Articles

Multidonor Ligands. 3.† Cyclopalladation of py{$SCH_2C(O)R$}-2 (py-2 = 2-pyridyl, R = Ph, Me, OMe) through a C(sp^3)−H Bond Activation

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$[PdCl_2(NCPh)_2]$ reacts with R−carbonylmethylenethiopyridines [py{$SCH_2C(O)R$}-2] to give, depending on the substituent R and the reaction conditions, $[Pd\{py\{SCHC(O)Ph\}\text{-}2\}(\mu\text{-}Cl)_2Pd\{py\{SCH_2C(O)Ph\}\text{-}2\}Cl]$ or the coordination complexes $[Pd\{py\{SCH_2C(O)R\}\text{-}2\}_2Cl_2]$ (R = Ph, Me, OMe). The latter can be doubly deprotonated by a base (Na_2CO_3 or NaH) to give dicyclometalated complexes *cis*-$[Pd\{py\{SCHC(O)R\}\text{-}2\}_2]$. These transmetalate one ligand to $[PdCl_2(NCPh)_2]$ to give $[Pd\{py\{SCHC(O)R\}\text{-}2\}(\mu\text{-}Cl)]_2$, which in turn reacts with $(Me_4N)Cl$ or with monodentate ligands L or with MeCN in the presence of $AgClO_4$ to give anionic $Me_4N[Pd\{py\{SCHC(O)Ph\}\text{-}2\}Cl_2]$, neutral $[Pd\{py\{SCHC(O)R\}\text{-}2\}Cl(L)]$ [R = Ph, L = PPh_3, py{$SCH_2C(O)Ph$}-2, ^{t}BuNC, $NH_2CH(Me)Ph$, pyridine (py), tetrahydrothiophene (tht); R = Me, L = PPh_3, py, tht], or cationic $[Pd\{py\{SCHC(O)R\}\text{-}2\}(NCMe)_2]ClO_4$ (R = Ph, Me, OMe) complexes, respectively. The latter react with PPh_3 or with bidentate ligands to give complexes $[Pd\{py\{SCHC(O)Ph\}\text{-}2\}(NCMe)(PPh_3)]ClO_4$ or $[Pd\{py\{SCHC(O)Ph\}\text{-}2\}L_2]ClO_4$ [L = PPh_3, L_2 = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) or 2,2′-bipyridine (bipy)]. The crystal structures of $[Pd\{py\{SCHC(O)R\}\text{-}2\}_2]$ and $[Pd\{py\{SCHC(O)R\}\text{-}2\}Cl\{py\{SCH_2C(O)R\}\text{-}2\}]$ have been determined.

Introduction

Cyclopalladated complexes are becoming increasingly important in organic synthesis.[2−14] Chiral cyclopalladated derivatives are being used for optical resolution purposes[15−21] and for enantioselective catalysis.[22] Many palladacycles have found use in the preparation of metallomesogens,[23−32] and some show antitumor activity.[33,34]

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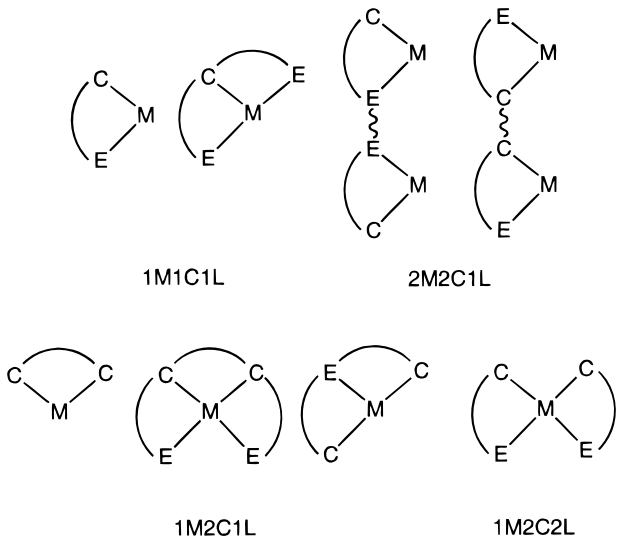
Cyclopalladation reactions involving a C(sp^2)−H activation are by far the best known, while those involving a C(sp^3)−H bond are a minority.[14,35−49] Those involving a prochiral C(sp^3)−H bond are very rare.[46,48,49] In this paper, we report the synthesis of a family of cyclopalladated complexes with a chiral C(sp^3) atom bonded to Pd.

We are interested in the coordination properties of ligands with several different donor atoms (multidonor ligands), particularly 2-substituted pyridine derivatives. Thus, we have synthesized a variety of mono- and polynuclear silver(I), gold(I),[50−55] and Pd(II) derivatives.[49,54] The polynuclear complexes of d^{10} metal ions offered us the possibility of studying metal−metal interactions, which are the subject of considerable interest,[51,56−58] whereas in the case of palladium, unusual dicationic $[PdCl_2L_2]^{2+}$ and neutral $[PdCl_3L]$ complexes [where L is the phosphonium cation $[To_3PCH_2(py\text{-}2)]^+$] were obtained, which underwent a facile double C−H activation process.[49] Recently we have studied the reactivity of 2-(R−carbonylmethylenthio)pyridine [py-{$SCH_2C(O)R$}-2, R = Ph, Me, OMe] toward Ag(I), Au(I), and Au(III) and discussed the differing abilities of these metal centers to coordinate to the various donor atoms of these ligands, as well as the capacity of Au(III) to metalate the methylene carbon atom.[53,59] In this paper, we report the first complexes of Pd(II) derived from these multidonor ligands, which, as far as we are aware, are the first bearing a sulfur atom between both coordinate atoms of a palladacycle.

Chart 1



Most cyclopalladation reactions involve one C−H activation per palladium atom. Those leading to mononuclear monopalladated complexes of a single ligand form the vast majority.[60,61] The notation 1M1C1L in Chart 1 means that the cyclometalated complex has one metal atom bonded to one C atom of one ligand. In this group of cyclopalladation reactions, those giving N,C,N or P,C,P pincer complexes[10,62−69] and dipalladated complexes obtained by cyclometalation of a single ligand (2M2C1L) are increasingly being reported.[10,62,64,70−79]

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Much more scarce are those cyclopalladation reactions involving two C−H bond activations per palladium atom. Two kinds of complexes have been isolated from these cyclopalladation reactions: 1M2C1L and 1M2C2L (see Chart 1). As far as we are aware, the double C−H bond activation reactions leading to 1M2C1L complexes are limited to palladation of a coordinated 2-pyridine-substituted phosphonium salt[49] and 2,6-pyridine-, 3,3′-bipyridine-, and 2-pyrazine-substituted ligands,[42,44,45] while those giving 1M2C2L complexes are known for 2-pyridine- and 2-pyrazine-substituted ligands.[43−45] In this paper we report new 1M2C2L complexes.

Experimental Section

The IR spectra, elemental analyses, conductance measurements in acetone, and melting point determinations were carried out as described earlier.[80] The neutral complexes **3**−**10** are nonconducting in acetone. Unless otherwise stated the reactions were carried out at room temperature without special precautions against moisture, the ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded with a Varian Unity-300 spectrometer in $CDCl_3$ solution, and chemical shifts are referred to TMS [^{1}H, ^{13}C{^{1}H}] or H_3PO_4 [^{31}P{^{1}H}]. 2-Mercaptopyridine (HSpy) and chloroacetone were purchased from Fluka, 2-bromoacetophenone [$BrCH_2C(O)Ph$] was from Aldrich, and methylchloroacetate was from Merck. The ligands py{$SCH_2C(O)R$}-2 (R = Ph, Me, OMe) were prepared as previously described.[1,53]

Synthesis of [Pd{py{SCHC(O)Ph}-2}(*μ*-Cl)$_2$Pd{py-{SCH$_2$C(O)Ph}-2}Cl] (1). A solution of py{$SCH_2C(O)Ph$}-2 (700 mg, 3.05 mmol) in acetone (5 mL) was added dropwise to a well-stirred solution of [$PdCl_2(NCPh)_2$] (1.17 g, 3.05 mmol) in acetone (5 mL). A red suspension immediately formed, which was stirred for 1 h and filtered. The solid was washed with acetone (3 × 5 mL) to give **1** as a red solid, which was dried in an oven at 80 °C overnight. Yield: 817 mg, 1.05 mmol, 69%. Mp: 193 °C. Anal. Calcd for $C_{26}H_{21}Cl_3N_2O_2S_2Pd_2$: C, 40.21; H, 2.73; N, 3.61; S, 8.26. Found: C, 40.15; H, 2.74; N, 3.48; S, 8.21. IR (cm^{-1}): *ν*(C═O), 1674, 1644; *ν*(PdCl), 356, 304, 272. ^{1}H NMR (300 MHz, dmso-d_6): *δ* 5.19 (s, 1 H, CH), 6.13 (s, br, 2 H, CH_2), 7.28−8.20 [m, 17 H, H5 (py)], 8.55 [d, 1 H, H6 (py), $^3J_{HH}$ = 5.5 Hz]. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): *δ* 40.42 (CH_2), 54.57 (CH), 119.82, 120.67, 121.23, 126.78, 127.59, 128.16, 128.19, 128.69, 128.78, 128.85, 132.17, 133.95, 138.53, 139.40, 150.73 (ternary carbon nuclei); 135.12, 138.50 (C_{ipso}), 174.67, 172.77 (CS), 193.58, 194.53 (CO).

Syntheses of [Pd{py{SCH$_2$C(O)R}-2}$_2$Cl$_2$] [R = Ph (2a), Me (2b), OMe (2c)]. To a solution of py{$SCH_2C(O)R$}-2 (ca. 2.3 mmol) in acetone (20 mL) was slowly added solid [$PdCl_2(NCPh)_2$] (ca. 1 mmol). A yellow (**2a,b**) or orange (**1c**) suspension immediately formed, which was stirred for 30 (**2a**) or 80 (**2b,c**) min and filtered. The solid was washed successively with acetone (10 mL) and diethyl ether (15 mL) to give yellow **2a**−**c.**

2a: Yield, 100%. Mp: 206 °C dec. Anal. Calcd for $C_{26}H_{22}Cl_2N_2O_2S_2Pd$: C, 49.11; H, 3.49; N, 4.41; S,10.08. Found: C, 48.69; H, 3.53; N, 4.54; S, 9.94. IR (cm^{-1}): *ν*(C═O), 1674; *ν*(PdCl), 348.

2b: Yield, 95%. Mp: 168 °C. Anal. Calcd for $C_{16}H_{18}Cl_2N_2O_2S_2Pd$: C, 37.55; H, 3.55; N, 5.47; S, 12.53. Found: C, 37.50; H, 3.61; N, 5.30; S, 12.46. IR (cm^{-1}): *ν*(C═O), 1644; *ν*(PdCl), 352.

2c: Yield, 95%. Mp: 226 °C dec. Anal. Calcd for $C_{16}H_{18}Cl_2N_2O_4S_2Pd$: C, 35.34; H, 3.34; N, 5.15; S,11.77. Found: C, 35.65; H, 3.36; N, 4.97; S, 11.24. IR (cm^{-1}): *ν*(C═O), 1746; *ν*(PdCl), 350.

Syntheses of [Pd{py{SCHC(O)R}-2}$_2$] [R = Ph (3a), Me (3b), OMe (3c)]. To a suspension of **2** (**a**, 705 mg, 1.11 mmol; **b**, 2.635 g, 5.15 mmol; **c**, 744 mg, 1.37 mmol) in acetone (**2a**,**b**, 20 mL) or chloroform (**2c**, 20 mL) was added solid Na_2CO_3 (**2a**, 282 mg, 2.66 mmol; **2b**, 819 mg, 7.72 mmol) or NaH (**2c**, 66 mg, 2.74 mmol), and the resulting mixture was refluxed for 7, 5, or 1.5 h, respectively. In the cases of **3a** and **3b** the solvent was removed under vacuum, the residue was extracted with CH_2Cl_2 (3 × 5 mL), and the combined extracts were filtered through Celite. In the case of **3c**, the reaction mixture was directly filtered through anhydrous $MgSO_4$. The resulting solution was concentrated (to ca. 2 mL), and diethyl ether (**3a**,**b**, 20 mL) or *n*-hexane (**3c**, 20 mL) was added to precipitate yellow **3a,b** or orange **3c**.

3a: Yield, 580 mg, 1.03 mmol, 93%. Mp: 213 °C. Anal. Calcd for $C_{26}H_{20}N_2O_2S_2Pd$: C, 55.47; H, 3.58; N, 4.97; S, 11.39. Found: C, 54.98; H, 3.58; N, 5.03; S, 11.20. IR (cm^{-1}): *ν*(C═O), 1644, 1626. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 3.95 (s, 1 H, CH), 6.98 [m, 1 H, H5 (py)], 7.53 [m, 4 H, H3 (py) + H3 (Ph) + H4 (Ph)], 7.58 [m, 1 H, H4 (py)], 7.69 [m, 2 H, H2 (Ph)], 7.80 [d, 1 H, H6 (py), $^3J_{HH}$ = 5.1 Hz]. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): *δ* 42.60 (s, CH), 119.96, 121.69, 127.17, 128.11, 131.02, 137.34, 148.72 (ternary carbon nuclei); 140.91 (C_{ipso}), 170.85 (CS), 197.38 (CO).

Crystal Structure. A yellow prism of **3a** of 0.44 × 0.22 × 0.12 mm, obtained by liquid diffusion of ^{i}Pr$_2$O into a $CHCl_3$ solution of **3a**, was mounted in inert oil on a glass fiber and transferred to the diffractometer (Siemens P4 with LT2 low-temperature attachment). The crystal data are summarized in Table 1. Unit cell parameters were determined from a least-squares fit of 63 accurately centered reflections (9.98° < 2*θ* < 24.9°). An absorption correction based on *ψ* scans was employed with transmission factor 0.756−0.601. The structure was solved by direct methods and refined anisotropically on F^2 (program SHELXL 93).[81] Hydrogen atoms were included using a riding model. The programs use the neutral atom scattering factors from International Tables for Crystallography.[82] A system of 266 restraints (to local ring symmetry and *U* components of neighboring light atoms) was employed. Maximum $\Delta/\sigma = 0.001$. Figure 1 shows the thermal ellipsoid plot of **3a**; Tables 1 and 2 give crystallographic data and selected bond lengths and angles, respectively.

3b: Yield, 1.956 g, 4.45 mmol, 87%. Mp: 228 °C. Anal. Calcd for $C_{16}H_{16}N_2O_2S_2Pd$: C, 43.78; H, 3.68; N, 6.38; S, 14.61

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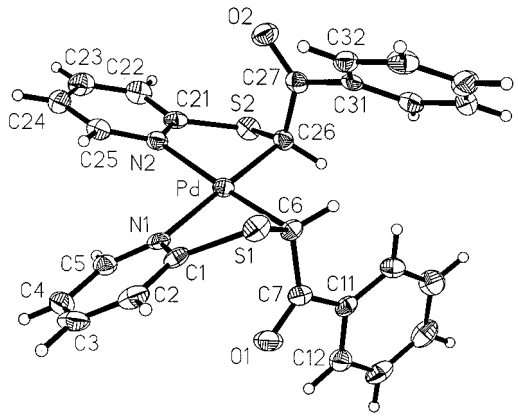


Figure 1. Thermal ellipsoid plot of **3a** (50% probability levels) with the labeling scheme.

Table 1. Crystal Data for Complexes 3a and 6·CDCl$_3$

	3a	**6**·$CDCl_3$
formula	$C_{26}H_{20}N_2O_2PdS_2$	$C_{27}H_{21}Cl_4DN_2O_2PdS_2$
M_r	562.96	719.80
space group	$P2_1/n$	$Pbca$
cell constants		
a (Å)	13.114(2)	11.8989(12)
b (Å)	9.8241(12)	18.244(2)
c (Å)	18.454(3)	26.688(2)
α (deg)	90	90
β (deg)	107.975(10)	90
γ (deg)	90	90
V (Å^3)	2261.5(5)	5793.5(10)
Z	4	8
D_x (Mg/m^3)	1.653	1.650
μ (mm^{-1})	1.033	1.183
T (K)	173(2)	173(2)
$2\theta_{max}$	50	50
λ (Å)	0.71073	0.71073
F(000)	1136	2880
no. of ind reflns	3984	5080
no. of params	298	343
no. of restraints	266	0
R1[a]	0.0331	0.0327
wR2[b]	0.0700	0.0644
$S(F^2)$	0.919	0.956
max. $\Delta\rho$ (e Å^{-3})	0.601	0.707

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for reflections with $I > 2\sigma I$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and a and b are constants set by the program.

Found: C, 43.64; H, 3.60; N, 6.17; S, 14.35. IR (cm^{-1}): ν(C═O), 1650. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.31 (s, 3 H, Me), 4.10 (s, 1 H, CH), 7.01 [m, 1 H, H4 (py)], 7.60 [m, 2 H, H3 + H5 (py)], 7.86 [d, 1 H, H6 (py), $^3J_{HH}$ = 5.6 Hz]. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 28.26 (Me), 46.38 (CH), 119.96, 121.94, 137.47, 148.76 (ternary carbon nuclei), 171.09 (CS), 203.81 (CO).

3c (1:1 mixture of diastereoisomers RR + SS and RS): Yield, 471 mg, 1.00 mmol, 73%. Mp: 220 °C. Anal. Calcd for $C_{16}H_{16}N_2O_4S_2Pd$: C, 40.82; H, 3.43; N, 5.95; S, 13.62. Found: C, 40.72; H, 3.58; N, 5.62; S, 13.25. IR (cm^{-1}): ν(C═O), 1682. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.65 (s, 3 H, Me), 3.69 (s, 3 H, Me), 4.04 (s, 1 H, CH), 4.32 (s, 1 H, CH), 6.98−7.03 (m, 2 H, py), 7.47−7.60 (m, 4 H, py), 7.90−7.95 (m, 2 H, py). When this mixture of stereoisomers is refluxed in chloroform for 19 h, a small amount of palladium is deposited. When the suspension is filtered through Celite, the solution concentrated (2 mL), and diethyl ether added, **3c** precipitates as the pair of enantiomers RR + SS or the RS isomer for which ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.65 (s, 3 H, Me), 4.04 (s, 1 H, CH), 6.98 [m, 1 H, H4 (py)], 7.45 [m, 2 H, H3 + H5 (py)], 7.94 [d, 1 H, H6 (py, $^3J_{HH}$ = 5.6 Hz). $^{13}C\{^1H\}$ (50 MHz, $CDCl_3$): δ 32.90 (Me), 51.70 (s, CH), 119.90, 121.87, 137.32, 148.92 (ternary carbon nuclei), 171.75 (CS), 176.71 (CO).

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Complexes 3a and 6·CDCl$_3$

3a		**6**·$CDCl_3$	
Pd−N(1)	2.093(3)	Pd−N(1)	2.040(2)
Pd−N(2)	2.112(3)	Pd−N(2)	2.045(2)
Pd−C(6)	2.071(3)	Pd−C(6)	2.048(3)
Pd−C(26)	2.056(4)	Pd−Cl(1)	2.3738(8)
S(1)−C(1)	1.745(4)	S(1)−C(11)	1.753(3)
S(2)−C(21)	1.745(4)	S(1)−C(5)	1.793(3)
S(1)−C(6)	1.813(3)	S(2)−C(21)	1.729(3)
S(2)−C(26)	1.803(4)	S(2)−C(6)	1.799(3)
N(1)−C(1)	1.360(5)	N(1)−C(11)	1.344(4)
N(2)−C(21)	1.345(4)	N(2)−C(21)	1.358(4)
C(26)−Pd−C(6)	97.08(14)	N(1)−Pd−C(6)	90.76(11)
C(6)−Pd−N(1)	82.25(13)	N(2)−Pd−C(6)	85.72(11)
N(1)−Pd−N(2)	96.74(11)	N(2)−Pd−Cl(1)	93.80(7)
C(26)−Pd−N(2)	84.08(13)	N(1)−Pd−Cl(1)	89.71(7)
Pd−C(6)−S(1)	103.9(2)	Pd−C(6)−S(2)	109.5(2)
Pd−C(26)−S(2)	109.2(2)	C(21)−S(2)−C(6)	99.23(14)
C(1)−S(1)−C(6)	97.0(2)	S(2)−C(21)−N(2)	118.0(2)
C(21)−S(2)−C(26)	100.2(2)	C(11)−S(1)−C(5)	103.8(2)

Syntheses of [Pd{py{SCHC(O)R}-2}(μ-Cl)]$_2$ [R = Ph (4a), Me (4b), OMe (4c)]. To a suspension of **3** (**a**, 1162 mg, 2.06 mmol; **b**, 1 g, 2.28 mmol; **c**, 160 mg, 0.34 mmol) in acetone (**a**, 15 mL; **b**, 40 mL; **c**, 25 mL) was added $[PdCl_2(NCPh)_2]$ (**a**, 792 mg, 2.06 mmol; **b**, 874 mg, 2.28 mmol; **c**, 130 mg, 0.34 mmol). A clear solution formed, from which an orange solid precipitated within a few minutes. After 2 (**4a**) or 1.5 (**4b**) or 24 (**4c**) h of stirring, the suspension was filtered (**4a**,**b**) or centrifuged (**4c**) and the orange solid washed with diethyl ether (**4a**, 15 mL) or acetone (**4b**, 3 × 10 mL; **4c**, 15 mL) and air-dried. The solid was recrystallized from dichloromethane/diethyl ether (**4a**) or suspended in chloroform (15 mL), the suspension refluxed for 15 h, the resulting solution concentrated (2 mL), and diethyl ether (15 mL) added to precipitate **4b,c**.

4a: Yield, 1.433 g, 1.90 mmol, 94%. Mp: 225 °C. Anal. Calcd for $C_{26}H_{20}Cl_2N_2O_2S_2Pd_2$: C, 42.18; H, 2.72; N, 3.78; S, 8.66. Found: C, 41.85; H, 2.71; N, 3.82; S, 8.54. IR (cm^{-1}): ν(C═O), 1644; ν(PdCl), 328, 294, 258. ^{1}H NMR (300 MHz, dmso-d_6): δ 5.21 (s, 1 H, CH), 7.24−7.97 [complex multiplets, 8 H, py + Ph], 8.59 [m, 1 H, H6 (py)]. $^{13}C\{^1H\}$ NMR (75 MHz, dmso-d_6): δ 54.62 (CH), 120.66, 121.22, 128.17, 128.74, 132.17, 139.37, 150.73 (ternary carbon nuclei), 138.48 (C_{ipso}), 172.25 (CS), 194.65 (CO).

4b: Yield, 1347 mg, 2.19 mmol, 96%. Mp: 235 °C. Anal. Calcd for $C_{16}H_{16}Cl_2N_2O_2S_2Pd_2$: C, 31.19; H, 2.62; N, 4.55; S, 10.40. Found: C, 30.74; H, 2.71; N, 4.29; S, 9.61. IR (cm^{-1}): ν(C═O), 1660; ν(PdCl), 314, 278, 254. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.32 (s, 3 H, Me), 4.74 [s, 1 H, CH), 7.00 [m 1 H, H4 (py)], 7.57 [m, 2 H, H 3 + H5 (py)], 8.11 [m, 1 H, H6 (py)].

4c: Yield, 178 mg, 0.27 mmol, 81%. Mp: 324 °C. Anal. Calcd for $C_{16}H_{16}Cl_2N_2O_4S_2Pd_2$: C, 29.65; H, 2.49; N, 4.32; S, 9.89. Found: C, 29.28; H, 2.44; N, 4.14; S, 9.21. IR (cm^{-1}): ν(C═O), 1697; ν(PdCl), 362, 334, 293, 265. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.71 (s, 1 H, CH), 3.73 (s, 3 H, Me), 6,99 [m, 1 H, H4 (py)] 7.48 [d, 1 H, H3 (py), $^3H_{HH}$ = 7.6 Hz], 7.60 [m, 1 H, H5 (py)], 8.24 [m, 1 H, H6 (py)].

Syntheses of [Pd{py{SCHC(O)R}-2}Cl(L)] [R = Ph, L = PPh$_3$ (5a), py{SCH$_2$C(O)Ph}-2 (6), ^{t}BuNC (7), *S*-NH$_2$CH(Me)Ph (8), py (9a), tetrahydrothiophene (tht) (10a); R = Me, L = PPh$_3$ (5b), py (9b), tht (10b)]. To a suspension of **4a** (or **4b**) (ca. 0.5 mmol) in dichloromethane (20 mL) was added 2 equiv (4 in the case of **7**) of the corresponding ligand. The resulting solution was stirred for 0.5 (**5a**, **6**), 1.5 (**5b**, **9b**), 3.5 (**7**), or 4.5 (**8**) h or overnight (**9a**, **10a**,**b**) and concentrated (to ca. 1 mL), and diethyl ether (20 mL) or *n*-pentane (**10b**, 15

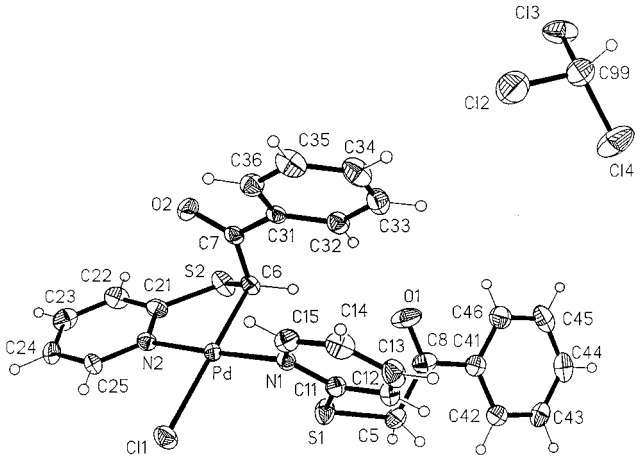


Figure 2. Thermal ellipsoid plot of **6**·$CDCl_3$ (50% probability levels) with the labeling scheme.

mL) was added to precipitate a yellow solid, which was filtered off and air-dried. In the case of **9b** refluxing in chloroform (15 mL) for 4.5 h, concentration of the solution (1 mL), and addition of diethyl ether (20 mL) were required to provide an analytically pure sample. Complexes **6**, **10a,** and **10b** were recrystallized from dichloromethane/diethyl ether. Additionally, complexes **6**, **8**, **9a**, **10a**, **9b,** and **10b** were dried in an oven at 80 °C (**9b**, 60 °C) overnight.

5a: Yield, 93%. Mp: 243 °C. Anal. Calcd for $C_{31}H_{25}ClNOPPdS$: C, 58.87; H, 3.98; N, 2.21; S, 5.06. Found: C, 58.77; H, 3.98; N, 2.24; S, 4.94. IR (cm^{-1}): ν(C=O), 1642; ν(PdCl), 304. ^1H NMR (300 MHz, $CDCl_3$): δ 4.41 (d, 1 H, CH, $^3J_{PH}$ = 2.7 Hz), 7.15 (m, 5 H, Ph) 7.45 [m, 18 H, PPh_3 + H3 + H4 + H5 (py)], 9.05 [m, 1 H, H6 (py)]. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 49.92 (s, CH), 120.23, 127.45, 128.12, 128.23, 128.45, 130.63, 131.34, 134.47, 134.69, 137.84, 150.59, 150.62 (ternary carbon nuclei), 129.84, 130.69, 130.89, 139.09 (quaternary carbon nuclei), 197.03 (CO). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 27.83 (s).

5b: Yield, 91%. Mp: 188 °C. Anal. Calcd for $C_{26}H_{23}ClNOPPdS$: C, 54.75; H, 4.06; N, 2.46; S, 5.62. Found: C, 54.67; H, 4.12; N, 2.32; S, 5.66. IR (cm^{-1}): ν(C=O), 1660; ν(PdCl), 294. ^1H NMR (300 MHz, $CDCl_3$): δ 1.86 (S, 3 H, Me), 3.54 (d, 1 H, CH, $^3J_{PH}$ = 3.3 Hz), 7.09 [m, 1 H, H4 (py)], 7.63 (m, 17 H, H3 + H5 (py) + PPh_3], 9.12 (m, 1 H, H6). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 29.82 (s).

6: Yield, 85%. Mp: 203 °C. Anal. Calcd for $C_{26}H_{21}ClN_2O_2PdS_2$: C, 52.10; H, 3.53; N, 4.67; S, 10.70. Found: C, 52.06; H, 3.56; N, 4.71; S, 10.98. IR (cm^{-1}): ν(C=O), 1690, 1630; ν(PdCl), 316. ^1H NMR (200 MHz, $CDCl_3$): δ 4.70 (AB system, 2 H, CH_2, $^2H_{HH}$ = 16 Hz), 5.28 (s, 1 H, CH), 6.47 (m, 1 H), 7.01(m, 4 H), 7.49 (m, 10 H) 8.10 (m, 2 H), 8.94 (d, 1 H, $^3J_{HH}$ = 5.9 Hz). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 39.73 (s, CH_2), 45.21 (CH), 119.52, 120.30, 121.04, 122.77, 127.20, 128.24, 128.54, 128.83, 129.08, 131.51, 134.31, 137.22, 152.68, 153.00 (ternary carbon nuclei), 99.19, 122.77, 132.06, 142.85, 143.13 (quaternary carbon nuclei), 192.44 (CO).

Crystal Data for 6·$CDCl_3$. A yellow parallelepiped of **6**·$CDCl_3$ of 0.70 × 0.60 × 0.35 mm was mounted and measured as described for **3a**. Unit cell parameters were determined from a least-squares fit of 58 accurately centered reflections (9° < 2θ < 25°). An absorption correction based on ψ-scans was employed, with transmisssion factors 0.725−0.812. The structure was solved and refined as described for **3a**. Figure 1 shows the thermal ellipsoid plot of **3a**; Tables 1 and 2 give crystallographic data and selected bond lengths and angles, respectively.

7: Yield, 90%. Mp: 174 °C. Anal. Calcd for $C_{18}H_{19}ClN_2OPdS$: C, 47.70; H, 4.22; N, 6.18; S, 7.07. Found: C, 47.36; H, 4.26; N, 6.15; S, 6.97. IR (cm^{-1}): ν(C=O), 1652; ν(PdCl), 310 or 296. ^1H NMR (300 MHz, $CDCl_3$): δ 1.24 (s, 9 H, ^{t}Bu), 5.60 (s, 1 H, CH), 7.08 [m, 1 H, H4 (py)], 7.51 [m, 6 H, H5 (py) + Ph], 7.97 [m, 1 H, H3 (py)], 8.98 (m, 1 H, H6 (py)]. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 29.60 (Me), 45.26 (CH), 119.84, 120.26, 128.09, 128.35, 132.13, 138.24, 151.08 (ternary carbon nuclei), 137.64 (C_{ipso}), 172.54 (CS), 196.78 (CO).

8: Yield, 88%. Mp: 156 °C. Anal. Calcd for $C_{21}H_{21}ClN_2OPdS$: C, 51.34; H, 4.30; N, 5.70; S, 6.53. Found: C, 51.22; H, 4.40; N, 5.75; S, 6.26. IR (cm^{-1}): ν(NH), 3242, 3198; ν(C=O), 1630; ν(PdCl), 340 or 296. ^1H NMR (300 MHz, $CDCl_3$): δ 1.62 (d, 3 H, Me, $^3J_{HH}$, 4.4 Hz), 1.88 (d, 3 H, Me, $^3J_{HH}$, 4.4 Hz), 2.7 (m, 2 H, NH_2), 3.36 (m, 2 H, NH_2), 4.38 (s, 1 H, CH), 4.99 (s, 1 H, CH), 4.45 (m, 2 H, NCH), 7.10 (m, 2 H), 7.21−7.58 (m, 20 H), 7.87 (m, 4 H) 9.20 (m, 2 H).

9a: Yield, 89%. Mp: 178 °C. Anal. Calcd for $C_{18}H_{15}ClN_2OPdS$: C, 48.12; H, 3.37; N, 6.23; S, 7.14. Found: C, 47.80; H, 3.40; N, 6.02; S, 6.96. IR (cm^{-1}): ν(C=O), 1632; ν(PdCl), 316. ^1H NMR (200 MHz, $CDCl_3$): δ 5.23 (s, 1 H, CH), 6.98−7.60 (m, 11 H), 8.37 (m, 2 H), 9.00 (m, 1 H).

9b: Yield, 68%. Mp: 296 °C. Anal. Calcd for $C_{13}H_{13}ClN_2OPdS$: C, 40.33; H, 3.38; N, 7.24; S, 8.28. Found: C, 40.66; H, 3.35; N, 7.28; S, 8.34. IR (cm^{-1}): ν(C=O), 1640; ν(PdCl), 348. ^1H NMR (300 MHz, $CDCl_3$): δ 2.19 (S, 3 H, Me), 4.16 (s, 1 H, CH), 7.00 (m, 1 H) 7.33−7.38 (m, 2 H), 7.60 (m, 1 H), 7.80 (m, 1 H), 8.70 (m, 2 H), 8.84 (m, 1 H), 9.13 (m, 1 H).

10a: Yield, 80%. Mp: 163 °C. Anal. Calcd for $C_{17}H_{18}ClNOPdS_2$: C, 44.55; H, 3.96; N, 3.06; S, 13.99. Found: C, 44.65; H, 4.03; N, 3.79; S, 13.77. IR (cm^{-1}): ν(C=O), 1630; ν(PdCl), 304 or 262. ^1H NMR (200 MHz, $CDCl_3$): δ 1.97 (s, 4 H, tht), 2.70 (s, 4 H, tht), 5.24 (s, 1 H, CH), 7.03 [m, 1 H], 7.44 (m, 5 H), 7.85 (m, 2 H), 8.90 (m, H6, 1 H).

10b: Yield, 80%. Mp: 191 °C. Anal. Calcd for $C_{12}H_{16}ClNOPdS_2$: C, 36.38; H, 4.07; N, 3.53; S, 16.18. Found: C, 35.83; H, 3.85; N, 3.80; S, 14.56. IR (cm^{-1}): ν(C=O), 1659; ν(PdCl), 311. ^1H NMR (200 MHz, $CDCl_3$): δ 2.10 (s, 4 H, tht), 3.24 (s, 4 H, tht), 2.22 (s, 3 H, Me), 4.10 (s, 1 H, CH), 6.97 [m, 1 H, H4 (py)], 7.40 [d, 1 H, H3 (py), $^3J_{HH}$ = 7.72 Hz], 7.53 [m, 1 H, H5 (py)], 9.00 [d, 1 H, H6 (py), $^3J_{HH}$ = 5.62 Hz].

Synthesis of Me_4N[Pd{py{SCHC(O)Ph}-2}Cl_2] (11). To a suspension of **4a** (150 mg, 0.20 mmol) in acetone (30 mL) was added (Me_4N)Cl (43.28 mg, 0.40 mmol). The suspension was stirred for 24 h and concentrated to dryness. The residue was extracted with dichloromethane (3 × 5 mL), and the combined extracts were filtered through Celite. The solution was concentrated (to ca. 2 mL) and diethyl ether (20 mL) added to give **11** as a yellow-orange solid, which was recrystallized from dichloromethane and diethyl ether and dried in an oven at 80 °C overnight. Yield: 157 mg, 0.33 mmol, 82%. Mp: 221 °C. Anal. Calcd for $C_{17}H_{22}Cl_2N_2OPdS$: C, 42.56; H, 4.62; N, 5.84; S, 6.68. Found: C, 42.74; H, 4.84; N, 5.93; S, 6.66. IR. (cm^{-1}): ν(C=O), 1630 ν(PdCl), 328, 296. ^1H NMR (300 MHz, dmso-d_6): δ 3.14 (s, 12 H, NMe_4), 5.38 (s, 1 H, CH), 7.10 [t, 1 H, H4 (py), $^3J_{HH}$ = 6 Hz], 7.67 [m, 7 H, H3 + H5 (py) + Ph], 8.70 [d, 1 H, H6 (py), $^3J_{HH}$ = 5.2 Hz].

Syntheses of [Pd{py{SCHC(O)R}-2}$(NCMe)_2$]ClO_4 [R = Ph (12a), Me (12b), OMe (12c)]. To a suspension of **4a**−**c** (ca. 0.15 mmol) in acetone (30 mL) was added 2 equiv of solid AgClO4. Immediate precipitation of AgCl was observed. The suspension was stirred for 3 (**12a**) or 6 h (**12b,c**) and filtered. The solution was concentrated (to ca. 1 mL) and diethyl ether (20 mL) added to precipitate yellow (**12a**,**b**) or orange (**12c**) complexes. **12b**,**c** were recrystallized from acetonitrile and diethyl ether, and **12c** was dried in an oven at 60 °C overnight.

12a: Yield, 93%. Mp: 293 °C. Anal. Calcd for $C_{17}H_{16}ClN_3O_5PdS$: C, 39.55; H, 3.12; N, 8.14; S, 6.21. Found: C, 39.10; H, 3.21; N, 8.05; S, 6.65. IR (cm^{-1}): ν(C=O), 1648; ν(ClO), 1110; δ(OClO), 624. ^1H NMR (300 MHz, CD_3CN): δ 1.97 (s, 3 H, free MeCN), 5.90 (s, 1 H, CH), 7.21 [m, 1 H, H4 (py)], 7.51−7.57 (m, 2 H), 7.63 (m, 1 H), 7.73 (m, 1 H), 7.83 (m, 1 H), 7.92

(m, 2 H), 8.05 [m, 1 H, H6 (py)]. $^{13}C\{^1H\}$ (75 MHz, CD_3CN): δ 44.25 (CH), 121.98, 122.03, 128.77, 129.34, 133.73, 140.64, 152.36 (ternary carbon nuclei), 138.22, 173.88 (quaternary carbon nuclei), 196.04 (CO).

12b: Yield, 84%. Mp: 279 °C dec. Anal. Calcd for $C_{12}H_{14}ClN_3O_5PdS$: C, 31.74; H, 3.11; N, 9.25; S, 7.06. Found: C, 30.94; H, 3.00; N, 8.62; S, 6.64. IR (cm^{-1}): ν(C═O), 1666; ν(ClO), 1085; δ(OClO), 624. ^1H NMR (300 MHz, CD_3CN): δ 1.98 (s, 3 H, MeCN), 2.21 (s, 3 H, MeCN), 2.24 [s, 3 H, C(O)Me], 4.89 (s, 1 H, CH), 7.19 [m, 1 H, H4 (py)], 7.66 [m, 1 H, H3 (py)], 7.81 [m, 1 H, H5 (py)], 8.06 [m, 1 H, H6 (py)].

12c: Yield, 83%. Mp: 243 °C. Anal. Calcd for $C_{12}H_{14}ClN_3O_6PdS$: C, 30.65; H, 3.00; N, 8.94 S, 6.82. Found: C, 28.91; H, 2.81; N, 8.05; S, 6.36. IR (cm^{-1}): ν(C═O), 1693; ν(ClO), 1089; δ(OClO), 620. ^1H NMR (300 MHz, CD_3CN): δ 2.06 (s, 3 H, MeCN), 2.31 (s, 3 H, MeCN), 3.77 (s, 3 H, OMe), 4.63 (s, 1 H, CH), 7.31 [m, 1 H, H4 (py)], 7.74 [m, 1 H, H3 (py)], 7.92 [m, 1 H, H5 (py)], 8.25 [m, 1 H, H6 (py)].

Synthesis of [Pd{py{SCHC(O)Ph}-2}(NCMe)(PPh_3)]ClO_4 (13). To a suspension of **12a** (90 mg, 0.17 mmol) in MeCN (20 mL) was added solid PPh_3 (46 mg, 0.17 mmol). The color changed immediately from yellow to orange. The suspension was stirred for 1 h and concentrated (to ca. 2 mL), and diethyl ether (20 mL) was added to precipitate **13** as an orange solid, which was recrystallized from dichloromethane/diethyl ether and dried in an oven at 80 °C overnight. Yield: 112 mg, 0.15 mmol, 88%. Mp: 159 °C. Anal. Calcd for $C_{33}H_{28}ClN_2O_5PPdS$: C, 53.74; H, 3.83; N, 3.80; S, 4.35. Found: C, 53.66; H, 3.92; N, 3.89; S, 4.17. IR (cm^{-1}): ν(C═O), 1650; ν(ClO), 1093; δ(OClO), 624. Λ_M, 142 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.80 (s, 3 H, MeCN), 4.32 (d, 1 H, CH, $^3J_{HP}$ = 5.7 Hz), 7.41 (m, 23 H, py + Ph + PPh_3), 8.63 [m, 1 H, H6 (py)]. $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$): δ 2.66 (Me), 45.22 (CH), 120.87, 127.94, 128.18, 129.13, 129.35, 131.93 (d, $^2J_{PC}$ = 2.6 Hz), 132.46, 133.85, 134.08, 139.11 (ternary carbon nuclei), 122.50, 127.40, 136.24, 151.43 (quaternary carbon nuclei), 198.93 (CO). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): 26.77 (s, PPh_3).

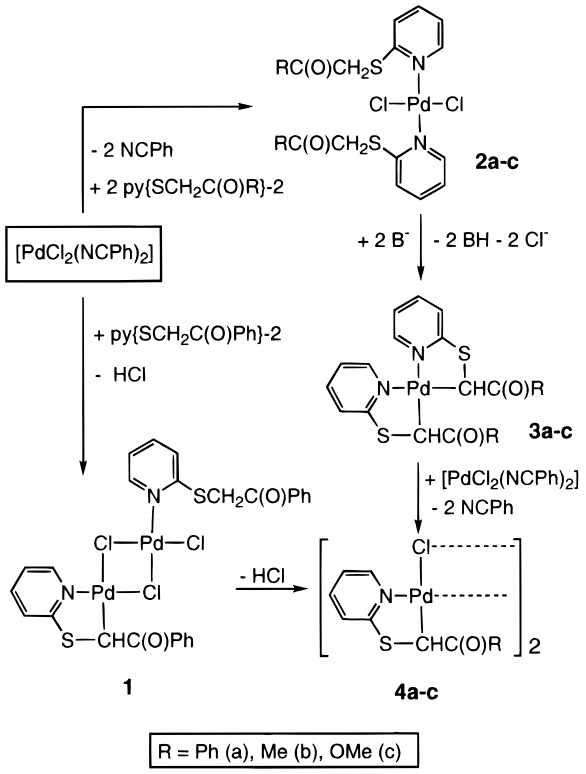
Syntheses of [Pd{py{SCHC(O)Ph}-2}L_2]ClO_4 [L = PPh_3 (14), L_2 = *N,N,N′,N′*-Tetramethylethylenediamine (tmeda) (15), 2,2′-Bipyridine (bipy) (16)]. To a solution of the appropriate ligand (PPh_3, ca. 1 mmol; tmeda, bipy, ca. 0.5 mmol) in dichloromethane (20 mL) was added solid **12a** (ca. 0.5 mmol). The resulting orange solution (**14**, **15**) or the orange suspension (**16**) was stirred for 2 or 24 h, respectively. The solution was filtered through anhydrous $MgSO_4$ and concentrated to ca. 1 mL, and diethyl ether (20 mL) was added to precipitate pale orange **14** or yellow **15**, which were recrystallized from dichloromethane and diethyl ether and dried in an oven at 80 °C overnight. The suspension obtained in the reaction with bipy was filtered off, and the solid was washed with dichloromethane (15 mL) and dried in an oven at 80 °C overnight to give **16** as a yellow solid.

14: Yield, 75%. Mp: 142 °C. Anal. Calcd for $C_{49}H_{40}ClNO_5P_2PdS$: C, 61.38; H, 4.20; N, 1.46 S, 3.34. Found: C, 61.36; H, 4.59; N, 1.56; S, 3.50. IR (cm^{-1}): ν(C═O), 1625; ν(ClO), 1090; δ(OClO), 624. Λ_M, 149 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.97 (d, 1 H, CH, $^3J_{PH}$ = 10.2 Hz), 6.88−7.42 (m, 38 H, py + Ph + PPh_3), 8.66 (m, 1 H, H6(py)]. $^{13}C\{^1H\}$ NMR: δ 65.72 (CH), 124.73, 125.17, 128.00, 128.29, 128.87, 129.09, 129.44, 131.41 (d, $^2J_{CP}$ = 2.3 Hz), 131.62 (d, $^2J_{CP}$ = 2.2 Hz), 132.99, 133.36 (d, $^2J_{CP}$ =2 Hz), 133.61(d, $^2J_{CP}$ = 1.2 Hz), 135.70 (ternary carbon nuclei), 129.91, 130.27, 130.78, 138.93, 151.45 (quaternary carbon nuclei), 193.00 (CO). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 23.44 (d, PPh_3, $^2J_{PP}$ = 45.7 Hz), 28.51 (d, PPh_3).

15: Yield, 76%. Mp: 184 °C. Anal. Calcd for $C_{19}H_{26}ClN_3O_5PdS$: C, 41.46; H, 4.76; N, 7.63; S, 5.82. Found: C, 41.48; H, 4.77; N, 7.46; S, 5.86. IR (cm^{-1}): ν(C═O), 1650; ν(ClO), 1090; δ(OClO), 620. Λ_M, 150 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (300 MHz, CD_2Cl_2): δ 2.09 (s, 3 H, Me), 2.56 (s, 3 H, Me), 2.76 (s, 3 H, Me), 2.77 (m, 4 H, CH_2), 2.90 (s, 3 H, Me), 4.47 (s, 1 H, CH), 7.00 [m, 1 H, H4 (py)], 7.58 [m, 7 H, H3 + H5 (py) +Ph], 7.95 [m, 1 H, H6 (py)]. $^{13}C\{^1H\}$ NMR: δ 45.73 (Me), 49.10 (Me), 50.98 (Me), 52.07 (Me), 60.91 (CH_2), 64.03 (CH_2), 52.60 (CH), 122.90, 123.09, 128.17, 129.55, 132.776, 139.86, 150.17 (ternary carbon nuclei), 140.74 (C_{ipso}), 172.75 (CS), 199.53 (CO).

16: Yield, 82%. Mp: 145 °C. Anal. Calcd for **16**·0.5CH_2Cl_2 $C_{23.5}H_{19}Cl_2N_3O_5PdS$: C, 44.60; H, 3.03; N, 6.64; S, 5.07. Found: C, 44.93; H, 2.99; N, 6.93; S, 5.33. IR (cm^{-1}): ν(C═O), 1650; ν(ClO), 1084; δ(OClO), 624. ^1H NMR (200 MHz, dmso-d_6): δ 5.68 (s, 1 H, CH), 5.76 (s, 1 H, CH_2Cl_2), 7.32−7.50 (m, 5 H), 7.78 (m, 2 H), 7.85−8.00 (m, 3 H), 8.31 (m, 2 H), 8.50−8.60 (m, 5 H).

Scheme 1



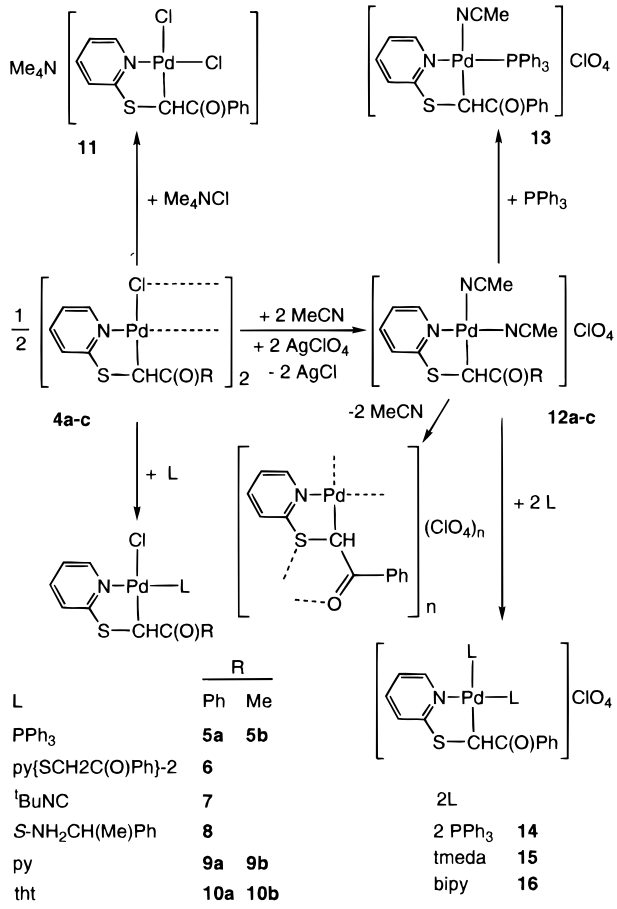
Results

Slow addition of an acetone solution of py{SCH_2C(O)Ph}-2 into a well-stirred solution of $[PdCl_2(NCPh)_2]$ in the same solvent causes spontaneous evolution of HCl and immediate precipitation of the dinuclear complex [Pd{py{SCHC(O)Ph}-2}(μ-Cl)$_2$Pd{py{SCH_2C(O)Ph}-2}-Cl] (**1**) in ca. 70% yield (see Scheme 1). The mother liquor is shown to contain (by ^1H NMR) a mixture of complexes that we could not separate. When py{SCH_2C(O)R}-2 (R = Me, OMe) are used instead, the same reaction workups also led to inseparable mixtures.

Coordination complexes [Pd{py{SCH_2C(O)R}-2}$_2Cl_2$] [R = Ph (**2a**), Me (**2b**), OMe (**2c**)] precipitate almost quantitatively by slow addition of $[PdCl_2(NCPh)_2]$ to an acetone solution containing ca. 2.3 equiv of the appropriate py{SCH_2C(O)R}-2 ligand (see Scheme 1). The order of addition of the reagents and their molar ratio must be observed because otherwise mixtures are obtained containing **2** and other insoluble species that we could not separate.

Dicyclometalated complexes *cis*-[Pd{py{SCHC(O)R}-2}$_2$] [R = Ph (**3a**), Me (**3b**), OMe (**3c**)] were obtained in

Scheme 2



L	R = Ph	R = Me
PPh_3	**5a**	**5b**
py{SCH2C(O)Ph}-2	**6**	
^{t}BuNC	**7**	
S-$NH_2CH(Me)Ph$	**8**	
py	**9a**	**9b**
tht	**10a**	**10b**

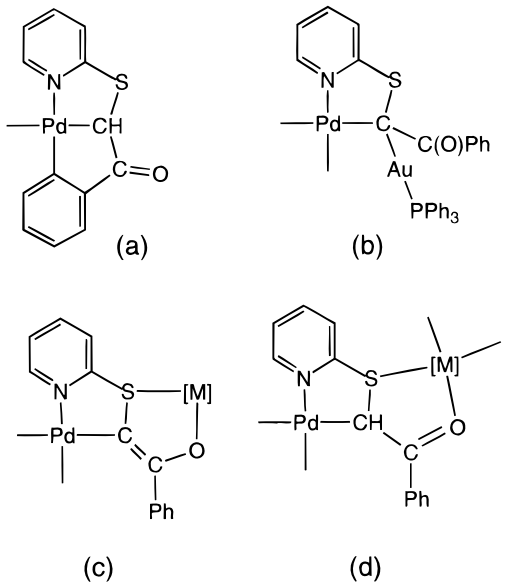
2L	
2 PPh_3	**14**
tmeda	**15**
bipy	**16**

good yields by deprotonation of both methylene groups present in complexes **2** (see Scheme 1). Thus, refluxing **2a** or **2b** with an excess of Na_2CO_3 allowed the synthesis of complex **3a** or **3b**, which were separated from the unreacted Na_2CO_3 and the byproduct NaCl by extraction with dichloromethane. Complex **2c** does not react with Na_2CO_3, but it does do so with NaH to give **3c**.

The spirocomplexes **3a**−**c** are efficient transmetalating agents toward $[PdCl_2(NCPh)_2]$, and the room-temperature reaction of equimolar amounts of both reagents in acetone gives high yields of the insoluble dinuclear complexes $[\overline{Pd\{py\{SCHC(O)R\}\text{-}2\}}(\mu\text{-}Cl)]_2$ [R = Ph (**4a**), Me (**4b**), OMe (**4c**)]. Complexes **4a**−**c** can also be obtained in good yield by reacting $[PdCl_2(NCPh)_2]$ with the appropriate py{$SCH_2C(O)R$}-2 (R = Ph, Me, OMe) ligand and Na_2CO_3 in 2:2:1 molar ratio.

Complexes **4a**,**b** have been used as starting materials for the synthesis of various cyclometalated neutral, anionic, and cationic species (see Scheme 2). Thus, addition of neutral ligands to suspensions of **4a,b** gives solutions from which neutral complexes $[\overline{Pd\{py\{SCHC(O)R\}\text{-}2\}}Cl(L)]$ [R = Ph, L = PPh_3 (**5a**), py{$SCH_2C(O)Ph$}-2 (**6**), ^{t}BuNC (**7**), *S*-$NH_2CH(Me)Ph$ (**8**), py (**9a**), tetrahydrothiophene (tht) (**10a**); R = Me, L = PPh_3 (**5b**), py (**9b**), tht (**10b**)], which result from bridge cleavage and coordination of the neutral ligand L, can be isolated. We could not separate the 1:1 *RS*-**8** + *SS*-**8** mixture even after recrystallizing it several times.

Chart 2



Similarly, the reaction of **4a** with Me_4NCl gives the anionic complex $Me_4N[\overline{Pd\{py\{SCHC(O)Ph\}\text{-}2\}}Cl_2]$ (**11**), whereas cationic complexes $[\overline{Pd\{py\{SCHC(O)R\}\text{-}2\}}(NCMe)_2]ClO_4$ [R = Ph (**12a**), Me (**12b**), OMe (**12c**)] can be obtained by reacting the corresponding complex **4** with 2 equiv of $AgClO_4$ in acetonitrile. After removing AgCl by filtration, the complexes precipitate upon addition of diethyl ether to the concentrated solution. Complex **12a** decomposes in dichloromethane or acetone to give a brick red insoluble product. In the case of dichloromethane, this product analyzes as "Pd{py{SCHC(O)Ph}}$(ClO_4)\cdot 0.5Cl_2CH_2$" (29% yield), and from the mother liquor complexes containing H_2O (by IR) could be isolated. Complexes **12b** and **12c** are rather more unstable, requiring recrystallization from acetonitrile. Despite this, they always give elemental analyses with low C, H, N, and S values that we attribute to contamination with palladium or palladium-rich decomposition products. This is why we decided to explore only the reactivity of the stable complex **12a**.

Complex **12a** reacts with neutral monodentate or chelating ligands to give various cationic derivatives (see Scheme 2) depending on the molar ratio of the reagents. Thus, complex $[\overline{Pd\{py\{SCHC(O)Ph\}\text{-}2\}}(NCMe)(PPh_3)]ClO_4$ (**13**) was obtained by addition of 1 equiv of PPh_3 to a suspension of **12a** in acetonitrile, whereas complexes $[\overline{Pd\{py\{SCHC(O)Ph\}\text{-}2\}}L_2]ClO_4$ [L = PPh_3 (**14**), L_2 = tmeda, (**15**), bpy (**16**)] were prepared by adding solid **12a** to a dichloromethane solution containing 2 equiv of PPh_3 or 1 equiv of tmeda or bpy, respectively. If the order of addition of the reagents is reversed, mixtures are obtained containing complexes **14**−**16** and the above-mentioned products that result when **12a** is dissolved in dichloromethane.

So far, starting from some of the above complexes, we have unsuccessfully attempted (i) to oxidize them to sulfoxides or sulfones, (ii) to deprotonate the CH group to give complexes a−c (Chart 2), (iii) to use them as sulfur or sulfur and oxygen donor ligands to prepare complexes of type d (See Chart 2), and (iv) to prepare

complexes resulting from insertion of alkynes, isocyanides, or carbon monoxide.

Discussion

Syntheses of Complexes. It is reasonable to assume that the slow addition of py{$SCH_2C(O)Ph$}-2 to [$PdCl_2(NCPh)_2$] first gives a monoadduct (e.g., [Pd{py{$SCH_2C(O)R$}-2}Cl(μ-Cl)]$_2$). This compound must be the precursor of **1** after a spontaneous cyclometalation (Scheme 1). The extreme insolubility of **1** prevents further cyclometalation to give **4a**. However, **4a** is obtained by reacting **1** with Na_2CO_3 (2:1) (Scheme 1). Equally reasonable is the assumption that the diadducts **2a**−**c**, formed by slow addition of [$PdCl_2(NCPh)_2$] to a solution of py{$SCH_2C(O)R$}-2, do not cyclometalate spontaneously because of their insolubility. However, the formation of the dicyclometalated complexes **3a**−**c** is possible if a base is added. In the case of **3a** (R = Ph) and **3b** (R = Me) Na_2CO_3 can be used as the base, but **2c** does not react with Na_2CO_3, and the stronger base NaH had to be used to achieve deprotonation. This difference may be attributed to the strong +I effect of the methoxy group, which decreases the acidity of the methylene protons in complex **2c**. Complexes **3a**−**c** are examples of the rare type of complexes obtained by cyclopalladation reactions involving two C−H bond activations of two ligands per palladium atom (1M2C2L in Chart 1). The transmetalation of one alkyl group from **3a**−**c** to [$PdCl_2(NCPh)_2$] gives complexes **4a**−**c**. We have used the same method in the synthesis of mono-*o*-nitrophenylpalladium complexes from bis-*o*-nitrophenylpalladium.[83]

Neutral and anionic complexes have been prepared by reacting **4a**−**c** with neutral or anionic ligands that cleave the chloro bridge (Scheme 2). The product of the reaction between **4a**−**c** and $AgClO_4$ in acetonitrile allows the preparation of the solvento complexes **12a**−**c**. Complex **12a** is stable in acetonitrile, but its solution in dichloromethane changes from yellow to orange and slowly precipitates as a brick red insoluble product analyzing as "Pd{py{SCHC(O)Ph}}(ClO_4)·0.5Cl_2CH_2". It is reasonable to asume that polymerization is achieved by coordination of the sulfur and the oxygen atoms (see Scheme 2). Complex **12a** has been used to prepare other cationic complexes **13**−**16.**

Structure of Complexes. The crystal structure of **3a** shows a spiro complex in which the palladium atom is coordinated to the nitrogen and methylene carbon atoms of two mutually cis-anionic py{SCHC(O)Ph}-2 ligands in a distorted square planar environment. The bite angles of the chelating ligands are narrower [82.25(13)° and 84.08(13)°] and, correspondingly, the other two angles are wider than the ideal value of 90° [97.08(14)°, 97.74(11)°]. The bond distances and angles differ marginally from one metalacycle to the other. The Pd−N [2.093(3) and 2.112(3) Å] and Pd−C [2.056(4) and 2.071(3) Å] bond distances are similar to those found for other Pd(II) complexes with pyridine trans to a secondary alkyl ligand.[84−86]

The crystal structure of **6**·$CDCl_3$ shows the palladium atom in a distorted square planar environment coordinated to a chelating py{SCHC(O)Ph}-2 and a chloro ligand and to the pyridinic nitrogen of a nonmetalated py{$SCH_2C(O)Ph$}-2 ligand. The palladium and the donor atoms are in a plane (mean deviation of the five atoms 0.007 Å) with the two nitrogen atoms mutually trans. The bond angles around the palladium atom are close to the expected 90° with the exception of the N(2)−Pd−C(6) angle [85.72(11)°] imposed by the chelating ligand. The bond distances and angles in the Pd−C(6)−S(2)−C(21)−N(2) heterocycle present in **6** are similar to their analogues in complex **3a**, except for the Pd−N bond distances, which in **6** [Pd−N(1), 2.040(2) Å; Pd−N(2), 2.045(2) Å] are appreciably shorter than that in **3a** [2.112(3) Å], consistent with the smaller trans-influence of nitrogen than carbon donor ligands. The bond distances in the nonmetalated ligand are similar to those in the chelating one, but the angles are appreciably different. In the absence of the restriction imposed by chelation, the Pd−N(1)−C(11) [120.4(2)°] and C(5)−S(1)−C(11) [103.8(2)°] are wider and closer to their ideal values. The Pd−Cl bond distance [2.3738(8) Å] is shorter than those found in some Pd(II) complexes with chloro trans to a secondary alkyl ligand [2.413−2.47 Å].[87−89] It is possible that the electron-withdrawing ability of the benzoyl group could reinforce the p(π)Cl−d(π)Pd bond component. Nonclassical hydrogen bonds C(12)−H(12)···O(2) [H···O 2.35 Å, C−H···O 156°] and C(99)−H(99)···Cl(1) [H···Cl 2.70 Å, C−H···Cl 149°] are observed.

^{1}H and ^{13}C NMR spectra of complex **1** could only be measured in dmso-d_6. As expected, they correspond to an equimolecular mixture of the two complexes resulting from bridge cleavage by the solvent, as shown by the singlet nature of the resonance due to the CH_2 protons (5.97 ppm). Otherwise, this should appear as an AB system as observed in complex **6** (4.70 ppm in $CDCl_3$). NMR spectra of complexes **2a**−**c** could not be measured because of their extreme insolubility. The ^{1}H NMR spectra of complexes **1** and **3**−**16** show the CH−Pd resonance in the range 3.95−5.97 (R = Ph), 3.54−4.74 (R = Me), or 3.71−4.63 ppm (R = OMe). The corresponding parent ligands show the CH_2 resonance at 4.71, 3.99, and 3.88 ppm, within the range of their complexes. As expected, in the series of complexes with R = Ph, the value of δ_{CH} is high for the cationic complex **14** (δ_{CH} = 5.97 ppm) and in the neutral complex **4a** (δ_{CH} = 5.21 ppm), where the electronegative Cl ligand is trans to the CH group, while complex **3a** shows the lowest value (δ_{CH} = 3.95 ppm). However, not all values of δ_{CH} are as easy to interpret on electronic grounds. Thus, that of the anionic complex **11** is 5.38 ppm, downfield shifted with respect to that in the neutral complex **5a** despite both having a chloro ligand trans to CH. Similarly, the CH proton is more deshielded in **3c** (4.06 ppm) than in **4c** (3.71 ppm), although both

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complexes are neutral and the latter has a more electronegative chloro ligand trans to CH.

Complexes **1**−**10** and **13** could be of cis or trans geometry, but, according to the NMR data obtained from those complexes sufficiently soluble in noncoordinating solvents (**3**−**10** and **13**), only one of the possible geometric isomers is obtained in all reactions. We propose a trans position of the pyridinic N atoms in complexes **2** and **9** because this is the geometry of complex **6**. Additionally, the IR spectrum of complex **9** suggests that the chloro ligand is trans to the carbon atom (see below). The NMR spectrum of complex **3c** (obtained after 1.5 h refluxing in chloroform of a mixture of **2c** and HNa) shows a double set of resonances, indicating a 1:1 mixture of the diastereoisomer RS and of the enantiomer pair RR + SS. However, the NMR spectrum of the analogous **3a** or **3b** (obtained after refluxing in acetone for 7 or 5 h a mixture Na_2CO_3 and **2a** or **2b**, respectively) shows that only the RS or the pair of enantiomers RR + SS is present in solution. We believe that in all three cases a mixture of the three stereoisomers initially forms and that on prolonged heating *RS*-**3** → *RR*-**3** + *SS*-**3**, or the reverse reaction, occurs. In fact, after refluxing **3c** in chloroform for 19 h and filtering off a small amount of precipitated palladium, the 1:1 mixture of stereoisomers transforms into *RS*-**3c** or *RR*-**3c** + *SS*-**3c**. According to the crystal structure of **3a** (q.v.), which shows it to be the RR isomer, this thermal reaction transforms *RS*-**3a** into *RR*-**3a** + *SS*-**3a**. A series of NOE experiments on complex **3a** prove that both chelating ligands also adopt a mutually cis disposition in solution. In fact, irradiation of the methynic C*H* proton enhances the resonance at 7.7 ppm, assigned to the ortho-proton of the phenyl group, but does not modify the intensity of the pyridinic H6 as would be expected for the trans isomer. Similarly, irradiation of H6 enhances the H4 resonance but not the CH resonance. The cis geometry of complexes **3** or the Cl trans to C disposition in complexes **5** or **7** accords with the inherent instability of Pd(II) complexes containing two carbon or one C and one P donor ligands in mutually trans positions (*transphobia*).[90,91]

The ^{1}H NMR spectrum of complex **4a** in dmso-d_6 shows one resonance for each type of proton, whereas in the case of complexes **4b** and **4c**, a double set of signals is observed. If, as expected, mononuclear species result from splitting of the chloro bridge and coordination of dmso, every set of resonances would correspond to one of the two possible geometrical isomers. The ^{1}H NMR spectrum of complex **8** shows duplicate resonances, indicating the formation of the isomers RS and SS in 1:1 molar ratio.

The resonance assignable to the H6 of the pyridine in the py{SCHC(O)R}-2 ligands can be unambiguously assigned in most complexes. In the R = Ph series, most complexes show this resonance downfield shifted [8.25−9.20 ppm] with respect to that in the free ligand (8.06 ppm), while in the spectra of **3a**, **12a,** and **15** it appears at 7.80, 8.05, and 7.95 ppm, respectively. All complexes with R = OMe show such resonance equally (**3c**, δ_{H6} = 8.24; **12c**, δ_{H6} = 8.25 ppm) or more (**3c**, δ_{H6} = 7.94 ppm) shielded than the free ligand (at 8.25 ppm).

The ^{13}C{^{1}H} NMR spectra of some of the reported complexes have also been measured and show the expected resonances due to the methyl [28.26 (**3b**), 32.90 (**3c**), 29.60 (**7**), 2.66 (**13**), 45.73, 49.10, 50.98, 52.07 (**15**) ppm], methylene [40.42 (**1**), 39.73 (**6**) 60.91, 64.03 (**15**) ppm], methyne [54.57 (**1**), 42.60 (**3a**), 46.38 (**3b**), 51.70 (**3c**), 54.62 (**4a**), 49.92 (**5a**), 45.21 (**6**), 45.26 (**7**), 44.25 (**12a**), 45.22 (**13**) 65.72 (**14**), 52.60 (**15**) ppm], aryl, pyridyl (range 119−175 ppm), and carbonyl [193.58, 194.53 (**1**), 197.38 (**3a**), 203.81 (**3b**), 176.71 (**3c**), 194.65 (**4a**), 197.03 (**5a**), 192.44 (**6**), 196.78 (**7**), 196.04 (**12a**), 198.93 (**13**), 193.00 (**14**), 199.53 (**15**) ppm] groups. The spectrum of **6** shows only one CO resonance (at 192.44 ppm), although two different carbonyl groups are present in the molecule. The spectrum of **7** does not show the quaternary ^{t}BuNC carbon nuclei even if it is measured overnight.

The ^{31}P{^{1}H} NMR spectra show singlet resonances for complexes **5a** (27.83 ppm), **5b** (29.82 ppm), and **13** (26.77 ppm) and two doublets for complex **14** (23.44, 28.51 ppm; $^2J_{PP}$ 45.7 Hz)

All complexes show one or in some cases two (**1**, **3a**, **6**) IR bands assignable to ν(C═O) mode in the ranges 1626−1690 (R = Ph), 1640−1690 (R = Me), and 1693−1746 cm^{-1} (R = OMe). The presence of two ν(C═O) bands in complexes **1** and **6** must be attributed to the presence of two different thiopyridine ligands, one N- and the other C,N-coordinated. Although two ν(C═O) bands should also be observed in the IR spectra of complexes **3a**−**c** and **4a**−**c**, with C_{2v} or lower symmetry, these are only observed in the spectrum of **3a**. Complexes **2a**, **6** (R = Ph), and **2c** (R = OMe), containing N-coordinated thiopyridine ligands, show the ν(C═O) band (1674, 1690, and 1746 cm^{-1}, respectively) close to that in the free ligand [1678 (R = Ph) and 1737 (R = OMe) cm^{-1}, respectively], while C,N-coordination causes the energy of this band to decrease by between 26 (**7**) and 55 (**3c**) cm^{-1}. Surprisingly, when R = Me (complexes **2b**−**10b** and **12b**), the ν(C═O) band (in the narrow range of 1640−1660 cm^{-1}) is of lower energy than that in the free ligand, irrespective of the coordination mode of the ligand or the charge of the complex.

The IR spectra of complexes **1** and **4a**−**c**, containing two bridging chloro ligands, show three or four medium bands in the 400−200 cm^{-1} region that could tentatively be assigned to ν(PdCl) modes [356, 304, 272 (**1**), 328, 294, 258 (**4a**), 314, 278, 254 (**4b**), 362, 334, 293, 265 (**4c**) cm^{-1}] according to the low symmetry of these complexes. In complexes **2**, the presence of only one band assignable to a ν(PdCl) mode is indicative of a trans geometry because two bands are expected for the cis C_{2v} isomers. In the IR spectrum of complex **11** the bands at 328 and 296 cm^{-1} must be assigned to the ν(PdCl) trans to nitrogen and carbon, respectively, according to the higher trans influence of carbon- than nitrogen-donor ligands. Most of the neutral complexes **5**−**10** show one ν(PdCl) band around 300 cm^{-1}, indicative of the chloro ligand being trans to carbon. However, unequivocal assingment of the ν(PdCl) bands in complexes **7** and **8** is not possible because they show two bands in the region 340−262 cm^{-1}, although according to NMR data their solutions contain only one geometrical isomer (see

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Experimental Section). In the case of **10b**, the unique band is observed in the middle of the range (311 cm^{-1}). Additionally, complex **7** shows a ν(CN) at 2232 cm^{-1}, **8** shows two ν(NH) bands at 3242, 3198 cm^{-1}, **11** shows at 952 cm^{-1} a band due to the NMe_4, and complexes **12**−**16** show two bands characteristic of the perchlorate anion in the ranges 1100−1090 [ν(ClO)] and 624−620 [δ(OClO)] cm^{-1}.

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Supporting Information Available: Tables giving crystal data and structure refinement details, atomic coordinates and equivalent isotropic displacement parameters, bond distances and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **3c** and **6**·$CDCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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