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Synthesis and characterization of dimeric organochalcogenido-bridged methylpalladium and allylpalladium complexes

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Abstract

Dimeric organochalcogenido-bridged methylpalladium and allylpalladium complexes of the types $[Pd_2Me_2(\mu\text{-}SR')_2(PR_3)_2]$ and $[Pd_2(\mu\text{-}ER')_2(\eta^3\text{-allyl})_2]$ (E = S or Se; R = Et, ^{i}Pr, ^{t}Bu, Ph, $C_6H_4CH_3$-4, C_6H_4Cl-4) have been synthesized and characterized by elemental analyses and nuclear magnetic resonance (^{1}H, ^{13}C and ^{31}P) spectroscopy. The methylpalladium complexes exist either as *cis* isomers or as a mixture of *cis* and *trans* forms, with the former predominating. The allylpalladium complexes exist in *syn* and *anti* forms. The dynamic behaviour in these complexes was studied by variable-temperature ^{1}H NMR spectroscopy. A few reactions of $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-allyl})_2]$ with free thiols were also investigated.

Keywords: Palladium; Allylpalladium; Methylpalladium; Dimeric; Organochalcogenide; NMR

1. Introduction

The role of σ-bonded organopalladium and η^3-allylpalladium compounds in several palladium-catalysed organic syntheses is now well established [1–4]. Organotransition metal thiolate complexes, besides their diverse structural features [5], are believed to be the key intermediates in metal-catalysed organic transformations [6] such as desulfurization of organosulfur compounds and the coupling reaction of organic halides with RS^- to give dialkyl sulfides. Recently, we have reported a number of dimeric organochalcogenide-bridged platinum and palladium complexes [7]. We have found that subtle changes in the nature of the ligand *trans* to the chalcogenide group and the nature of R group on the RE^- moiety control the thermodynamically preferred configuration.

In view of the above and in pursuance of our work on dimeric platinum and palladium complexes, we have now synthesized a series of dimeric methylpalladium and allylpalladium complexes containing bridging organochalcogenide groups. The results of this work are reported herein.

2. Results and discussion

The reaction of $[Pd_2Me_2(\mu\text{-}Cl)_2(PR_3)_2]$ or $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-allyl})_2]$ with $Pb(ER')_2$ (E = S or Se) in acetone readily gave dimeric thiolato/selenato-bridged methylpalladium and allylpalladium complexes.

$$[Pd_2Me_2(\mu\text{-}Cl)_2(PR_3)_2] + Pb(SR')_2 \rightarrow [Pd_2Me_2(\mu\text{-}SR')_2(PR_3)_2] + PbCl_2 \quad (1)$$

$$[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-allyl})_2] + Pb(ER')_2 \rightarrow [Pd_2(\mu\text{-}ER')_2(\eta^3\text{-allyl})_2] + PbCl_2 \quad (2)$$

When the reactions of chloro-bridged allylpalladium complexes with thiols (R'SH) were carried out in the absence or presence of pyridine, an insoluble orange–red product was isolated. Microanalysis of these products showed the formation of $[Pd(SR')_2]_n$ and or $[Pd(Cl)(SR')]_n$ [8], depending on the nature of R' group on sulfur. The IR spectra did not show absorptions attributable to the allyl group. However, the spectra displayed absorptions for ν Pd–S and/or ν Pd–Cl stretchings [9] (see Experimental). The cleavage of the allyl–palladium bond has been reported in a number of reactions [2,9]. For example, in the complex $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-allyl})_2]$, treatment with 5–6 mol of PPh_3 cleaves the palladium–allyl bond [10].

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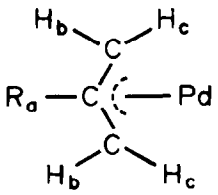
Table 1
$^{31}P\{^1H\}$ and ^1H NMR data for $[Pd_2Me_2(\mu\text{-}SR')_2(PR_3)_2]$ and $[Pd_2(RC_3H_4)_2(\mu\text{-}SR')_2]$ complexes (R = H or Me) [i]

Complex	^{31} (δ, ppm)P	^{1}H NMR data [ii]
$[Pd_2Me_2(\mu\text{-}SPh)_2(PBu_3)_2]$	13.0 CI [iii] 13.6 TI (1:3)	0.04 (d, 3.3 Hz, PdMe, CI); 0.14 (d, 3.0 Hz, PdMe, TI); 0.89 (t, 7 Hz, PCCCMe); 1.28–1.50 (m, PC–CH_2CH_2–); 1.63 (m, PCH_2–); 7.00–7.15 (m), 7.60 (d, 7.6 Hz), 7.81 (d, 7.0 Hz) (Ph)
$[Pd_2Me_2(\mu\text{-}SEt)_2(PMe_2Ph)_2]$	−2.3 CI [iii] −1.6 TI (10:1)	0.27 (d, 4.3 Hz, PdMe, CI); 0.25 (d, PdMe, TI); 1.11(t), 1.32(t), (7.3 Hz each, $SCCH_3$, CI); 1.35 (t, 7.3 Hz, SCMe, TI) 1.63 (d, 9.0 Hz, PMe_2, CI); 1.68 (d, 9.0 Hz, PMe_2, TI); 2.44 (q, 7.3 Hz, SCH_2–, CI); 2.49 (m, SCH_2–, CI + TI); 7.38 (br), 7.71 (br) (Ph)
$[Pd_2Me_2(\mu\text{-}S^iPr)_2(PMe_2Ph)_2]$	−2.6 CI	0.33 (d, 4.9 Hz, PdMe); 1.19 (d), 1.45(d) (each 6.7 Hz, SC-Me_2); 1.61 (d, 9.1 Hz, PMe_2); 3.15 (m) 3.27 (m) (SCH <); 7.35 (br), 7.72 (br) (Ph)
$[Pd_2Me_2(\mu\text{-}S^tBu)_2(PMe_2Ph)_2]$	−2.0 CI	0.42 (d, 5.2 Hz, PdMe); 1.38(s), 1.51 (s) ($SCMe_3$); 1.64 (d, 9.1 Hz, PMe_2) 7.36 (m), 7.72 (m) (Ph)
$[Pd_2Me_2(\mu\text{-}SPh)_2(PMe_2Ph)_2]$	0.6 TI −0.9 CI [iii] (1:3)	0.15 (d, 4.2 Hz, PdMe, CI); 0.18 (d, 4.4 Hz, PdMe, TI); 1.39 (d, 9.1 Hz, PMe_2, TI); 1.59 (d, 8.9 Hz, PMe_2, CI); 6.98–7.71 (m, Ph)
$[Pd_2Me_2(\mu\text{-}Stol)_2(PMe_2Ph)_2]$	0.3 TI −1.2 CI [iii] (1:3)	0.15 (d, 4.3 Hz, PdMe, CI); 0.17 (d, 4.3 Hz, PdMe, TI); 1.39 (d, 9.0 Hz, PMe_2, TI); 1.59 (d, 9.1 Hz, PMe_2, CI); 2.23 (s), 2.26(s) (tol-Me, CI); 2.25(s, tol-Me, TI); 6.79 (d), 6.96 (d), 7.44 (d), 7.48 (d) (7.7 Hz each, C_6H_4, CI); 6.48 (d), 7.58 (d) (7.7 Hz each, C_6H_4, TI); 7.36 (br), 7.66 (br) (Ph)
$[Pd_2Me_2(\mu\text{-}S^iPr)_2(PMePh_2)_2]$	15.8 TI 15.6 CI [iii] (1:4)	0.23 (d, 5.2 Hz, PdMe, TI); 0.27 (d, 4.7 Hz, PdMe, CI); 1.07 (d), 1.48 (d) (6.8 Hz each, $SCMe_2$, CI); 1.37 (d, 6.8 Hz, $SCMe_2$, TI); 1.88 (d, 8.8 Hz, PMe, CI); 1.99 (d, 9.0 Hz, PMe, TI); 2.99–3.36 (m, SCH, CI + TI); 7.27–7.69 (m, Ph).
$[Pd_2Me_2(\mu\text{-}SEt)_2PPh_3]_2]$	9.0 CI [iii] 8.5 TI (1:4)	0.24 (d, 4.2 Hz, PdMe, TI); 0.26 (d, 4.5 Hz, PdMe, CI); 1.20 (t), 1.22(t) (7.1 Hz, each, SC-Me, CI); 1.68 (t, 7.1 Hz, SC-Me, TI); 2.26 (q), 2.32 (dq) (SCH_2, CI); 2.62 (m, SCH_2, TI); 7.36 (m), 7.66 (m) (Ph)
$[Pd_2Me_2(\mu\text{-}S^tBu)(PPh_3)_2]$ [iv]		0.40 (d, TI); 0.55 (d, 5.4 Hz, CI); 1.36 (s), 1.41 (s), ($SCMe_3$, CI); 1.60 (s, $SCMe_3$, TI); 7.27–7.69 (Ph)

Table 1(continued)

Complex	^{31} (δ, ppm)P	^{1}H NMR data [ii]
$[Pd_2(\mu\text{-}S^tBu)_2(\eta^3\text{-}C_3H_5)_2]$		1.48 (s, $SCMe_3$); 3.15 (br, *anti* CH [c]); 4.27 (br, *syn* CH [b]); 5.48 (br, CH [a])
$[Pd_2(\mu\text{-}SPh)_2(\eta\text{-}^3C_3H_5)_2]$		2.91 (d, 12.6 Hz, *anti* CH [c]); 3.59 (br, *syn* CH [b]); 5.34 (m, CH [a]); 7.13 (m), 7.63(br) (Ph)
$[Pd_2(\mu\text{-}SePh)_2(\eta^3\text{-}C_3H_5)_2]$		2.93 (d, 12.3 Hz, *anti* CH [c]); 3.79 (br, *syn* CH [b]); 5.27 (br, CH [a]); 7.10 (br), 7.70 (br) (Ph)
$[Pd_2(\mu\text{-}Stol)_2(\eta^3\text{-}C_3H_5)_2]$		2.28 (s, tol-Me); 2.90 (d, 13 Hz, *anti* CH [c]); 3.60 (br, *syn* CH [b]); 5.40 (br, CH [a]); 6.93 (d), 7.53 (d) (8 Hz each, C_6H_4)
$[Pd_2(\mu\text{-}SC_6H_4Cl\text{-}4)_2(\eta^3\text{-}C_3H_5)_2]$		2.99 (d, 12.5 Hz, *anti* CH [c]); 3.77 (br, *syn* CH [b]) 5.40 (sept, 6.7 Hz, CH [a]); 7.10 (d), 7.56 (d) (8.5 Hz each, C_6H_4)
$[Pd_2(\mu\text{-}S^tBu)_2(\eta^3\text{-}C_4H_7)_2]$		1.41 (s, S^tBu); 1.88 (s), 1.92 (s) (Me); 2.76 (s), 2.73(s) (*anti* CH [c]); 3.81 (s, *syn* CH [b]).
$[Pd_2(\mu\text{-}SPh)_2(\eta^3\text{-}C_4H_7)_2]$		1.95 (s), 1.99 (s) (Me); 2.79 (s), 2.82 (s) (*anti* CH [c]); 3.32 (s), 3.34 (s) (*syn* CH [b]); 7.05–7.14 (m), 7.65–7.73 (m) (Ph)
$[Pd_2(\mu\text{-}SePh)_2(\eta^3\text{-}C_4H_7)_2]$		1.90 (br, Me); 2.83 (br, *anti* CH [c]); 3.50 (br, *syn* CH [b]); 7.11 (br), 7.75 (br) (Ph)
$[Pd_2(\mu\text{-}Stol)_2(\eta^3\text{-}C_4H_7)_2]$		1.96 (br, Me); 2.30 (s, tol-Me); 2.80 (br, *anti* CH [c]); 3.31 (br, *syn* CH [b]); 6.93 (d), 7.53 (d) (7.8 Hz each, C_6H_4)
$[Pd_2(\mu\text{-}SC_6H_4Cl)_2(\eta^3\text{-}C_4H_7)_2]$		2.02 (s, Me); 2.88(br, *anti* CH [c]); 3.54 (br, *syn* CH [b]); 7.10 (d), 7.61 (d) 8.3 Hz each) (Ph)

[i] CI = *cis* isomer; TI = *trans* isomer.
[ii] s = Singlet; d = doublet; t = triplet; q = quartet; dq = doublet of quartets; m = multiplet; br = broad.

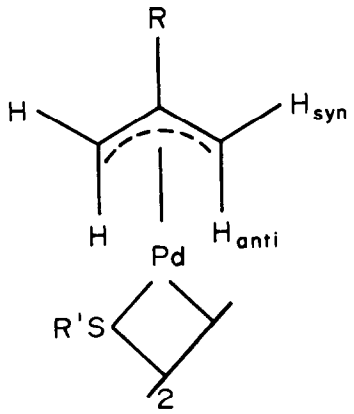


[iii] More abundant isomer.
[iv] Recorded at 200 MHz.

Dimeric thiolato/selenato-bridged methylpalladium and allylpalladium complexes are yellow–orange crystalline solids. Methylpalladium complexes are stable under ambient conditions for several months, whereas the allylpalladium complexes darken and eventually turn black with time.

2.1. NMR spectra of methylpalladium complexes

Thiolato-bridged methylpalladium complexes were formed exclusively in the *cis* form or as a mixture of *cis* and *trans* isomers, with the *cis* form predominating. Thus, each isomer gave a single resonance in the ^{31}P NMR spectra (Table 1). The ^{1}H NMR spectra displayed separate doublets attributable to Pd–Me protons for *cis* and *trans* isomers. It may be noted that the chloro-bridged complexes are in a dynamic equilibrium [11,12] whereas the pyrazolato-bridged complexes $[Pd_2Me_2(\mu\text{-}pz)_2(PR_3)_2]$ exist exclusively in the *trans* form [11]. The palladium methyl resonances in the thiolato-bridged complexes are more shielded than those of the corresponding chloro-bridged precursors [11]. The *cis* isomer exhibited two sets of resonances for SR′ protons; one was attributed to the SR′ group *trans* to phosphine and the other to the SR′ group *trans* to the terminal methyl group. The *trans* isomer, as expected, displayed a sin-



(I)

gle set of resonances attributable to SR′ protons. Each isomer of the complexes containing dimethylphenylphosphine showed a single doublet for PMe_2 protons.

2.2. NMR spectra of allylpalladium complexes

^1H NMR spectra of thiolato/selenato-bridged allylpalladium complexes showed the expected integration and peak multiplicities (Table 1). The ER′ (E = S or Se) protons showed a single set of resonances. The *anti* protons (**I**) (allyl group) (H-2 and H-3) of the terminal CH_2 group are most shielded ($\delta \approx 2.9$ ppm in C_3H_5 and 2.28 ± 0.06 ppm in C_4H_7 complexes) and appear to be little influenced by the nature of the R′ group on the bridging ER′ moiety. The *syn* proton (H-1 and H-4) resonances of the terminal CH_2 group are markedly influenced by the nature of the R′ group on ER′ (δ 3.59–3.79 ppm in C_3H_5 and 3.56 ± 0.25 ppm in C_4H_7 complexes).

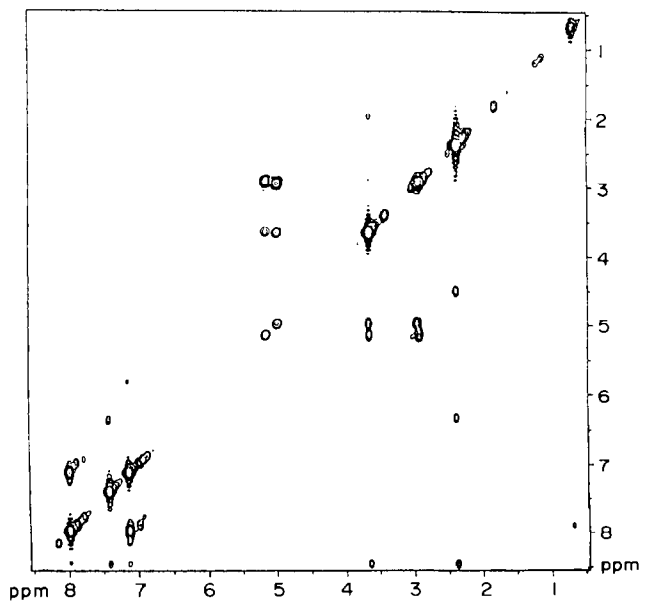


Fig. 1. COSY NMR spectrum of $[Pd_2(\mu\text{-Stol})_2(\eta^3\text{-}C_3H_5)_2]$ in $CDCl_3$ at 500 MHz.

The NMR spectra of allyl complexes exhibited a doublet for *anti* protons due to coupling with the central carbon proton. However, *syn* protons gave a broad singlet. The central carbon proton (H-5) resonance appeared as a broad singlet or as a multiplet at the lowest field. Various proton–proton interactions can be clearly seen in the 2D-COSY NMR spectrum of $[Pd_2(\mu\text{-Stol})_2(\eta^3\text{-}C_3H_5)_2]$ (Fig. 1). The CH-5 proton resonance showed correlation with both *syn* and *anti* protons; however, *syn* and *anti* interactions, i.e. geminal couplings usually < 1.0 Hz, could hardly be detected.

The NMR spectra of the methylallyl complexes displayed either two closely spaced singlets or broad singlets each for the methyl group *syn* and *anti* protons of terminal CH_2 groups. For the complexes $[Pd_2(\mu\text{-}S^tBu)_2(\eta^3\text{-}C_4H_7)_2]$ singlets for methyl, *syn* and *anti* protons (δ 1.58, 2.54 and 3.61 ppm, respectively) have been reported at 100 MHz [13]. The spectrum at 500 MHz reported in this paper gave two separate resonances each for the methyl group and *anti* protons.

The dimeric allylpalladium complexes $[Pd_2(\mu\text{-}X)_2(\eta^3\text{-allyl})_2]$ (X = single donor atom ligand) are expected to exist in two geometrical isomers, i.e. *syn* (**II**) and *anti* (**III**) depending on the arrangements of allyl groups with respect to each other. In the solid state, the chloro-bridged allyl complexes usually exist in an *anti* configuration [14]; however, a *syn* structure is reported in the case of $[Pd_2(\mu\text{-Cl})_2(\eta^3\text{-Me(CH)}_3\text{Me})_2]$ [15]. Only one set of resonances are observed in the NMR spectra in non-coordinating solvents at various temperatures [9].

The NMR spectra of the thiolato-bridged complexes reported here indicate that both the *syn* (**II**) and *anti* (**III**) isomers exist in solution. In some cases isomerization is slow on the NMR time-scale to give separate resonances for two isomeric forms, whereas in others the process is relatively rapid, resulting in broad signals at room temperature. In order to ascertain the dynamic behaviour, a variable-temperature ^1H NMR spectrum of $[Pd_2(\mu\text{-SPh})_2(\eta^3\text{-}C_3H_5)_2]$ was recorded at 300 MHz. Two separate resonances for the *syn* protons (H-1 and H-4) of the terminal CH_2 group (two doublets) and the central carbon proton (two multiplets) were observed at 0°C (Fig. 2). The spectrum did not show any noticeable change on further lowering of the temperature to −45°C. The chemical shift for the *anti* protons of the terminal CH_2 group appears to degenerate as only one doublet was observed at all temperatures.

3. Experimental details

The complexes $[Pd_2Me_2(\mu\text{-}Cl)_2(PR_3)_2]$ [11], $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$ [16], $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_4H_7)_2]$ [17] and $Pb(ER')_2$ (E = S or Se) were prepared by standard methods. All preparations were carried out in a nitrogen atmosphere. Elemental analyses were carried out by the Analytical Chemistry Division of this research centre.

^1H and $^{31}P\{^1H\}$ NMR spectra were recorded in $CDCl_3$ solutions on a Bruker-AMX 500 spectrometer. Chemical shifts are reported in ppm from internal $SiMe_4$ for ^1H and 85% H_3PO_4 for ^{31}P. $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC-200 spectrometer operating at 50 MHz. The chemical shifts are reported in ppm from internal chloroform peak at 77.0 ppm. The 2D-COSY NMR spectrum was recorded on a Bruker AMX-500 spectrometer. Variable-temperature ^1H NMR spectra were recorded on a Varian XLR-300 spectrometer. IR spectra were recorded as Nujol mulls on a Perkin-Elmer Model 577 spectrometer. Melting points were determined in capillary tubes in the open and were uncorrected.

3.1. Preparation of $[Pd_2Me_2(\mu\text{-}S^tBu)_2(PMe_2Ph)_2]$

To a dry acetone solution of $[Pd_2Me_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ (108 mg, 0.18 mmol) was added solid $Pb(S^tBu)_2$ (78 mg, 0.20 mmol) under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 3 h and the solvent removed under reduced pressure. The residue was extracted with benzene and filtered. The filtrate, on concentration in vacuo, gave a yellow solid, which was recrystallized from benzene–hexane (yield 62 mg, 48%). Other thiolato-bridged methylpalladium complexes were prepared similarly. Pertinent data are summarized in Table 2.

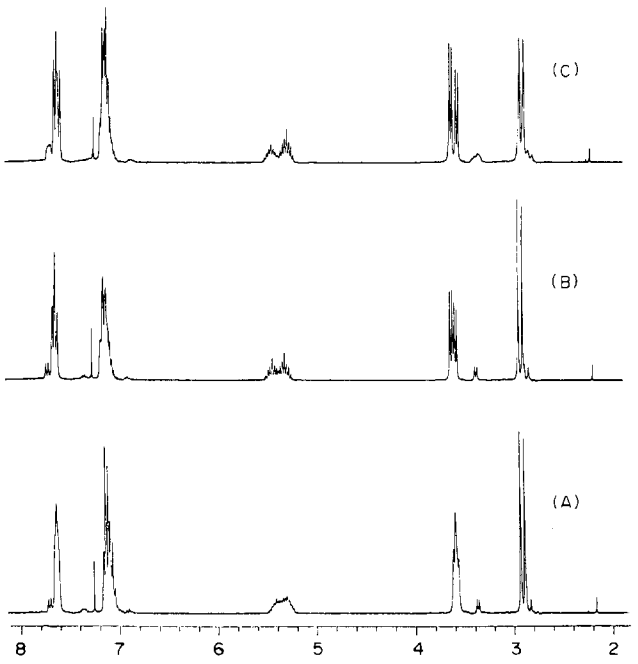


Fig. 2. Variable-temperature ^1H NMR spectrum of $[Pd_2(\mu\text{-}SPh)_2(\eta^3\text{-}C_3H_5)_2]$ in $CDCl_3$ at (A) 25, (B) 0 and (C) −45°C.

3.2. Preparation of $[Pd_2(\mu\text{-}SPh)_2(\eta^3\text{-}C_3H_5)_2]$

Solid $Pb(SPh)_2$ (122 mg, 0.29 mmol) was added to a stirred, dry acetone solution (20 ml) of $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$ (105 mg, 0.29 mmol) at 5°C under a nitrogen atmosphere. The reaction mixture was stirred for 40 min at 0–5°C, during which lead chloride precipitated. The solvent was stripped off under vacuum and the residue

Table 2
Physical and analytical data for $[Pd_2Me_2(\mu\text{-}SR')_2(PR_3)_2]$ and $[Pd_2(RC_3H_4)_2(\mu\text{-}SR')_2]$ complexes (R = H or Me)

Complex	Recrystallization solvent	Yield (%)	M.p. (°C)	Analysis: found (calcd.) (%)	
				C	H
$[Pd_2Me_2(\mu\text{-}SPh)_2(PBu_3)_2]$	Pentane	51	60	52.6 (52.7)	9.2 (8.1)
$[Pd_2Me_2(\mu\text{-}SEt)_2(PMe_2Ph)_2]$	C_6H_6–pentane	49	130–132 (d)	40.9 (41.2)	5.8 (6.0)
$[Pd_2Me_2(\mu\text{-}S^iPr)_2(PMe_2Ph)_2]$	CH_2Cl_2–hexane	77	110	42.8 (43.0)	6.2 (6.3)
$[Pd_2Me_2(\mu\text{-}S^tBu)_2(PMe_2Ph)_2]$	C_6H_6–hexane	48	131	44.7 (44.8)	6.4 (6.6)
$[Pd_2Me_2(\mu\text{-}SPh)_2(PMe_2Ph)_2]$	CH_2Cl_2–MeOH	60	126	48.2 (48.8)	5.1 (5.2)
$[Pd_2Me_2(\mu\text{-}Stol)_2(PMe_2Ph)_2]$	CH_2Cl_2–hexane	53	150–155 (d)	49.8 (50.2)	4.7 (5.5)
$[Pd_2Me_2(\mu\text{-}S^iPr)_2(PMePh_2)_2]$	C_6H_6–hexane	50	105–108	50.5 (51.5)	5.2 (5.8)
$[Pd_2Me_2(\mu\text{-}SEt)_2(PPh_3)_2]$	CH_2Cl_2–hexane	63	135–140 (d)	56.0 (56.7)	5.4 (5.2)
$[Pd_2Me_2(\mu\text{-}S^tBu)_2(PPh_3)_2]$	CH_2Cl_2–hexane	43	115(d)	59.9 (58.4)	5.3 (5.7)
$[Pd_2(\mu\text{-}S^tBu)_2(\eta^3\text{-}C_3H_5)_2]$	CH_2Cl_2–hexane	74	103–107 (d)	35.8 (35.5)	6.0 (6.0)
$[Pd_2(\mu\text{-}SPh)_2(\eta^3\text{-}C_3H_5)_2]$	Acetone–MeOH	59	118–120 (d)	42.0 (42.1)	3.9 (3.9)
$[Pd_2(\mu\text{-}SePh)_2(\eta^3\text{-}C_3H_5)_2]$	C_6H_6–hexane	64	89–90 (d)	35.7 (35.6)	3.3 (3.3)
$[Pd_2(\mu\text{-}Stol)_2(\eta^3\text{-}C_3H_5)_2]$	C_6H_6–hexane	74	128–132 (d)	44.3 (44.4)	4.3 (4.5)
$[Pd_2(\mu\text{-}SC_6H_4Cl\text{-}4)_2(\eta^3\text{-}C_3H_5)_2]$	Acetone–hexane	76	125–127 (d)	37.4 (37.1)	3.1 (3.1)
$[Pd_2(\mu\text{-}S^tBu)_2(\eta^3\text{-}C_4H_7)_2]$	CH_2Cl_2–hexane	65	135–138 (d)	38.2 (38.3)	6.1 (6.4)
$[Pd_2(\mu\text{-}SPh)_2(\eta^3\text{-}C_4H_7)_2]$	Acetone–hexane	79	116	44.2 (44.4)	4.4 (4.5)
$[Pd_2(\mu\text{-}SePh)_2(\eta^3\text{-}C_4H_7)_2]$	C_6H_6–hexane	68	110 (d)	38.0 (37.8)	3.8 (3.8)
$[Pd_2(\mu\text{-}Stol)_2(\eta^3\text{-}C_4H_7)_2]$	Acetone–hexane	69	135–140 (d)	46.2 (46.4)	5.1 (5.0)
$[Pd_2(\mu\text{-}SC_6H_4Cl\text{-}4)_2(\eta^3\text{-}C_4H_7)_2]$	Acetone–hexane	67	150–155 (d)	39.1 (39.4)	3.4 (3.6)

was extracted with acetone (3 × 5 ml) and filtered. The volume of the filterate was reduced to 5 ml and methanol was added. The resulting solution on slow evaporation gave yellow crystals of the title complex (yield 87 mg, 59%). Other allylpalladium complexes were prepared in a similar manner.

^{13}C NMR data

$[Pd_2(\mu\text{-}S^tBu)_2(\eta^3\text{-}C_4H_7)_2]$, δ 23.6 (Me of allyl), 34.9 (SC-Me_3), 41.8 (SC <), 59.8 (terminal CH_2 of allyl), 124.7 ppm (central carbon of allyl).

$[Pd_2(\mu\text{-Stol})_2(\eta^3\text{-}C_4H_7)_2]$, δ 20.9 (tol-Me), 23.6 (Me of allyl), 64.2 (terminal CH_2 of allyl), 128.2 (C-3,5 of Stol), 132.7 (C-2,6 of Stol), 133.7 (central carbon of allyl), 134.4 (C-4 Stol), 138.9 ppm (C-1 of Stol).

3.3. Reaction between $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$ and ^tBuSH

To a chloroform solution of $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$ (167 mg, 0.456 mmol) was added tert-butanethiol (0.1 ml, 0.914 mmol) and the mixture was stirred at room temperature for 3 h. During the reaction, an orange–red solid precipitated, which was filtered, washed with hexane and dried in vacuo (yield 120 mg). C, 19.3; H, 3.6; calculated for $[PdCl(S^tBu)]_n$, C, 20.8; H, 3.9%. IR in Nujol: 270s (ν Pd–Cl), 300sh, 365m (ν Pd–S). Similarly, reactions with EtSH (C, 16.6; H, 2.4; calculated for $[Pd(SEt)_2]_n$, C, 21.0; H, 4.4%; $[PdCl(SEt)]_n$, C, 11.8; H, 2.5%), ^{i}PrSH (C, 19.2; H, 3.7%; calculated for $[Pd(S^iPr)_2]_n$, C, 28.1, H, 5.5%; $[PdCl(S^iPr)]_n$, C, 16.6; H, 3.2%) and PhSH (C, 41.4; H, 3.7%; calculated for $Pd(SPh)_2$, C, 44.4; H, 3.1%; $[PdCl(SPh)]_n$, C, 28.7; H, 2.0%) (IR: 355w ν Pd–S) were carried out.

3.4. Reaction between $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$ and EtSH in the presence of pyridine

To a benzene solution of $[Pd_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_2]$ (194 mg, 0.53 mmol), pyridine (0.1 ml) was added with stirring, which was continued for 10 min. To the resulting pale-yellow solution, ethanethiol (0.16 ml, 2.2 mmol) was added and the mixture was stirred at room temperature for 3 h, during which an orange–yellow product precipitated. This was filtered, washed with water until the washings were free from chloride ion (from pyridine hydrochloride) and then with acetone and diethyl ether and air dried (yield 196 mg); C, 20.5; H, 4.0%; IR: 365w, 315vw, 285vw. Similarly, reactions with PhSH (C, 41.8, H, 3.0; IR: 355m) and ^{t}BuSH (C, 18.2; H, 3.4%) were carried out.

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