Cyclopalladated compounds derived from a [C,N,S] terdentate ligand: synthesis, characterization and reactivity. Crystal and molecular structures of $[Pd\{2\text{-}ClC_6H_3C(H)=NCH_2CH_2SMe\}(Cl)]$ and $[\{Pd[2\text{-}ClC_6H_3C(H)=NCH_2CH_2SMe]\}_2\{\mu\text{-}Ph_2P(CH_2)_4PPh_2\}]\text{-}[CF_3SO_3]_2$

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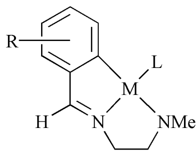
Treatment of the Schiff base $2\text{-}ClC_6H_4C(H)=NCH_2CH_2SMe$, **1**, with palladium(II) acetate in dry toluene gave the mononuclear cyclometallated complex $[Pd\{2\text{-}ClC_6H_3C(H)=NCH_2CH_2SMe\}(O_2CMe)]$, **2**. Reaction of **2** with aqueous sodium chloride gave $[Pd\{2\text{-}ClC_6H_3C(H)=NCH_2CH_2SMe\}(Cl)]$, **3**, after a metathesis reaction. The X-ray crystal structure of **3** was determined and shows that the palladium atom is bonded to four different donor atoms: C, N, S and Cl. Treatment of **3** with triphenylphosphine in acetone gave the mononuclear cyclometallated complex $[Pd\{2\text{-}ClC_6H_3C(H)=NCH_2CH_2SMe\}(Cl)(PPh_3)]$ with cleavage of the Pd–S bond. However, treatment of **3** with silver triflate and triphenylphosphine gave $[Pd\{2\text{-}ClC_6H_3C(H)=NCH_2CH_2SMe\}(PPh_3)][CF_3SO_3]$, **10**, in which the Pd–S bond is retained. Reaction of **3** with the diphosphines dppm, dppb or dppf in a 2 : 1 molar ratio gave the dinuclear cyclometallated complexes $[\{Pd[2\text{-}ClC_6H_3C(H)=NCH_2CH_2SMe](Cl)\}_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}]$, ($n=1$, **5**; $n=4$, **6**), and $[\{Pd[2\text{-}ClC_6H_3C(H)=NCH_2CH_2SMe](Cl)\}_2(\mu\text{-}Ph_2PC_5H_4FeC_5H_4PPh_2)]$, **7**. Treatment of **3** with dppb in a 2 : 1 molar ratio and $AgCF_3SO_3$ gave the dinuclear cyclometallated complex $[\{Pd[2\text{-}ClC_6H_3C(H)=NCH_2CH_2SMe]\}_2\{\mu\text{-}Ph_2P(CH_2)_4PPh_2\}][CF_3SO_3]_2$, **11**, which was characterized by X-ray crystal structure analysis. Reaction of **3** with dppe in a 1 : 1 molar ratio and sodium perchlorate gave the mononuclear complex $[Pd\{2\text{-}ClC_6H_3C(H)=NCH_2CH_2SMe\}\{Ph_2P(CH_2)_2PPh_2\text{-}P,P\}][ClO_4]$, **8**. Treatment of **3** with bis(2-diphenylphosphinoethyl)phenylphosphine in a 1 : 1 molar ratio, followed by treatment with sodium perchlorate gave $[Pd\{2\text{-}ClC_6H_3C(H)=NCH_2CH_2SMe\}\{(Ph_2PCH_2CH_2)_2PPh\text{-}P,P,P\}][ClO_4]$, **9**, in which the triphosphine is bonded to the palladium atom through the three phosphorus atoms.

Introduction

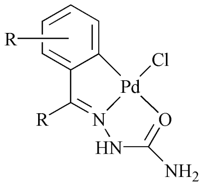
The study of cyclometallated compounds has attracted much attention over the last three decades.[1–5] They have numerous applications in organic and organometallic synthesis,[6] insertion reactions,[7] the synthesis of new metal mesogenic compounds[8] and biologically active compounds[9,10] and as catalytic materials.[11] By far the most widely studied examples of cyclometallated complexes are five-membered palladacycles with nitrogen donor atoms. Among these, cyclometallated complexes derived from potentially terdentate [C,N,N] and [C,N,S] ligands have been described.[12–23] In previous work, we have shown that potentially terdentate ligands, such as Schiff bases **I**,[24–27] semicarbazones **II**[28,29] and thiosemicarbazones **III**,[30,31] undergo facile metallation with palladium(II), palladium(0) and platinum(II) to give compounds with two five-membered fused rings at the metal centre. The Schiff base and semicarbazone derivatives are monomeric species but the complexes derived from thiosemicarbazones present a tetranuclear structure.

As part of our studies on the synthesis and reactivity of cyclometallated complexes derived from multidentate

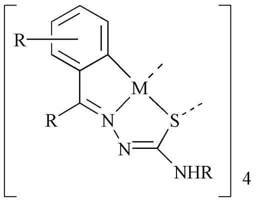


L = Cl, Me
M = Pd, Pt

I



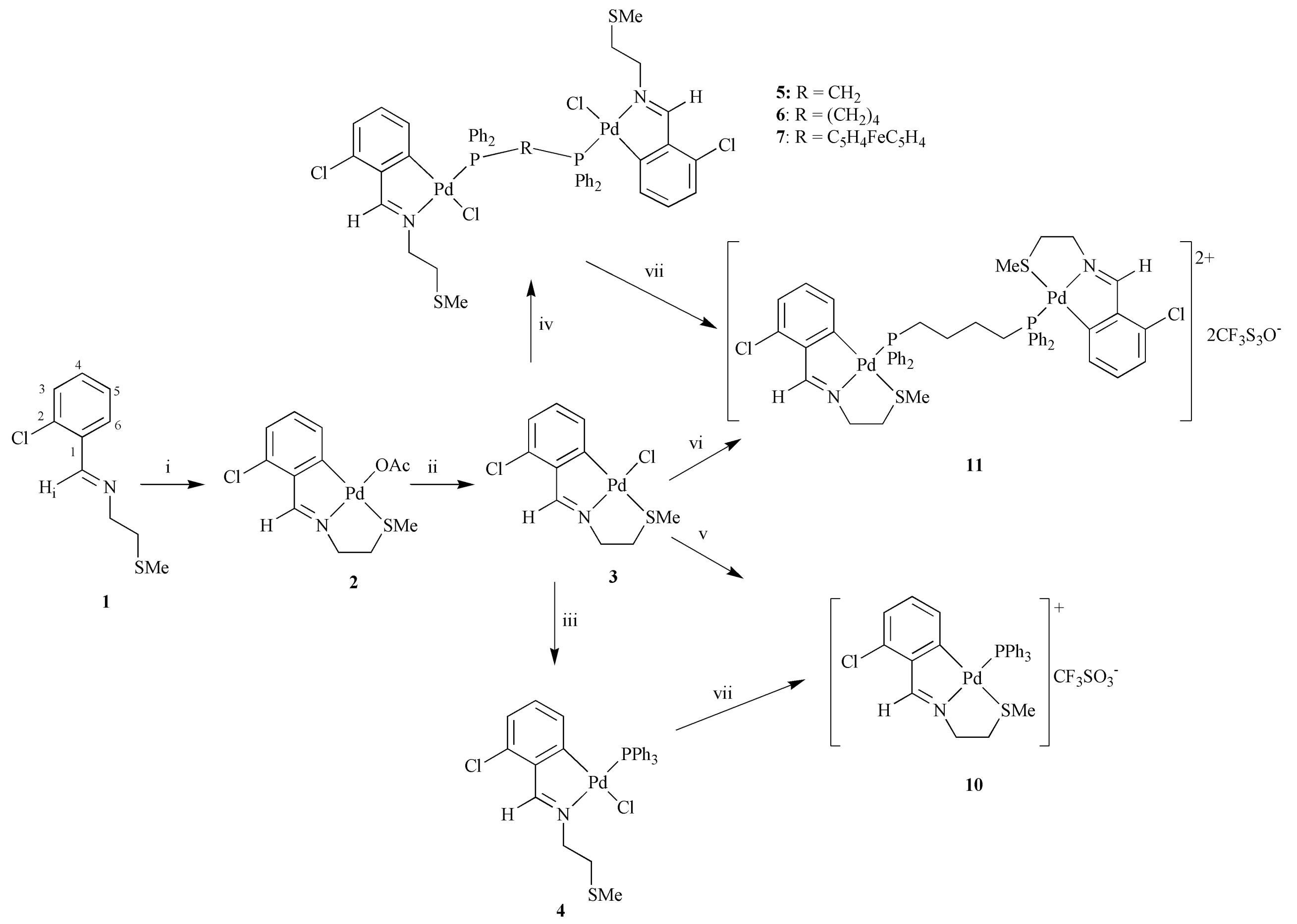
II



M = Pd, Pt

III

DOI: 10.1039/b106511d

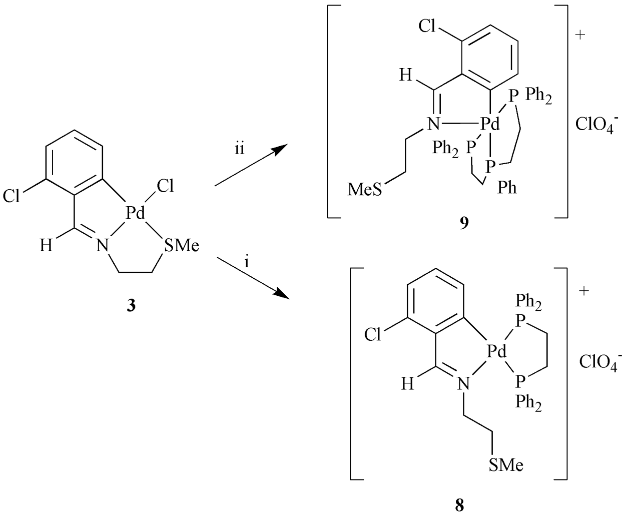


Scheme 1 (i) $Pd(AcO)_2$, (toluene); (ii) NaCl (acetone–water); (iii) PPh_3 (acetone); (iv) dppm, dppb or dppf (acetone, 2 : 1 molar ratio); (v) $AgCF_3SO_3$, PPh_3 (acetone); (vi) $AgCF_3SO_3$, dppb (acetone, 2 : 1 molar ratio); (vii) $AgCF_3SO_3$ (acetone).

ligands, we synthesized the potentially [C,N,S] Schiff base $2\text{-}ClC_6H_4C(H){=}NCH_2CH_2SMe$, **1**, where metallation may occur by activation of a C–H bond or by oxidative addition across the C–Cl bond, in order to study its reactivity and also the behavior of the subsequent metal compounds derived from **1**. Therefore, in the present work, we report the reaction of **1** with the metallating reagents $Pd(AcO)_2$, $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone) and $Li_2[PdCl_4]$. In the resulting complexes, the ligand behaves as [C, N, S] terdentate yielding the monomeric species **2** and **3**, in contrast with the tetrameric structure observed for the [C, N,S] thiosemicarbazone cyclometallated derivatives. Moreover, the reactivity of **3** with tertiary phosphines such as triphenylphosphine, bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), 1,4-bis(diphenylphosphino)butane (dppb), 1,1′-bis(diphenylphosphino)ferrocene (dppf) and the triphosphine bis(2-diphenylphosphinoethyl)phenylphosphine (triphos), may be regulated to give compounds where the Pd–S bond may be retained or cleaved, which is achieved by the use of a chloride removing agent, usually a silver(I) salt, in the reaction media. In the former case, the coordination vacancy is occupied by the phosphine, and in the latter, opening of the coordination ring occurs. Such a reactivity pattern differs from that observed for the related thiosemicarbazones.

Results and discussion

For the convenience of the reader, the compounds and reactions are shown in Schemes 1 and 2. The compounds described in this paper were characterised by elemental analysis (C, H, N), IR spectroscopy (data in the Experimental section), ^1H, $^{31}P\text{-}\{^1H\}$ (see Table 1) and, in part, $^{13}C\text{-}\{^1H\}$ NMR spectroscopy, and FAB mass spectrometry (see Experimental section).



Scheme 2 (i) dppe, $NaClO_4$ (acetone–water, 1 : 1 molar ratio); (ii) triphos, $NaClO_4$ (acetone, 1 : 1 molar ratio).

Treatment of the Schiff base $2\text{-}ClC_6H_4C(H){=}NCH_2CH_2SMe$, **1**, with palladium(II) acetate in dry toluene gave the mononuclear cyclometallated complex $[Pd\{2\text{-}ClC_6H_3C(H){=}NCH_2CH_2SMe\}(O_2CMe)]$, **2**, in 21% yield, which was fully characterized. The ^1H NMR spectrum shows a singlet resonance at δ 7.93, assigned to the HC=N proton,

Table 1 ^{31}P-{^{1}H}^{a} and ^{1}H NMR$^{b–d}$ data

	^{31}P	Aromatic	Others
1		7.70 [m, 3H, H^3, H^4, H^5] 8.02[dd, 1H, H^6 6.9^f, 2.3^e]	8.73 [t, 1H, H$_i$ 1.5^e] 3.88 [2H, (CH$_2$)^g 13.6^h] 2.85 [2H, (CH$_2$)^i] 2.16 [s, 3H, Me]
2		7.25 [d, 1H, H^5 7.8^f] 7.15 [t, 1H, H^4 7.8^f, 7.8^f] 7.00 [dd, 1H, H^3 7.8^f 1.0^e]	8.34 [s, 1H, H$_i$] 3.94 [2H, (CH$_2$)^g 12.2^h] 2.94 [2H, (CH$_2$)^i] 2.64 [s, 3H, Me] 2.11 [s, 3H, OC(Me)O]
3		7.64 [dd, 1H, H^5 7.8^f, 1.0^e] 7.11 [t, 1H, H^4 7.8^f] 6.96 [dd, 1H, H^3 7.8^f, 1.0^e]	8.23 [t, 1H, H$_i$ 1.7^e] 4.02 [2H, (CH$_2$)^g 12.2^h] 3.11 [2H, (CH$_2$)^i] 2.57 [s, 3H, Me]
4	42.3s	6.87 [d, 1H, H^3 7.8^f] 6.49 [t, 1H, H^4 7.8^f] 6.28 [d, 1H, H^5 7.8^f]	8.64 [s, 1H, H$_i$] 4.19 [2H, (CH$_2$)^g 13.2^h] 3.10 [2H, (CH$_2$)^i] 2.18 [s, 3H, Me]
5^i	30.1s	6.79 [d, 1H, H^3 7.6^f] 6.43 [t, 1H, H^4 7.6^f] 5.90 [m, 1H, H^5]	8.44 [s, 1H, H$_i$] 4.05 [2H, (CH$_2$)^g] 3.04 [2H, (CH$_2$)^i 11.2^h] 2.19 [s, 3H, Me]
6	34.0s	6.83 [d, 1H, H^3 7.8^f] 6.42 [t, 1H, H^4 7.8^f] 6.27 [dd, 1H, H^5 7.8^f, 5.4^k]	8.49 [d, 1H, H$_i$ 7.8^k] 4.12 [2H, (CH$_2$)^g] 3.08 [2H, (CH$_2$)^i 12.6^h] 2.20 [s, 3H, Me]
7^j	31.1s	6.88 [d, 1H, H^3 7.3^f] 6.51 [br, 1H, H^4] 6.21 [m, 1H, H^5]	8.57 [br, 1H, H$_i$] 4.16 [2H, (CH$_2$)^g] 3.07 [2H, (CH$_2$)^i] 2.17 [s, 3H, Me]
8	62.5 [d, 27.1^m] 44.6d	6.99 [d, 1H, H^3 7.8^f] 6.73 [dt, 1H, H^4 7.8^f, 3.0^k] 6.55 [q, 1H, H^5 7.8^f, 7.8^k]	8.69 [d, 1H, H$_i$ 6.8^k] 3.51 [2H, (CH$_2$)^g] 2.65 [2H, (CH$_2$)^i] 1.89 [s, 3H, Me]
9	90.1 [t, 26.3^m] 45.4d	6.86 [d, 1H, H^3 7.8^f] 6.38 [dt, 1H, H^4 7.8^f, 2.3^k] 6.84 [t, 1H, H^5 7.8^f, 7.8^k]	8.35 [s, 1H, H$_i$] 3.27 [2H, (CH$_2$)^g 13.6^h] 2.69 [2H, (CH$_2$)^i] 1.85 [s, 3H, Me]
10	37.8s	6.95 [dd, 1H, H^3 7.8^f, 1.0^e] 6.63 [t, 1H, H^4 7.8^f] 6.28 [dd, 1H, H^5 7.8^f, 1.0^e]	8.76 [s, 1H, H$_i$] 4.40 [2H, (CH$_2$)^g 12.6^h] 3.22 [2H, (CH$_2$)^i] 1.81 [s, 3H, Me]
11	32.5s	6.95 [d, 1H, H^3 7.8^f] 6.74 [t, 1H, H^4 7.8^f] 6.40 [dd, 1H, H^5 7.8^f, 5.5^k]	8.49 [d, 1H, H$_i$ 7.8^k] 4.24 [2H, (CH$_2$)^g 12.6^h] 3.23 [2H, (CH$_2$)^i] 1.98 [s, 3H, Me]

[a] In $CDCl_3$. Measured at 80.9 MHz (*ca.* ±20 °C); chemical shifts (δ) in ppm (±0.1) to high frequency of 85% H_3PO_4. [b] In $CDCl_3$. Measured at 200 MHz (*ca.* ±20 °C); chemical shifts (δ) in ppm (±0.01) to high frequency of $SiMe_4$. [c] Coupling constants in Hz. [d] s, singlet; d, doublet; dd, doublet of doublets; t, triplet; dt, doublet of triplets; q, quadruplet; m, multiplet; br, broad. [e] ^4J(HH). [f] ^3J(HH). [g] HC$=$NCH_2. [h] *N* values. [i] CH_2SMe. [j] δ(PCH$_2$P) $=$ 4.70 t. [k] *J*(PH). [l] δ(CH$^{\text{Ferrocene}}$) $=$ 5.06 [br, 2H], 4.50 [br, 2H]. [m] *J*(PP).

shifted to lower frequency due to coordination of the imine group to the palladium atom *via* the lone pair of the nitrogen atom.[32] Coordination of the palladium atom to the C=N moiety is confirmed by the shift to lower wavenumbers of the ν(C=N) band in the IR spectrum (1635s, **1**, 1613sh s cm^{-1}, **2**).[33,34] The C=N–CH_2CH_2–SMe resonances appear as well-defined virtual triplets at δ 3.94 and 2.94, respectively ($N = 13.6$ Hz). A singlet at δ 2.64 was assigned to the SMe protons. This signal is shifted to higher frequency from its value in the free ligand due to coordination of the sulfur atom. The ^{13}C-{^{1}H} spectrum shows resonances at δ 172.4 (C=N), 161.4 (C6) and 145.6 (C1) shifted to higher frequency from the free ligand values, thus confirming formation of the cyclometallated ring.[24,35] The signal at 18.1, assigned to the SMe group, is also shifted to higher frequency upon coordination of the sulfur atom. The FAB mass spectrum of the complex shows peaks assigned to [M − O$_2$CMe]$^+$ and [2M + O$_2$CMe]$^+$, both with chemically reasonable isotopic patterns. These data suggest the formulation [{Pd[2-ClC$_6$H$_3$C(H)=NCH$_2$CH$_2$SMe]}$_2$(μ-O$_2$CMe)]$^+$[O$_2$CMe]$^-$ for complex **2**. However, the low conductivity shown by the complex in acetonitrile solution precludes an ionic formulation. Consequently, the signal assignable to [2M + O$_2$CMe] can be explained by the dimerization produced in the ionization chamber, as has been described for related cyclometallated complexes.[27] In order to improve the poor yield of the metallation reaction of **1** we attempted oxidative addition reactions with Pd(0) compounds, but with little or no success. For instance, treatment of **1** with [Pd$_2$(dba)$_3$] in dry toluene gave a large residue of metallic palladium as a black powder, and similarly, reaction of **1** with Li$_2$[PdCl$_4$] in methanol did not yield the expected cyclometallated complex.

Reaction of **2** with aqueous sodium chloride gave [Pd{2-ClC$_6$H$_3$C(H)=NCH$_2$CH$_2$SMe}(Cl)], **3**, as a pure air-stable solid which was fully characterized (see Table 1 and Experimental section). The ^{1}H NMR spectrum of the complex shows a singlet resonance at δ 2.57 assigned to the SMe protons (shifted to higher frequency by 0.41 ppm as compared with the free ligand) and the ^{13}C-{^{1}H} spectrum shows a signal assigned to the SMe methyl carbon at δ 18.4 (also shifted to higher frequency), showing coordination of the sulfur atom to palladium. This was confirmed by the determination of the molecular structure of complex **3** by X-ray single crystal diffraction. Treatment of **3** with triphenylphosphine in acetone gave the mononuclear cyclometallated complex $[Pd\{2\text{-}ClC_6H_3C(H){=}NCH_2CH_2SMe\}(Cl)(PPh_3)]$, **4**, which was fully characterized (see Experimental section and Table 1). The low conductivity value observed for complex **4** precludes the alternative formulation as a 1 : 1 electrolyte $[Pd\{2\text{-}ClC_6H_3C(H){=}NCH_2CH_2SMe\}(PPh_3)]Cl$, after displacement of the chloride ligand rather than the thioether from the palladium coordination sphere. Furthermore, the SMe resonance in the ^1H NMR spectrum appears at δ 2.18 (2.16 for **1**) and at 15.9 (16 for **1**) in the ^{13}C NMR spectrum, suggesting the SMe group is not coordinated to the palladium atom as in the complexes **10** and **11** (*vide infra*), in which cases δ values under 2 (^1H NMR) and 16 (^{13}C NMR) would be expected for complex **4**. Also, the IR spectrum of **4** shows a band assigned to the ν(Pd–Cl) stretch, at 306 m cm^{-1}, which was absent in the IR spectra of compounds **10** and **11**. The $^{31}P\text{-}\{^1H\}$ spectrum of **4** shows a singlet resonance at δ 42.3, in accordance with coordination of the phosphine ligand *trans* to the nitrogen atom.

Reaction of **3** with the diphosphines dppm, dppb and dppf in a 2 : 1 molar ratio the dinuclear gave the cyclometallated complexes $[\{Pd[2\text{-}ClC_6H_3C(H){=}NCH_2CH_2SMe](Cl)\}_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}]$, ($n = 1$, **5**; $n = 4$, **6**) and $[\{Pd[2\text{-}ClC_6H_3C(H){=}NCH_2CH_2SMe](Cl)\}_2(\mu\text{-}Ph_2PC_5H_4FeC_5H_4PPh_2)]$, **7**, respectively (see Experimental section and Table 1). The ^1H (and $^{13}C\text{-}\{^1H\}$ NMR in the case of compound **6**) data are in agreement with Pd–S bond cleavage. The $^{31}P\text{-}\{^1H\}$ NMR spectra show a singlet resonance, indicating the compounds to be centrosymmetric. Reaction of **3** with $AgCF_3SO_3$ followed by PPh_3 (1 : 1 molar ratio) or by $Ph_2P(CH_2)_4PPh_2$ (2 : 1 molar ratio), gave the mono- and dinuclear species $[Pd\{2\text{-}ClC_6H_3\text{-}C(H){=}NCH_2CH_2SMe\}(PPh_3)][CF_3SO_3]$, **10**, and $[\{Pd[2\text{-}ClC_6H_3C(H){=}NCH_2CH_2\text{-}SMe]\}_2\{\mu\text{-}Ph_2P(CH_2)_4PPh_2\}][CF_3SO_3]_2$, **11**, respectively, after halide extraction. The IR spectra support the presence of the $[CF_3SO_3]^-$ anion, showing the characteristic stretching bands of the free anion,[36] *ca.* 1271, 1228, 1157 and 1028 cm^{-1}. The ^1H spectra of the complexes show singlet signals for the SMe protons at δ 1.81 and 1.98, we suggest these low values are due to shielding of the phosphine phenyl rings.[24] Nevertheless, the resonance at δ 22.7 in the $^{13}C\text{-}\{^1H\}$ NMR spectrum of **11** is in agreement with coordination of the sulfur atom to palladium. Complexes **10** and **11** can also be prepared by treatment of **4** and **6**, respectively, with silver triflate.

Treatment of **3** with dppe in a 1 : 1 molar ratio and sodium perchlorate gave the mononuclear cyclometallated complex $[Pd\{2\text{-}ClC_6H_3C(H){=}NCH_2CH_2SMe\}\{Ph_2P(CH_2)_2PPh_2\text{-},P,P\}][ClO_4]$, **8** (see Experimental section and Table 1). The $^{31}P\text{-}\{^1H\}$ NMR spectrum shows two doublets [$J(PP) = 27.1$ Hz], the resonance at lower frequency was assigned to the phosphorus nucleus *trans* to the phenyl carbon atom in accordance with the higher *trans* influence of the latter with respect to the C=N nitrogen atom.[37] The HC=N resonance in the ^1H NMR spectrum is only coupled to the ^{31}P nucleus *trans* to nitrogen and the H5 resonance is coupled to both phosphorus nuclei. The SMe resonance is shifted to lower frequency as a consequence of Pd–S bond cleavage. Reaction of **3** with the tertiary triphosphine bis(2-diphenylphosphinoethyl)phenylphosphine in a 1 : 1 molar ratio, followed by treatment with sodium perchlorate gave $[Pd\{2\text{-}ClC_6H_3C(H){=}NCH_2CH_2\text{-}SMe\}\{(Ph_2PCH_2CH_2)_2PPh\text{-}P,P,P\}][ClO_4]$, **9**. The phosphorus resonances in the $^{31}P\text{-}\{^1H\}$ NMR spectrum of the complex are downfield shifted from their values in the free phosphine, suggesting coordination of the three phosphorus atoms to the metal centre. A triplet resonance at δ 62.5 was assigned to the central ^{31}P nucleus, *trans* to the phenyl carbon atom, and a doublet signal at δ 45.4 was assigned to the two equivalent mutually *trans* phosphorus nuclei. The latter signal appears at lower frequency, in accordance with the high *trans* influence of the phosphine ligand.[37] The resonance of the proton in the *ortho* position to the metallated carbon appears as a triplet showing coupling to the central ^{31}P atom [$J(PH) = 7.8$ Hz]; no coupling was observed to the terminal phosphorus nuclei. The shift of the ν(C=N) stretching vibration to lower wavenumbers,[33,34] as well as the upfield shift of the HC=N proton resonance in the ^1H NMR spectrum,[32] indicates the existence of palladium–nitrogen interaction in solution. In agreement with the results previously obtained by us for related species in solution and in the solid state,[26,38] these data strongly agree with a penta-coordinate palladium(II) compound in which the metallated ring is nearly perpendicular to the plane defined by the three phosphorus atoms, and point towards a square-pyramidal geometry in solution. These observations were confirmed by selective decoupling experiments (see Scheme 2). Recently, the chemistry of the related ligand $C_6H_5C(H){=}NCH_2CH_2SEt$, bearing no chlorine atom, has been reported and two compounds similar to **3** and **4** have been described. It should be noted that direct metallation of this Schiff base with $Na_2[PdCl_4]$ and $Na(CH_3COO)$ in methanol gave $[Pd\{C_6H_4C(H){=}NCH_2CH_2SEt\}(Cl)]$ in good yield, as opposed to ligand **1** in the present paper, where metallation was achieved only by reaction with palladium(II) acetate.

Crystal structure of $[Pd\{2\text{-}ClC_6H_3C(H){=}NCH_2\text{-}CH_2SMe\}(Cl)]$ (3)

Crystal data are given in Table 2 and selected bond distances and angles with estimated standard deviations are shown in Table 3. Suitable crystals of the title compound were grown by slowly evaporating a chloroform solution. The molecular structures, which are illustrated in Fig. 1 and 2, consist of discrete molecules separated by van der Waals distances.

The structure of **3** comprises two molecules of $[Pd\{2\text{-}ClC_6H_3C(H){=}NCH_2CH_2SMe\}(Cl)(PPh_3)]$ *per* asymmetric unit (these are slightly different and will be labelled as **3a** and **3b**). In both cases, the palladium atom is bonded in a slightly distorted square-planar geometry to the carbon atom of the

Table 2 Crystal and structure refinement data for **3** and **11**

	3	**11**
Formula	$C_{10}H_{11}NCl_2SPd_2$	$C_{50}H_{50}N_2O_6F_6Cl_2P_2S_4Pd_2$
M_r	354.56	1362.80
T/K	293(2)	173(2)
λ/Å	0.71073	0.71073
Crystal syst.	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	8.241(1)	10.350(1)
b/Å	15.229(1)	11.126(1)
c/Å	13.367(1)	12.780(2)
α/°		74.691(3)
β/°	90.207(1)	82.642(3)
γ/°		82.434(3)
U/Å^3	2430.6(1)	1400.7(4)
Z	4	1
μ/mm^{-1}	2.103	1.012
$2\theta_{max}$/°	56.6	56.6
Collected refl.	16 370	9629
Unique refl.	5963 ($R_{int} = 0.04$)	6726 ($R_{int} = 0.04$)
R^a	0.0372	0.0515
wR^b	0.0856	0.1513
max ρ/eÅ^3	0.946	0.832

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $[F > 4\sigma(F)]$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, all data.

Table 3 Selected bond lengths [Å] and angles [°] for **3**

3a		3b	
Pd(1)–C(1)	1.999(4)	Pd(2)–C(11)	2.005(4)
Pd(1)–N(1)	1.989(3)	Pd(2)–N(2)	1.985(3)
Pd(1)–S(1)	2.413(1)	Pd(2)–S(2)	2.422(1)
Pd(1)–Cl(1)	2.314(1)	Pd(2)–Cl(3)	2.314(1)
C(1)–C(6)	1.420(5)	C(11)–C(16)	1.423(5)
C(6)–C(7)	1.447(5)	C(16)–C(17)	1.450(5)
C(7)–N(1)	1.276(5)	C(17)–N(2)	1.279(4)
Cl(2)–C(5)	1.750(4)	Cl(4)–C(15)	1.747(4)
C(1)–Pd(1)–N(1)	80.78(14)	C(11)–Pd(2)–N(2)	81.45(14)
C(1)–Pd(1)–Cl(1)	96.66(11)	C(11)–Pd(2)–Cl(3)	96.69(11)
C(1)–Pd(1)–S(1)	165.10(11)	C(11)–Pd(2)–S(2)	165.94(11)
N(1)–Pd(1)–Cl(1)	176.92(10)	N(2)–Pd(2)–Cl(3)	179.09(9)
N(1)–Pd(1)–S(1)	84.46(10)	N(2)–Pd(2)–S(2)	84.49(9)
Cl(1)–Pd(1)–S(1)	98.03(4)	Cl(3)–Pd(2)–S(2)	97.34(4)
Pd(1)–C(1)–C(6)	112.1(3)	Pd(2)–C(11)–C(16)	111.0(3)

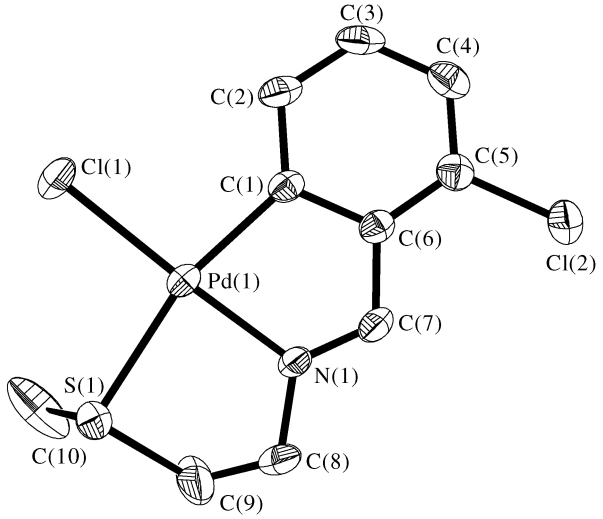


Fig. 1 Molecular structure of [Pd{2-ClC$_6$H$_3$C(H)=NCH$_2$CH$_2$SMe}(Cl)] (**3a**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

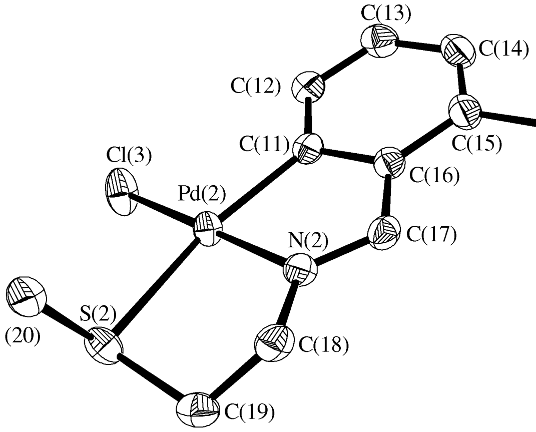


Fig. 2 Molecular structure of [Pd{2-ClC$_6$H$_3$C(H)=NCH$_2$CH$_2$SMe}(Cl)] (**3b**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

phenyl ring, the imine nitrogen atom, the sulfur atom and to a chlorine atom. The angles between adjacent atoms in the coordination sphere of palladium are close to the expected value of 90°, with the most noticeable distortions corresponding to the C(1)–Pd(1)–N(1) and C(11)–Pd(2)–N(2) angles of 80.78(14) and 81.45(14)° for **3a** and **3b**, respectively. The sum of the angles about palladium is approximately 360° in both cases. The Pd–N bond distances [1.989(3), **3a**, and 1.985(3) Å, **3b**], as well as the Pd–Cl bond distances [2.314(1) Å, **3a**, **3b**] are in accordance with previously reported values.[24,25,27,30] The Pd–C bond distances of 1.999(4), **3a**, and 2.005(4) Å, **3b**, are somewhat shorter than predicted from their covalent radii[39] but similar to values found earlier.[24,25,27] The Pd–S bond lengths of 2.413(1), **3a**, and 2.422(1) Å, **3b**, reflect the strong *trans*-influence of the metallated carbon atom.[13–16,30]

The geometry around the palladium atom [Pd, C, N, S, Cl] is planar (r.m.s. = 0.0122 and 0.0371 Å for **3a** and **3b**, respectively; planes 1 and 2). The metallated rings [Pd(1), C(1), C(6), C(7), N(1) and Pd(2), C(11), C(16), C(17), N(2)] are also planar (r.m.s. = 0.0156 and 0.0256 Å for **3a** and **3b**, respectively; planes 3 and 4). Angles between planes are as follows: plane 1/plane 3 = 0.3 °; plane 2/plane 4 = 4.6 °. The two molecules of the asymmetric unit are nearly parallel (plane 1/plane 2 = 3.2 °; plane 3/plane 4 = 5.3 °). As expected, the coordination rings [Pd(1), N(1), C(8), C(9), S(1) and Pd(2), N(2), C(18), C(19), S(2)] show large deviations from planarity with C(8) [C(19) for **3b**] lying above the least square plane and C(9) [C(18) for **3b**] below. Recently, a structure similar to **3** has been reported[40] where the asymmetric unit consists of three molecules, in contrast to the two found in the structure of compound **3**. The bond distances and bond angles show values very close to those observed in the present case.

Crystal structure of [{Pd[2-ClC$_6$H$_3$C(H)=NCH$_2$CH$_2$SMe]}$_2$-(μ-Ph$_2$P(CH$_2$)$_4$PPh$_2$)][CF$_3$SO$_3$]$_2$ (11)

Crystal data are given in Table 2 and selected bond distances and angles with estimated standard deviations are shown in Table 4. The molecular structure is illustrated in Fig. 3. Suitable crystals of the title compound were grown by slowly evaporating a dichloromethane solution.

The crystal structure comprises a centrosymmetric dinuclear cation (half the cation per asymmetric unit) and two triflate anions. Each four-coordinate palladium is bonded to the terdentate Schiff base ligand through the aryl C(1) carbon, the imine N(1) nitrogen and the sulfur atom, and to the phosphorus atom of the 1,4-bis(diphenylphosphine)butane, which bridges the two metal atoms.

The geometry around each metal atom is similar to that shown by complex **3**, with each palladium atom coordinated in a slightly distorted square-planar environment [mean deviation from the Pd(1), C(1), N(1), S(1), P(1) least square plane of 0.014 Å]. The most noticeable distortions being the C(1)–Pd(1)–N(1) and N(1)–Pd(1)–S(1) angles of 81.1(2) and 81.95(13) °, respectively.

The Pd(1)–C(1) bond length [2.030(6) Å] is shorter than the expected value of 2.081.[24,25,27] The Pd(1)–N(1) bond distance [2.044(4) Å] is longer than the values found for complex **3** [1.989(3), **3a**, and 1.985(3) Å, **3b**], reflecting the *trans* influence of the P(1) phosphorus donor ligand.[41] The Pd(1)–S(1) bond distance [2.399(2) Å] and the Pd(1)–P(1) length [2.279(1) Å]

Table 4 Selected bond lengths [Å] and angles [°] for **11**

Pd(1)–C(1)	2.030(6)	Pd(1)–N(1)	2.044(4)
Pd(1)–S(1)	2.399(2)	Pd(1)–P(1)	2.279(1)
C(1)–C(6)	1.424(7)	C(6)–C(7)	1.456(8)
C(7)–N(1)	1.283(7)	Cl(1)–C(5)	1.745(6)
C(1)–Pd(1)–N(1)	81.1(2)	C(1)–Pd(1)–P(1)	97.17(16)
C(1)–Pd(1)–S(1)	162.90(16)	N(1)–Pd(1)–P(1)	177.17(13)
N(1)–Pd(1)–S(1)	81.95(13)	P(1)–Pd(1)–S(1)	99.73(5)
Pd(1)–C(1)–C(6)	110.3(4)	C(1)–C(6)–C(7)	116.6(5)
C(7)–N(1)–Pd(1)	115.7(4)		

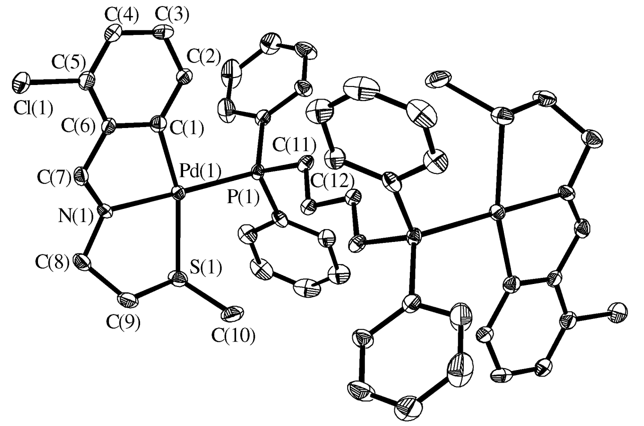


Fig. 3 Molecular structure of [{Pd[2-ClC$_6$H$_3$C(H)=NCH$_2$CH$_2$SMe]}$_2${μ-Ph$_2$P(CH$_2$)$_4$PPh$_2$}][CF$_3$SO$_3$]$_2$ (**11**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

are within the expected range and similar to values reported for related complexes.[25,28,41] Thus, as for compound **3**, the palladium atom in **11** is bonded to four different donor atoms: C, N, S and P.

The palladium coordination plane [Pd(1), C(1), N(1), S(1), P(1)] and the metallated ring [C(1), C(6), C(7), N(1), Pd(1)] are coplanar (angle between planes 5.3 °).

Experimental

General

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared and handled with great caution.

Solvents were purified by standard methods.[42] Chemicals were reagent grade. The phosphines PPh$_3$, Ph$_2$PCH$_2$PPh$_2$ (dppm), Ph$_2$P(CH$_2$)$_4$PPh$_2$ (dppb), Ph$_2$PC$_5$H$_4$FeC$_5$H$_4$PPh$_2$ (dppf) and (Ph$_2$PCH$_2$CH$_2$)$_2$PPh (triphos), were purchased from Aldrich-Chemie. Microanalyses were carried out using a Carlo Erba Model 1108 elemental analyser. IR spectra were recorded from Nujol mulls or polythene discs on a Perkin-Elmer 1330 and a Mattson spectrophotometer. NMR spectra were obtained from CDCl$_3$ solutions, referenced to SiMe$_4$ (^{1}H, ^{13}C-{^{1}H}) or 85% H$_3$PO$_4$ (^{31}P-{^{1}H}) and were recorded on a Bruker AC-2005 spectrometer. All chemical shifts are reported downfield from the standards. The FAB mass spectra were recorded using a VG Quatro mass spectrometer with a Cs ion gun; 3-nitrobenzyl alcohol was used as the matrix.

Syntheses

Preparation of 2-ClC$_6$H$_4$C(H)=NCH$_2$CH$_2$SMe (1). 2-chlorobenzaldehyde (1.166 g, 8.29 mmol) was added to a solution of 2-(methylthio)ethylamine (0.716 g, 7.85 mmol) in 50 cm^3 of dry chloroform. The solution was heated under reflux in a Dean–Stark apparatus for 4 h. After cooling to room temperature (r.t.), the chloroform was removed to give a yellow oil. Yield 95%. IR: ν(C=N) 1635s cm^{-1}. ^{13}C-{^{1}H} NMR (50.28 MHz, CDCl$_3$): δ 158.6 (C=N); 135.0, 133.0 (C1, C2); 131.5, 129.7, 128.3, 126.9 (C3–C6); 61.1 (N–CH$_2$), 34.9 (CH$_2$–S); 15.9 (SMe).

Preparation of [Pd{2-ClC$_6$H$_3$C(H)=NCH$_2$CH$_2$SMe}(O$_2$CMe)] (2). A pressure tube containing 2-ClC$_6$H$_4$C(H)=NCH$_2$CH$_2$SMe (305 mg, 1.42 mmol), palladium(II) acetate (316 mg, 1.41 mmol) and 20 cm^3 of dry toluene was sealed under argon. The resulting mixture was heated at 60 °C for 12 h. After cooling to r. t., the solution was filtered through Celite to remove the black palladium formed. The solvent was removed under vacuum to give a brown oil, which was chromatographed on a column packed with silica gel. Elution with dichloromethane–ethanol (7%) afforded an orange oil after solvent removal, which was recrystallized from dichloromethane–hexane to give the desired product as an orange solid. Yield 21%. Anal. found: C, 38.5; H, 3.4; N, 3.6; C$_{12}$H$_{14}$NO$_2$SClPd requires C, 38.1; H, 3.7; N, 3.7%. IR: ν(C=N) 1613sh s; ν$_{as}$(COO) 1571s; ν$_s$(COO), 1328m cm^{-1}. ^{13}C-{^{1}H} NMR (50.28 MHz, CDCl$_3$): δ 178.4 [OC(CH$_3$)O]; 172.4 (C=N); 161.4 (C6); 145.6 (C1); 131.0 (C2), 132.3, 130.0, 125.5 (C3–C5); 56.5 (N–CH$_2$), 37.3 (CH$_2$–S); 23.4 (OC(CH$_3$)O); 18.1 (SMe). FAB-MS: $m/z = 320$ [M – AcO]$^+$, 697 [2M + AcO]$^+$.

Preparation of [Pd{2-ClC$_6$H$_3$C(H)=NCH$_2$CH$_2$SMe}(Cl)] (3). An aqueous solution of NaCl (*ca.* 10^{-2} M) was added dropwise to a solution of **2** (218 mg, 0.29 mmol) in 15 cm^3 of acetone. The resulting mixture was stirred for 24 h. The yellow precipitate formed was filtered off, washed with water, dried under vacuum and recrystallized from dichloromethane–hexane to give complex **3** as a yellow crystalline solid. Yield 98%. Anal. found: C, 38.7; H, 3.1; N, 4.0; C$_{10}$H$_{11}$NSCl$_2$Pd requires C, 38.9; H, 3.1; N, 3.9%) IR: ν(C=N), 1612s cm^{-1}. ^{13}C-{^{1}H} NMR (50.28 MHz, CDCl$_3$): δ 172.4 (C=N); 162.1 (C6); 146.3 (C1); 131.1 (C2), 132.6, 132.5, 125.4 (C3–C5); 56.8 (N–CH$_2$), 38.6 (CH$_2$–S); 18.4 (SMe). FAB-MS: $m/z = 355$ [M]$^+$; 320 [M – Cl]$^+$.

Preparation of [Pd{2-ClC$_6$H$_3$C(H)=NCH$_2$CH$_2$SMe}(Cl)(PPh$_3$)] (4). PPh$_3$ (7.7 mg, 0.029 mmol) was added to a suspension of **3** (11 mg, 0.030 mmol) in acetone (15 cm^3). The mixture was stirred for 12 h and the solvent removed to give a white solid which was recrystallized from dichloromethane–hexane. Yield 46%. Anal. found: C, 54.0; H, 3.9; N, 2.0; C$_{28}$H$_{26}$NPSCl$_2$Pd requires C, 54.5; H, 4.2; N, 2.3%. IR: ν(C=N) 1617s, ν(Pd–Cl), 306m cm^{-1}. ^{13}C-{^{1}H} NMR (50.28 MHz, CDCl$_3$): δ 174.6 (C=N); 160.3 (C6); 145.0 (C1); 132.2 (C2), 136.6, 131.5, 125.1 (C3–C5); 59.0 (N–CH$_2$), 35.3 (CH$_2$–S); 16.0 (SMe); P–phenyl; 130.5 [d, C$_i$, J(PC) = 46.1 Hz], 135.3 [d, C$_o$, J(PC) = 12.0 Hz], 128.2 [d, C$_m$, J(PC) = 11.3 Hz], 131.0 [d, C$_p$, J(PC) = 2.2 Hz]. FAB-MS: $m/z = 582$ [M – Cl]$^+$.

Compounds **5**–**7** were obtained following a similar procedure as white (**5**, **6**) or orange (**7**) solids, but using a 2 : 1 complex **3** to diphosphine molar ratio.

[{Pd[2-ClC$_6$H$_3$C(H)=NCH$_2$CH$_2$SMe](Cl)}$_2$(μ-Ph$_2$PCH$_2$PPh$_2$)] (5). Yield 65%. Anal. found: C, 47.3; H, 3.7; N, 2.3; C$_{45}$H$_{44}$N$_2$P$_2$S$_2$Cl$_4$Pd$_2$ · CH$_2$Cl$_2$ requires C, 46.9; H, 3.9; N, 2.4%. IR: ν(C=N) 1616s cm^{-1}. FAB-MS: $m/z = 1058$ [M – Cl]$^+$; 1021 [M – 2Cl]$^+$; 704 [(**1** – H)Pd(dppm)]$^+$.

[{Pd[2-ClC$_6$H$_3$C(H)=NCH$_2$CH$_2$SMe](Cl)}$_2${μ-Ph$_2$P(CH$_2$)$_4$PPh$_2$}] (6). Yield 76%. Anal. found: C, 50.7; H, 4.4; N, 2.3; C$_{48}$H$_{50}$N$_2$P$_2$S$_2$Cl$_4$Pd$_2$ requires C, 50.8; H, 4.4; N, 2.5%. IR: ν(C=N), 1615s, ν(Pd–Cl), 308m cm^{-1}. ^{13}C-{^{1}H} NMR (50.28 MHz, CDCl$_3$): δ 174.0 (C=N); 160.0 (C6); 144.5 (C1); 132.1 (C2), 132.9, 131.5, 125.0 (C3–C5); 58.7 (N–CH$_2$), 34.9 (CH$_2$–S); 16.0 (SMe); P–phenyl: 129.9 [d,C$_i$, J(PC) = 46.1 Hz], 133.9 [d,C$_o$, J(PC) = 12.0 Hz], 128.6 [d, C$_m$, J(PC) = 10.6 Hz], 130.9(C$_p$) FAB-MS: $m/z = 1101$ [M – Cl]$^+$; 1064 [M – 2Cl]$^+$; 746 [(**1** – H)Pd(dppb)]$^+$.

[{Pd[2-ClC$_6$H$_3$C(H)=NCH$_2$CH$_2$SMe](Cl)}$_2$(μ-Ph$_2$PC$_5$H$_4$Fe-C$_5$H$_4$PPh$_2$)] (7). Yield 97%. Anal. found: C, 51.2; H, 4.4; N, 2.3; C$_{54}$H$_{50}$N$_2$P$_2$S$_2$Cl$_4$FePd$_2$ requires C, 51.3; H, 4.0; N, 2.2%.

IR: ν(C=N) 1622s cm^{-1}. FAB-MS: $m/z = 1192$ [M − 2Cl]$^+$; 874 [(**1** − H)Pd(dppf)]$^+$.

Preparation of [Pd{2-ClC$_6$H$_3$C(H)=NCH$_2$CH$_2$SMe}{Ph$_2$P-(CH$_2$)$_2$PPh$_2$-*P*,*P*}][ClO$_4$] (8). PPh$_2$(CH)$_2$PPh$_2$ (4.9 mg, 0.012 mmol) was added to a suspension of **3** (4.3 mg, 0.012 mmol) in acetone (20 cm^3). The mixture was stirred for 1 h, after which an excess of sodium perchlorate was added. The complex was the precipitated out by addition of water, filtered off and dried *in vacuo*. Recrystallization from dichloromethane–hexane gave the final compound as a yellow solid. Yield 94%. Anal. found: C, 51.3; H, 4.4; N, 1.5; $C_{36}H_{35}NO_4P_2SCl_2Pd \cdot 0.5CH_2Cl_2$ requires C, 51.0; H, 4.2; N, 1.6%. IR: ν(C=N), 1607s cm^{-1}. FAB-MS: $m/z = 718$ [M − ClO$_4$]$^+$.

[Pd{2-ClC$_6$H$_3$C(H)=NCH$_2$CH$_2$SMe}{(Ph$_2$PCH$_2$CH$_2$)$_2$PPh-*P*,*P*,*P*}][ClO$_4$] (9). Yield 72%. Anal. found: C, 52.3; H, 4.4; N, 1.5; $C_{44}H_{44}NO_4P_3SCl_2Pd \cdot CH_2Cl_2$ requires C, 52.0; H, 4.5; N, 1.3%. IR: ν(C=N) 1615s cm^{-1}. FAB-MS: $m/z = 854$ [M − ClO$_4$]$^+$.

Preparation of [Pd{2-ClC$_6$H$_3$C(H)=NCH$_2$CH$_2$SMe}-(PPh$_3$)][CF$_3$SO$_3$] (10). A solution of **3** (10.4 mg, 0.029 mmol) in acetone (15 cm^3) was treated with silver trifluoromethanesulfonate (7.4 mg, 0.029 mmol) and stirred for 2 h. The resulting solution was filtered through Celite to remove the AgCl precipitate. PPh$_3$ (7.0 mg, 0.028 mmol) was added to the filtrate, the solution stirred for another 4 h and the solvent removed to give a yellow solid which was recrystallized from dichloromethane–hexane. Yield 89%. Anal. found: C, 48.5; H, 3.7; N, 1.7; $C_{29}H_{26}NO_3F_3PS_2ClPd$ requires C, 47.7; H, 3.6; N, 1.9%. IR: ν(C=N), 1628s cm^{-1}.

Compound **11** was obtained following a similar procedure as a white solid but using a 2 : 1 complex **3** to diphosphine molar ratio.

[{Pd[2-ClC$_6$H$_3$C(H)=NCH$_2$CH$_2$SMe]}$_2${μ-Ph$_2$P(CH$_2$)$_4$PPh$_2$}]-[CF$_3$SO$_3$]$_2$ (11). Yield 50%. Anal. found: C, 44.2; H, 3.7; N, 1.9; $C_{50}H_{50}N_2O_6F_6P_2S_4Cl_2Pd_2$ requires C, 44.1; H, 3.7; N, 2.1%. IR: ν(C=N) 1626s cm^{-1}. ^{13}C-{^{1}H} NMR (50.28 MHz, CDCl$_3$): δ 172.3 (C=N); 157.6 (C6); 145.6 (C1); 132.4 (C2), 135.5, 129.3, 125.5 (C3–C5); 58.1 (N–CH$_2$), 36.1 (CH$_2$–S); 22.7 (SMe). P-phenyl: 129.8 [d, C$_i$, J(PC) = 46.8 Hz], 133.7 [d, C$_o$, J(PC) = 10.6 Hz], 128.8 [d, C$_m$, J(PC) = 9.2 Hz], 131.2(C$_p$) FAB-MS: $m/z = 1213$ [M − CF$_3$SO$_3$]$^+$; 746 [(**1** − H)Pd(dppb)]$^+$.

X-Ray crystallographic study

Three-dimensional, room temperature X-ray data were collected on a Siemens Smart CCD diffractometer by the ω scan method using graphite-monochromated Mo-Kα radiation. All the measured reflections were corrected for Lorentz and polarisation effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined by full matrix least squares on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0372$ and 0.515 (for complexes **3** and **11**, respectively, observed data, F) and $wR_2 = 0.0856$ and 0.1513 (for complexes **3** and **11**, respectively, unique data, F^2), with allowance for thermal anisotropy of all non-hydrogen atoms. The structure solution and refinement were carried out using the program package SHELX-97.[43]

CCDC reference numbers 157897 and 157898. See http://www.rsc.org/suppdata/nj/b1/b106511d/ for crystallographic data in CIF or other electronic format.

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