion parameters. The hydrogen atoms were included in the calculated positions [C–H bond lengths: 0.93 (aromatic), 0.97 (methylene) and 0.96 (methyl) Å] and assigned $U_{iso}(H) = 1.2\ U_{eq}(C)$ (aromatic and methylene) or 1.5 $U_{eq}(C)$ (methyl). The phenyl ring in the structure of **5** were constrained to regular hexagons with C–C distances of 1.39 Å.

4. Supplementary material

Crystallographic data (CIF files) have been deposited at the Cambridge Crystallographic Data Centre under the deposition numbers CCDC-235449 (**2** · 3CH_2Cl_2), −235447 (**3**), −235448 (**5**), −235450 (**6**), and −235451 (**8**). Copies of the data may be obtained free of charge upon request to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk, www: http://www.ccdc.cam.ac.uk).

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