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Linkage Isomerism in Thiophene Cyclometallated Palladium(II) Complexes. Crystal and Molecular Structure of the Isomers [Pd{n-$SC_4H_2C(H){=}NCy$}-(O_2CMe-*O*)(PPh_3)] (n = 3, 4)

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Dedicated to Professor Joachim Strähle on the Occasion of his 70th Birthday

Abstract. Treatment of 2-$SC_4H_3C(H){=}NCy$, **a**, or 3-$SC_4H_3C(H){=}NCy$, **b**, with palladium(II) acetate in toluene gave the dinuclear cyclometallated complexes [Pd{n-$SC_4H_2C(H){=}NCy$}(O_2CMe)]$_2$ (n = 5, **1a**; n = 3, **1b**; n = 4, **1b′**), the latter two as a 1:1 mixture of linkage isomers, whose subsequent reactions produced isomeric mixtures in all cases. Reaction of **1a** and **1b**, **1b′** with aqueous sodium chloride or bromide yielded the corresponding halide-bridged complexes [Pd{n-$SC_4H_2C(H){=}NCy$}(X)]$_2$ (n = 5: X = Cl, **2a**; X = Br, **3a**; n = 3,4: X = Cl, **2b**, **2b′**; X = Br, **3b**, **3b′**) after metathesis. Reactions of the dinuclear compounds with tertiary phosphines in the appropriate molar ratio gave the mononuclear [Pd{n-$SC_4H_2C(H){=}NCy$}(Cl)(PPh_3)] (n = 5, **6a**; n = 3, 4 **4b**, **4b′**) and [Pd{5-$SC_4H_2C(H){=}NCy$}{($Ph_2PCH_2CH_2)_2PPh$-*P,P,P*}](Cl), (**5a**), and the dinuclear [{Pd[5-$SC_4H_2C(H){=}NCy$](O_2CMe)}$_2$-{μ−$Ph_2P(CH_2)_nPPh_2$}] (n = 2, **7a**; n = 3, **8a**; n = 4, **9a**) complexes. The X-ray crystal structure of complex **4b**, **4b′** is described, establishing the presence of two isomers in the crystal lattice.

Keywords: Palladium; Cyclometallation; C-H activation; Isomerism; Phosphines

1 Introduction

Cyclometallation, of which palladacycles constitute a more than fair percentage, represents a flourishing topic in organometallic chemistry for which several reviews have appeared [1−5]. Most significant amongst their characteristics are the outstanding applications they show, such as their use as intermediates in organic and organometallic synthesis [5, 6], the design of liquid crystals [7] or their pharmacological usage [8] inclusive of their antitumoral activities [9−12].

Although many organic ligands are known to undergo metallation by palladium the majority hold phenyl rings, with cyclometallated heterocycles being more scarce. In the case of thiophene derivatives the presence of the *N,N*-dimethyl group at the C=X (X = S, Se) atom has proven to be a good substituent that promotes cyclometallation; thus, thiophene palladacycles have been reported for *N,N*-dimethylthiophene- carboseleno and thioamides [13], as well as for thienylbipyridine [14]. Nevertheless, similar palladium species with thiophene Schiff base ligands bearing no substituents at the imine nitrogen atom are to the best of our knowledge outstanding, more so when the question of regioselectivity arises, as is the case of ligand **b** described below, where metallation may come about through the C2 or C5 atoms. In previous findings [13a] where more than one metallation site was possible only one species was obtained, namely that pertaining to the metallation of the carbon atom in *ortho* to the sulfur atom, with the alleged isomerism being due only to the *cis* or *trans* arrangement of the ligands at palladium; this was also the case for related platinocycles with an unsubstituted imine carbon atom [15].

Herein we report the first examples of Schiff base thiophene palladacyles which demonstrate that absence of bulky groups at the imine carbon atom are unneeded to establish palladation of the organic moiety, as was found for the related platinocycles [15], and that regioselectivity allows formation of species holding different metallated carbon atoms thus giving rise to linkage isomerism in these complexes. Moreover, the 1:1 mixture of isomers derived from ligand **b** proved to be inseparable to the point that both moieties co-crystallized in an unprecedented structure that deemed indistinguishable the two isomers throughout the crystal array.

2 Experimental Section

General procedures

Solvents were purified by standard methods [16]. Chemicals were reagent grade. Palladium(II) acetate was purchased from

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Alfa Products. The phosphines, PPh_3, $Ph_2P(CH_2)_2PPh_2$, $Ph_2P(CH_2)_3PPh_2$, $Ph_2P(CH_2)_4PPh_2$, and thallium acetylacetonate, Tl(acac), were purchased from Aldrich-Chemie. Microanalyses were carried out at the Servicio de Análisis Elemental at the Universidad of Santiago de Compostela using a Carlo Erba Elemental Analyzer Model EA1108. IR spectra were recorded as Nujol mulls or KBr discs with a Perkin-Elmer 1330, with a IR-FT Mattson Model Cygnus-100 and with a Bruker Model IFS-66V spectrophotometers. NMR spectra were obtained as $CDCl_3$ solutions and referenced to $SiMe_4$ (^1H) or H_3PO_4 ($^{31}P\ \{^1H\}$) and were recorded with Bruker AMX 300, AMX 500 and WM250 spectrometers. All chemical shifts are reported downfield from standards. The FAB mass spectra were recorded with a Fisons Quatro mass spectrometer with a Cs ion gun; 3-nitrobenzyl alcohol was used as the matrix.

Syntheses

Preparation of $2\text{-}SC_4H_3C(H){=}NCy$ (a). Thiophen-2-carboxyaldehyde (4 g, 35.7 mol) and cyclohexylamine (3.9 g, 39.2 mmol) were refluxed together in chloroform (25 cm^3) in a Dean-Strak apparatus for 4 h, after which the solvent was removed under vacuum to give a dark-yellow oily liquid, which was dried under vacuum. Yield: 656 mg, 95 %. Anal. Found: C 68.2; H 7.7; N 7.3; S 16.5; $C_{11}H_{15}NS$ (193.3 g/mol) requires C 68.4; H 7.8; N 7.3; S 16.6 %.

IR (cm^{-1}): ν(C=N) 1632s. **^{1}H NMR** ($CDCl_3$, δ ppm, *J* Hz): 8.39 (s, 1H, *H*C=N), 7.35, 7.28, 7.05 (ABX, 3H, H2, H3, H4, [^3J(H2H3) 4.9, ^3J(H3H4) 4.5, ^4J(H2H4) 1.1]), 3.16 (m, H_{ipso}Cy). FAB-MS: *m*/*z* 193 $[M]^+$.

Ligand **b** was prepared similarly.

$3\text{-}SC_4H_3C(H){=}NCy$ (b). Yield: 663 mg, 96 %. Anal. Found: C 68.1; H 7.8; N 7.2; S 16.4; $C_{11}H_{15}NS$ (193.3 g/mol) requires C 68.4; H 7.8; N 7.3; S 16.6 %.

IR (cm^{-1}): ν(C=N) 1636s. **^{1}H NMR** ($CDCl_3$, δ ppm, *J* Hz): 8.31 (s, 1H, *H*C=N), 7.55, 7.53, 7.29 (ABX, 3H, H2, H4, H5, [^4J(H2H4) 1.1, ^4J(H2H5) 2.9, ^3J(H4H5) 5.1]), 3.12 (m, H_{ipso}Cy). **FAB-MS**: *m*/*z* 193 $[M]^+$.

Preparation of $[Pd\{5\text{-}SC_4H_2C(H){=}NCy\}(O_2CMe)]_2$ (1a). $2\text{-}SC_4H_3C(H){=}NCy$ (0.27 g, 1.3 mmol) and palladium(II) acetate (0.3 g, 1.3 mmol) were added to 25 cm^3 of dry toluene to give a yellow solution which was heated at 80 °C for 3 h under argon. After cooling to room temperature the solution was filtered to eliminate the small amount of black palladium formed. The solvent was removed under vacuum to give an orange solid which was chromatographed on a column packed with silica gel. Elution with dichloromethane / methanol (1 %) afforded the final product after concentration, which was recrystallized from chloroform/*n*-hexane. Yield: 288 mg, 62 %. Anal. Found: C 43.5; H 4.9; N 3.8; S 8.9; $C_{26}H_{34}N_2O_4S_2Pd_2$ (715.53 g/mol) requires C 43.6; H 4.8; N 3.9; S 9.0 %.

IR (cm^{-1}): ν(C=N) 1608m, ν_{as}(COO) 1580m, ν_s(COO) 1518m. **^{1}H NMR** ($CDCl_3$, δ ppm, *J* Hz): 7.87 (s, 1H, *H*C=N), 7.36 (d, 1H, H3, ^3J(H3H4) 4.9), 7.23 (d, 1H, H4, ^3J(H3H4) 4.9), 3.58 (m, H_{ipso}Cy), 1.94 (s, 3H, O_2CMe). **FAB-MS**: *m*/*z* 715 $[M]^+$.

Compiund **1b** was synthesized in a similar fashion as a mixture of isomers.

$[Pd\{n\text{-}SC_4H_2C(H){=}NCy\}(O_2CMe)]_2$ (n = 3, 1b; n = 4, 1b′). Yield: 340 mg, 73 %. Anal. Found: C 43.5; H 4.6; N 3.8; S 9.0; $C_{26}H_{34}N_2O_4S_2Pd_2$ (715.53 g/mol) requires C 43.6; H 4.8; N 3.9; S 9.0 %.

IR (cm^{-1}): ν(C=N) 1610m, ν_{as}(COO) 1575m, ν_s(COO) 1417m. **^{1}H NMR** ($CDCl_3$, δ ppm, *J* Hz): 7.27, 7.25 (s, 1H, *H*C=N), 6.96 (d, 1H, H4, ^3J(H4H5) 5.4), 6.90 (s, 1H, H3), 6.85 (d, 1H, H5, ^3J(H4H5) 5.4), 6.77 (s, 1H, H5), 3.05, 3.1 (m, H_{ipso}Cy), 2.17, 2.13 (s, 3H, O_2CMe). **FAB-MS**: *m*/*z* 715 $[M]^+$.

Preparation of $[Pd\{5\text{-}SC_4H_2C(H){=}NCy\}(Cl)]_2$ (2a). To a solution of **1a** (100 mg, 0.14 mmol) in 25 cm^3 of acetone, an aqueous solution of sodium bromide (*ca.* 10^{-2} M) was added and the mixture stirred at room temperature for 3 h, after which water was added and the solid formed was filtered off and dried *in vacuo*. Yield: 691 mg, 74 %. Anal. Found: C 39.4; H 4.2; N 4.1; S 9.4; $C_{22}H_{28}Cl_2N_2S_2Pd_2$ (668.35 g/mol) requires C 39.5; H 4.2; N 4.2; S 9.6 %.

IR (cm^{-1}): ν(C=N) 1613m, ν(Pd−Cl) 290m, 246m. **^{1}H NMR** ($CDCl_3$, δ ppm, *J* Hz): 7.71 (s, 1H, *H*C=N), 7.36 (d, 1H, H3, ^3J(H3H4) 4.9), 7.12 (d, 1H, H4, ^3J(H3H4) 4.9), 3.56 (m, H_{ipso}Cy). **FAB-MS**: *m*/*z* 668 $[M]^+$.

Compounds **3a**, **2b** and **3b** were prepared analogously.

$[Pd\{5\text{-}SC_4H_2C(H){=}NCy\}(Br)]_2$ (3a). Yield: 763 mg, 72 %. Anal. Found: C 34.7; H 3.6; N 3.7; S 8.3; $C_{22}H_{28}Br_2N_2S_2Pd_2$ (757.25 g/mol) requires C 34.9; H 3.7; N 3.7; S 8.5 %.

IR (cm^{-1}): ν(C=N) 1614m. **^{1}H NMR** ($CDCl_3$, δ ppm, *J* Hz): 7.76 (s, 1H, *H*C=N), 7.36 (d, 1H, H3, ^3J(H3H4) 4.9), 7.23 (d, 1H, H4, ^3J(H3H4) 4.9), 3.73 (m, H_{ipso}Cy). **FAB-MS**: *m*/*z* 757 $[M]^+$.

$[Pd\{n\text{-}SC_4H_2C(H){=}NCy\}(Cl)]_2$ (n = 3, 2b; n = 4, 2b′). Yield: 730 mg, 78 %. Anal. Found: C 39.3; H 4.1; N 4.1; S 9.5; $C_{22}H_{28}Cl_2N_2S_2Pd_2$ (668.35 g/mol) requires C 39.5; H 4.2; N 4.2; S 9.6 %.

IR (cm^{-1}): ν(C=N) 1612m, ν(Pd−Cl) 287m, 241m. **^{1}H NMR** ($CDCl_3$, δ ppm, *J* Hz): 7.76, 7.65 (s, 1H, *H*C=N), 7.03 (d, 1H, H4, ^3J(H4H5) 5.3), 6.95 (s, 1H, H3), 6.84 (d, 1H, H5, ^3J(H4H5) 5.3), 6.75 (s, 1H, H5), 3.85 (m, H_{ipso}Cy). **FAB-MS**: *m*/*z* 668 $[M]^+$.

$[Pd\{n\text{-}SC_4H_2C(H){=}NCy\}(Br)]_2$ (n = 3, 3b; n = 4, 3b′). Yield: 859 mg, 72 %. Anal. Found: C 34.6; H 3.6; N 3.7; S 8.4; $C_{22}H_{28}Br_2N_2S_2Pd_2$ (757.25 g/mol) requires C 34.9; H 3.7; N 3.7; S 8.5 %.

IR (cm^{-1}): ν(C=N) 1620m. **^{1}H NMR** ($CDCl_3$, δ ppm, *J* Hz): 7.66, 7.58 (s, 1H, *H*C=N), 7.05 (d, 1H, H4, ^3J(H4H5) 5.3), 7.0 (s, 1H, H3), 6.95 (d, 1H, H5, ^3J(H4H5) 5.3), 6.88 (s, 1H, H5), 3.85 (m, H_{ipso}Cy). **FAB-MS**: *m*/*z* 757 $[M]^+$.

Preparation of $[Pd\{5\text{-}SC_4H_2C(H){=}NCy\}(MeCOCHCOMe\text{-}\mathit{O,O})]$ (4a). The chloro-bridged complex, **2a**, (20 mg, 0.03 mmol) and thallium acetylacetonate (18 mg, 0.16 mmol) were stirred together in chloroform (25 cm^3) at room temperature for 2 h. The resulting mixture was chromatographed on a column packed with silica gel. Elution with dichloromethane/chloroform (3:1) gave a yellow residue after concentration, which was recrystallised from dichloromethane/hexane to give the required complex as a yellow solid. Yield: 203 mg, 85 %. Anal. Found: C 48.1; H 5.2; N 3.5; S 8.0; $C_{16}H_{21}NO_2SPd$ (397.83 g/mol) requires C 48.3; H 5.3; N 3.5; S 8.1 %.

IR (cm^{-1}): ν(C=N) 1600m, acac: ν(C−C) 1576s, ν(C−O) 1518s. **^{1}H NMR** ($CDCl_3$, δ ppm, *J* Hz): 7.73 (s, 1H, *H*C=N), 7.09 (d, 1H, H3, ^3J(H3H4) 4.9), 6.96 (d, 1H, H4, ^3J(H3H4) 4.9), 5.34 (s, 1H, C*H*), 3.54 (m, H_{ipso}Cy), 2.05 (s, 3H, C*Me*), 2.01 (s, 3H, C*Me*). **FAB-MS**: *m*/*z* 398 $[M]^+$.

Preparation of $[Pd\{5\text{-}SC_4H_2C(H){=}NCy\}\{(Ph_2PCH_2CH_2)_2PPh\text{-}\mathit{P,P,P}\}](Cl)$ (5a). To a solution of **1a** (21 mg, 0.03 mmol) in acetone (15 cm^3) $(Ph_2PCH_2CH_2)_2PPh$ (16 mg, 0.06 mmol) was added. The resulting mixture was stirred at room temperature for 24 h after which the complex was then precipitated out by addition of water, filtered off, dried *in vacuo* and recrystallized from dichloromethane/n-hexane. Yield: 395 mg, 79 %. Anal. Found: C 64.7; H 5.6; N 1.7; S 3.8; $C_{45}H_{47}NP_3SPd$ (833.27 g/mol) requires C 64.9; H 5.7; N 1.7; S 3.9 %.

IR (cm^{-1}): ν(C=N) 1618m. **^{1}H NMR** ($CDCl_3$, δ ppm, J Hz): 7.93 (s, 1H, *H*C=N), 7.01 (dd, 1H, H3, ^4J(PH) 5.7, ^3J(H3H4) 4.9), 3.58 (m, H_{ipso}Cy). **^{31}P {^{1}H} NMR** ($CDCl_3$, δ ppm, J Hz): 91.7 (t, 1P, J(PP) 27.1), 41.4 (d, 2P, J(PP) 27.1). **FAB-MS**: *m*/*z* 833 [M]$^+$.

Preparation of [Pd{5-SC_4H_2C(H)=NCy}(Cl)(PPh_3)] (6a). To **2a**, (50 mg, 0.075 mmol) in dichloromethane (15 cm^3), PPh_3 (39 mg, 0.15 mmol) was added in a halide-bridged complex/phosphine 1:2 molar ratio. The mixture was stirred for 4 h, filtered over celite to remove Pd(0), and the solvent eliminated under reduced pressure. The residue was recrystallised from dichloromethane/hexane. Yield: 79 mg, 88 %. Anal. Found: C 58.1; H 4.7; N 2.3; S 5.3; $C_{29}H_{29}ClNPPdS$ (596.46 g/mol) requires C 58.4; H 4.9; N 2.4; S 5.4 %.

IR (cm^{-1}): ν(C=N) 1613m. **^{1}H NMR** ($CDCl_3$, δ ppm, J Hz): 8.1 (d, 1H, *H*C=N, ^4J(PH) 7.2), 6.95 (d, 1H, H4, ^3J(H3H4) 5.1), 5.90 (dd, 1H, H3, ^4J(PH) 5.5, ^3J(H3H4) 5.1), 3.60 (m, H_{ipso}Cy). **^{31}P {^{1}H} NMR** ($CDCl_3$, δ ppm): 26.6s **FAB-MS**: *m*/*z* 596 [M]$^+$.

Compound **4b** was prepared analogously from **1b**.
[Pd{n-SC_4H_2C(H)=NCy}(O_2CMe)(PPh_3)] (n = 3, 4b; n = 4, 4b′) − Yield: 882 mg, 79 %. Anal. Found: C 60.0; H 5.1; N 2.3; S 5.1; $C_{31}H_{32}NO_2PSPd$ (620.3 g/mol) requires C 60.1; H 5.2; N 2.3; S 5.2 %.

IR (cm^{-1}): ν(C=N) 1615m, ν_{as}(COO) 1503m, ν_s(COO) 1387m. **^{1}H NMR** ($CDCl_3$, δ ppm, J Hz): 7.93, 7.86 (d, 1H, *H*C=N, ^4J(PH) 6.8), 7.01 (d, 1H, H4, ^3J(H4H5) 4.9), 6.90 (d, 1H, H3, ^4J(PH) 5.2), 6.78 (d, 1H, H5, ^3J(H4H5) 5.3), 6.72 (s, 1H, H5), 3.58 (m, H_{ipso}Cy), 2.10 (s, 3H, O_2C*Me*). **^{31}P {^{1}H} NMR** ($CDCl_3$, δ ppm): 34.7s, 34.1s.

Preparation [{Pd[5-SC_4H_2C(H)=NCy](O_2CMe)}$_2${μ−$Ph_2P(CH_2)_2$-PPh_2-*P,P*}] (7a). 1,2-bis(diphenylphosphino)ethane (28 mg, 0.07 mmol) was added to a solution of complex **1a** (50 mg, 0.07 mmol) in acetone (15 cm^3). The mixture was stirred for 3 h, and the resulting orange solid filtered off and dried. Yield: 64 mg, 82 %. Anal. Found: C 56.0; H 5.3; N 2.4; S 5.7; $C_{52}H_{58}N_2O_4P_2Pd_2S_2$ (1113.95 g/mol) requires C 56.1; H 5.3; N 2.5; S 5.8 %.

IR (cm^{-1}): ν(C=N) 1618m, ν_{as}(COO) 1505m, ν_s(COO) 1390m. **^{1}H NMR** ($CDCl_3$, δ ppm): 7.84 (d, 1H, *H*C=N, ^4J(PH 7.7), 7.0 (d, 1H, H4, ^3J(H3H4) 4.6), 5.97 (dd, 1H, H3, ^4J(PH) 5.7, ^3J(H3H4) 4.6), 3.65 (m, H_{ipso}Cy), 1.95 (s, 3H, O_2C*Me*). **^{31}P {^{1}H} NMR** ($CDCl_3$, δ ppm): 26.6s.

Compounds **8a** and **9a** were prepared analogously.
Preparation of [{Pd[5-SC_4H_2C(H)=NCy](O_2CMe)}$_2${μ−Ph_2P-$(CH_2)_3PPh_2$-*P,P*}] (8a). Yield: 67 mg, 85 %. Anal. Found: C 56.2; H 5.3; N 2.4; S 5.5; $C_{53}H_{60}N_2O_4P_2Pd_2S_2$ (1127.97 g/mol) requires C 56.4; H 5.4; N 2.5; S 5.7 %.

IR (cm^{-1}): ν(C=N) 1618m, ν_{as}(COO) 1501m, ν_s(COO) 1385m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): **^{1}H NMR** ($CDCl_3$, δ ppm, J Hz): 7.95 (d, 1H, *H*C=N, ^4J(PH 7.5), 6.8 (d, 1H, H4, ^3J(H3H4) 4.8), 6.0 (dd, 1H, H3, ^4J(PH) 5.2, ^3J(H3H4) 4.8), 3.48 (m, H_{ipso}Cy), 1.90 (s, 3H, O_2C*Me*). **^{31}P {^{1}H} NMR** ($CDCl_3$, δ ppm): 23.5 s.

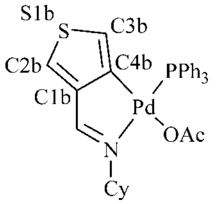
Preparation of [{Pd[5-SC_4H_2C(H)=NCy](O_2CMe)}$_2${μ−Ph_2P-$(CH_2)_4PPh_2$-*P,P*}] (9a). Yield: 63 mg, 79 %. Anal. Found: C 56.5; H 5.4; N 2.4; S 5.6; $C_{54}H_{62}N_2O_4P_2Pd_2S_2$ (1142.0 g/mol) requires C 56.8; H 5.5; N 2.5; S 5.6 %.

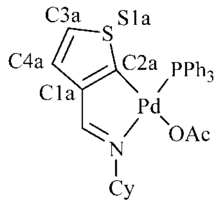
IR (cm^{-1}): ν(C=N) 1618m, ν_{as}(COO) 1504m, ν_s(COO) 1389m. **^{1}H NMR** ($CDCl_3$, δ ppm, J Hz): 7.93 (d, 1H, *H*C=N, ^4J(PH 7.8), 6.9 (d, 1H, H4, ^3J(H3H4) 4.4), 6.01 (dd, 1H, H3, ^4J(PH) 5.3, ^3J(H3H4) 4.4), 3.6 (m, H_{ipso}Cy), 1.89 (s, 3H, O_2C*Me*). **^{31}P {^{1}H} NMR** ($CDCl_3$, δ ppm): 24.8 s.

Crystal structure

Crystals of complex **4b**, **4b′** were mounted on a glass fiber and transferred to the diffractometer. Three-dimensional, room temperature X-ray data were collected in the θ range 1.84 to 28.28° on a Siemens Smart CCD diffractometer by the omega/2-theta scan method, using monochromated Mo-K_α radiation. Of the 9858 reflections measured, all of which were corrected for Lorentz and polarisation effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections, 5963 independent reflections exceeded the significance level $|F|/\sigma|F| > 4.0$. The structure was 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.

The two isomers **4b** and **4b′** crystallized with all their atoms occupying the same crystallographic positions except C(1a), S(1a) and C(2b), S(1b). In view of the close overlap between C(1a) and S(1b), and C(2b) and S(1a) bond length restrains were imposed during the refinement. The occupancies of the two pairs of positions were tied to give an overall value of 1.0 and then refined giving values of, approximately 0.5 for each component. All the measured reflections were corrected for Lorentz and polarization effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections [T_{max}/T_{min} = 0.7658 and 0.6889]. The structure was 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 = 0.0290 (wR_2 = 0.0719 for all 6574 data, 336 parameters, mean and maximum δ/σ = 0.000, 0.001) with allowance for thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density −0.673 and 0.423 eÅ^{-3}. The structure solution and refinement were carried out using the program package SHELX-97 [17].





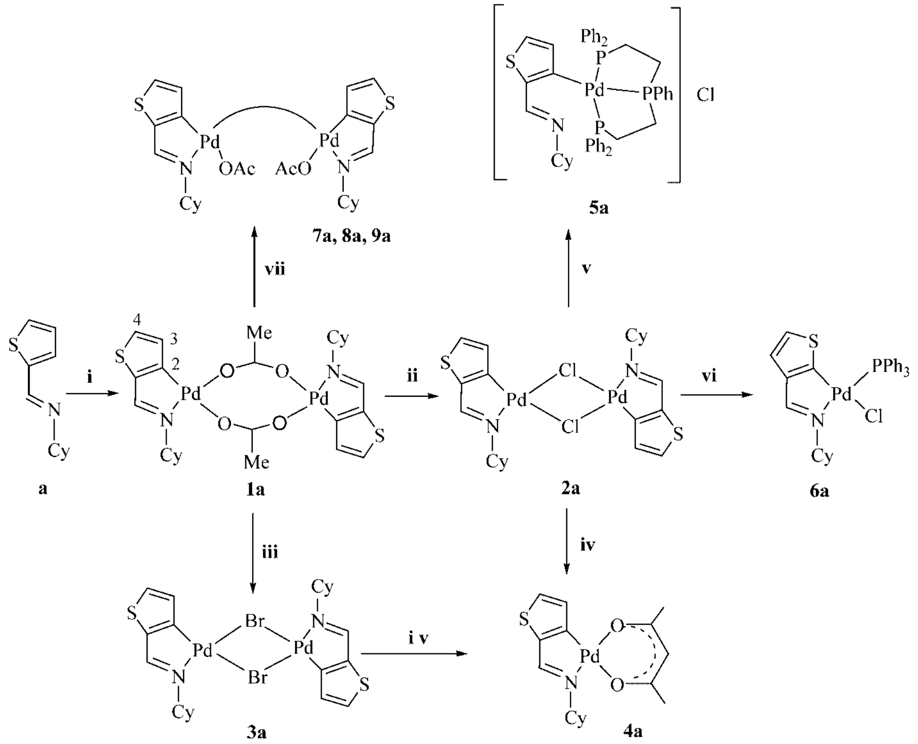
Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 631115. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

3 Results and Discussion

Synthesis and characterization

The compounds and reactions are shown in Schemes 1 and 2. The compounds were characterized by elemental analysis and by IR and by ^{1}H and ^{31}P {^{1}H} NMR spectroscopy, and (in part) by FAB mass spectrometry.

Treatment of 2-SC_4H_3C(H)=NCy, **a**, with palladium(II) acetate in toluene at 80 °C for two hours gave a yellow crystalline solid identified as the cyclometallated product derived from C-H activation at the 2-position, **1a**. The ^{1}H NMR spectrum for **1a** showed the absence of the ABX pattern in the parent ligand; thus, two doublets at δ = 7.23 and δ = 7.36 were assigned to the AB system for the H3



Scheme 1 (i) $Pd(AcO)_2$ / Toluene; (ii) NaCl/ acetone/water; (iii) NaBr/ acetone/water; (iv) Tl(acac) / $CHCl_3$; (v) $(Ph_2PCH_2CH_2)_2PPh$ / acetone; (vi) PPh_3 / acetone; (vii) $Ph_2P(CH_2)_nPPh_2$ / acetone (n = 2, **7a**; n = 3, **8a**; n = 4, **9a**)

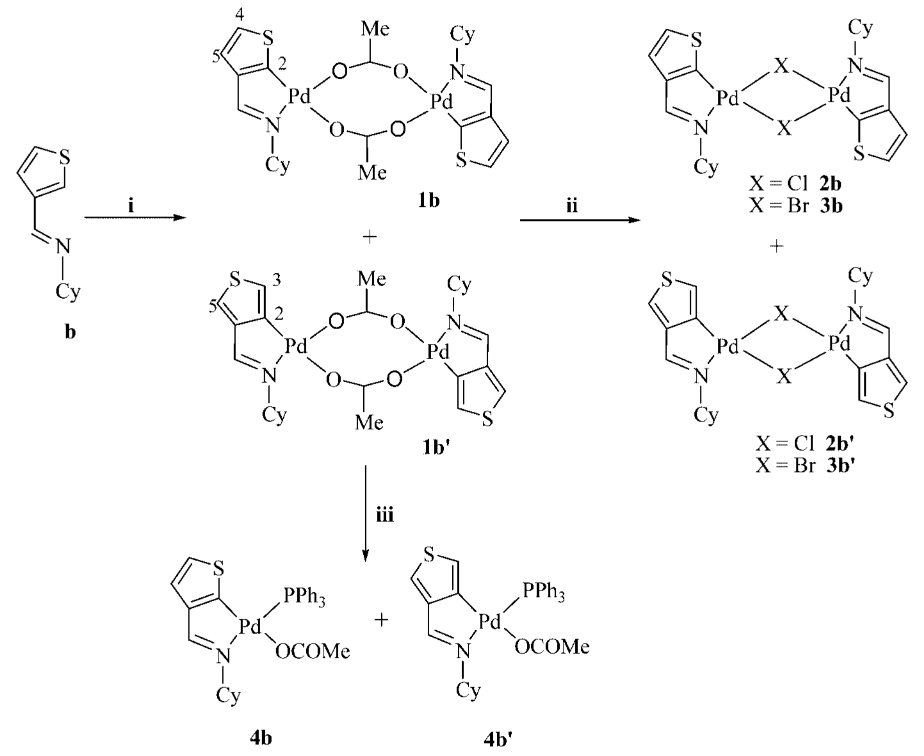
and H4 protons [^3J(HH = 4.9 Hz], respectively, with the signal for the H2 nucleus absent upon metallation at C2. In the IR spectra of the complexes the ν(C=N) stretch appeared at lower frequency than the corresponding one in the free ligand in accordance with nitrogen coordination to metal atom [18]. This was supported by the upfield shift of the NMR signal for the *H*C=N proton, *ca.* 1 ppm [19]. The ν_{as}(COO) and ν_s(COO) values were consistent with bridging acetato groups [20], the singlet resonance at *ca.* 2.00 in the ^{1}H NMR spectra was assigned to the equivalent methyl acetate protons, in agreement with a *trans* geometry of the two cyclometallated moieties [21].

Treatment of **1a** with an aqueous solution of sodium chloride or bromide gave the chloro- or bromo-bridged dinuclear compounds **2a** and **3a**, respectively (see Experimental). The IR and NMR data was in accordance with absence of the acetate ligands after metathesis; for **2a** bands at 290 and 273 cm^{-1} were ascribed to the ν(Pd-Cl) stretches.

Reaction of the halide-bridged complexes **2a** or **3a** with thallium 2,4-pentanedionate gave the soluble complex **4a** as an air-stable solid, which was fully characterized (see Experimental). The ^{1}H NMR spectrum showed singlets ca. δ = 7.73 assigned to the *H*C=N proton resonance. Singlet resonances at δ = 5.34 and at δ = 2.05, δ = 2.01 were assigned to the C*H* and to the two non-equivalent methyl groups, respectively.

Reaction of **2a** with triphos in a water/acetone mixture yielded the mononuclear cyclometallated complex [Pd{2-$SC_4H_2C(H)$=NCy}{$(Ph_2PCH_2CH_2)_2PPh$-*P,P,P*}](Cl), (**5a**), as an air-stable solid which was fully characterized. The phosphorus resonances in the ^{31}P {^{1}H} NMR spectra of the complex were downfield shifted from their values in the free phosphine suggesting coordination of all the phosphorus atoms to the metal center. A triplet resonance at δ = 91.7 was assigned to the central ^{31}P nucleus, which was *trans* to the phenyl carbon atom, and a doublet signal at δ = 41.1 was assigned to the two equivalent mutually *trans* phosphorus nuclei. The latter signal appeared at lower frequency in accordance with the high *trans* influence of the phosphine ligand [22]. The resonance of the proton in the *ortho* position to the metallated carbon, H3, appeared as a doublet of doublets showing coupling to the central ^{31}P atom [*J*(PH) 5.7 Hz]; no coupling was observed to the terminal phosphorus nuclei. These data are in accordance with a disposition in which the metalated ring is nearly perpendicular to the plane defined by the three phosphorus atoms; these observations were confirmed by selective decoupling experiments. The absence of the ν(Pd-Cl) band in the IR spectrum confirmed Pd-Cl bond cleavage upon coordination of the palladium atom to the three phosphorus atoms. No noticeable shift of the ν(C=N) stretching vibration to lower wavenumbers [18] or upfield shift of the *H*C=N proton resonance in the ^{1}H NMR spectra [19] was observed indicating absence of palladium−nitrogen interaction in solution. Conductivity measurements show the expected values for a 1:1 electrolyte [23].

Reaction of **1a** or **2a** with tertiary phosphines gave mononuclear and dinuclear compounds. Thus, treatment of



Scheme 2 (i) $Pd(AcO)_2$ / Toluene; (ii) NaX (X = Cl, Br)/ acetone/water; (iii) PPh_3 / acetone.

1a with $Ph_2P(CH_2)_nPPh_2$ in 1:2 molar ratio gave compounds [{Pd[5-$SC_4H_2C(H){=}NCy](O_2CMe)\}_2\{\mu{-}Ph_2P(CH_2)_nPPh_2\}$] (n = 2, **7a**; n = 3, **8a**; n = 4, **9a**) as pure air-stable solids, which were fully characterised (see Experimental section and Scheme 1). The ^{1}H NMR spectra showed the *H*C=N resonance to higher frequency with respect to **1a**, as a doublet owing to coupling to the phosphorus nucleus. The H3 resonance was shifted to lower frequency by *ca.* 1 ppm with respect to **1a**, owing to shielding by the phosphine phenyl rings, in accordance with a phosphorus *trans* to nitrogen geometry. The ^{31}P chemical shift values were also consistent with a phosphorus *trans* to nitrogen arrangement [22, 24−26]. Reaction of **2a** and triphenylphosphine produced the mononuclear compound **6a**, with the phosphorus ligand *trans* to the nitrogen atom (see Experimental).

The chemical behavior of 3-$SC_4H_3C(H){=}NCy$, **b**, was very similar to that of ligand **a**, giving rise to the dinuclear, **1b**, **2b**, **3b**, and mononuclear species, **4b**, as air-stable products which were unequivocally determined (see Experimental Section for details of characterization) and shall not be discussed in detail. However, it is most noteworthy to point out that as opposed to ligand **a**, in the case **b**, there are two possible positions for palladation giving rise to compounds with the sulfur atom at the 3 (palladation at the C_{ortho} to sulfur) or 4 (palladation at the C_{meta} to sulfur) sites, resulting in the formation of two linkage isomers. Thus, reaction of **b** and palladium acetate in toluene gave the dinuclear acetate-bridged complexes [Pd{n-$SC_4H_2C(H){=}NCy\}(O_2CMe)]_2$ (n = 3, **1b**; n = 4, **1b′**) in *ca.* 1:1 ratio as determined by ^{1}H NMR spectroscopy; attempts to separate both isomers deemed unsuccessful. The ^{1}H NMR spectrum showed two doublets assigned to the AB pattern of the H4 and H5 protons for **1b**, and two singlet resonances assigned to the H3 and H5 protons for **1b′**. Treatment of the acetato-bridged compounds with aqueous sodium chloride or bromide yielded the halide-bridged (**2b**, **2b′** X = Cl; **3b**, **3b′** X = Br) complexes (see Experimental Setion), whereas reaction with triphenylphosphine gave **4b**, **4b′** with a terminal acetato group; the spectroscopic data was in accordance with a *trans* P−Pd−N geometry.

Molecular structure of **[Pd{n-$SC_4H_2C(H){=}NCy\}(O_2CMe)(PPh_3)$] (n = 3, 4b; n = 4, 4b′)**. Suitable crystals were grown by slowly evaporating a dichloromethane/n-hexane solution of the complexes. The molecular structures are illustrated in Figures 1 and 2. Crystal data are given in Table 1 and selected bond distances and angles with estimated standard deviations are shown in Table 2.

The crystal consists of discrete molecules separated by van der Waals distances. The two isomers share the same crystallographic position (except the sulfur and a carbon atom, of the thiophene ring) with occupancies of approximately 50 % for each isomer. In both isomers the four-coordinated paladium atom is bonded to one carbon atom (C(2) and C(4) [27], for the isomers **a** and **b**, respectively) of the thiophene ring and the imine nitrogen of the Schiff base ligand, one monodentate acetate ligand and to the phosphorus atom of the triphenylphosphine ligand. The coordi-

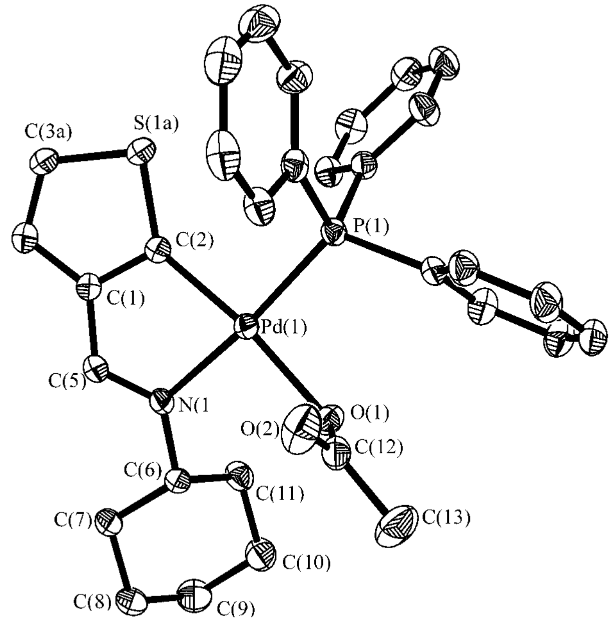


Figure 1 Molecular structure of [Pd{4-$SC_4H_2C(H)$=NCy}-(O_2CMe)(PPh_3)] (**4b**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

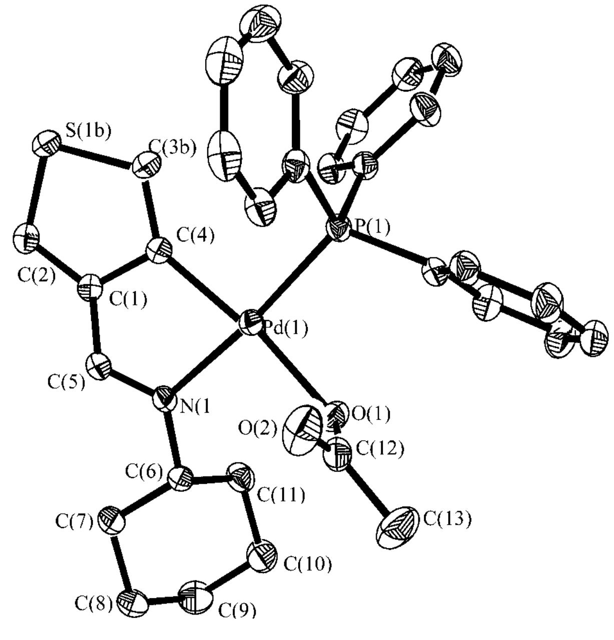


Figure 2 Molecular structure of [Pd{3-$SC_4H_2C(H)$=NCy}-(O_2CMe)(PPh_3)] (**4b′**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

nation sphere of the palladium atom may be described as slightly distorted square-planar. The angles between adjacent atoms in the coordination sphere of palladium atom are close to the expected value of 90° with the most noticeable distortion corresponding to the bite angle C(2)/C(4)-Pd(1)-N(1) of 80.34(8)°. The sum of the angles about palladium is approximately 360°.

Table 1 Crystal data and structure refinement data for compound **4b**, **4b′**.

Empirical formula	$C_{31}H_{32}NO_2PPd$ S	
Formula weight	620.01	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P $\bar{1}$	
Unit cell dimensions	a = 8.2478(1) Å	α = 80.449(1)°
	b = 11.4224(2) Å	β = 88.429(1)°
	c = 15.7151(1) Å	γ = 78.557(1)°
Volume	1430.95(3) Å^3	
Z	2	
Density (calculated)	1.439 Mg/m^3	
Absorption coefficient	0.805 mm^{-1}	
F(000)	636	
Crystal size	0.50 x 0.50 x 0.35 mm^3	
θ range for data collection	1.84 to 28.28°.	
Index ranges	−10< h< 10, −15< k< 14, −20< l< 12	
Reflections collected	9858	
Independent reflections	6754 [R(int) = 0.0146]	
Completeness to θ = 28.28°	95.5 %	
Max. and min. transmission	0.7658 and 0.6889	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6754 / 6 / 336	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2σ(I)]	R1 = 0.0290, wR2 = 0.0684	
R indices (all data)	R1 = 0.0361, wR2 = 0.0719	
Largest diff. peak and hole	0.423 and −0.673 e Å^{-3}	

Table 2 Selected bond distances /Å and angles /° for compound **4b**, **4b′**.

Pd(1)-N(1)	2.118(2)	Pd(1)-C(2a/4b)	1.990(2)
Pd(1)-O(1)	2.091(2)	Pd(1)-P(1)	2.2487(6)
C(2/4)-Pd(1)-N(1)	80.34(8)	C(2/4)-Pd(1)-P(1)	94.23(6)
N(1)-Pd(1)-P(3)	173.81(5)	C(2/4)-Pd(1)-O(1)	172.25(8)
N(1)-Pd(1)-O(1)	93.19(5)	P(1)-Pd(1)-O(1)	93.19(5)

The Pd-C bond distance of 1.990(2) Å is somewhat shorter than the value predicted from the sum of the van der Walls radii of palladium and carbon atoms [28] but similar to values reported previously [13a, 29, 30] for ortho-palladated thiophene rings. The Pd(1)-N(1) bond distance of 2.118(2) Å is longer than the predicted value based on the sum of the covalent radii of palladium atom an N(sp^2) radii [28] showing the high *trans* influence of the phosphine phosphorus [31, 32]. The Pd(1)-P(1) bond distance of 2.091(2) Å is in agreement with the values previously reported [31]. The Pd-O bond distance is also within the expected values [31−33].

The coordination sphere around palladium atom is planar [mean deviation from the least square plane Pd(1), C(2/4), N(1), P(1), O1(1), (plane 1), of 0.0394 Å] and approximately co-planar with the metallated ring [Pd(1), C(2/4), C(1), C(5), N(1); mean deviation 0.0329 Å (plane 2)] and with the thiophene ring [planes 3a and 3b, mean deviation of 0.0178, 0.0213 Å, for isomer **a** and **b**, respectively] (angles between planes are: plane 1:2, 3.6°; plane 1:3a, 4.0°; 1:3b, 4.3°; 2:3a, 2.9°; 2:3b, 3.4°).

No intra or intermolecular interactions were observed for the thiophene sulfur.

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References

[1] I. Omae, in: *Organometallic Intramolecular-coordination Compounds*. Elsevier Science. Amsterdam-New York, **1986**.

[2] V. V. Dunina, O. A. Zalevskaya, V. M. Potapov, *Russ. Chem. Rev.* **1984**, *571*, 250.

[3] G. R. Newkome, W. E. Puckett. W. K. Gupta. G. E. Kiefer, *Chem. Rev.* **1986**, *86*, 451.

[4] A. D. Ryabov, *Chem. Rev.* **1990**, *90*, 403.

[5] M. Pfeffer, *Recl. Trav. Chim. Pays-Bas.* **1990**, *109*, 567.

[6] (a) J. Spencer, M. Pfeffer, *Avd. Organomet. Chem.* **1994**, *3*, 1; (b) I. Omae, *Applications of Organometallic Compounds*, Wiley, Chichester, **1998**; (c) J. Dupont, M. Pfeffer, J. Spencer, *Eur. J. Inorg. Chem.* **2001**, 1917.

[7] J. L. Serrano (Ed.), *Metallomesogens. Synthesis, Properties and Applications*, VCH, Weinheim.

[8] K. J. Duffty, A. N. Shaw, E. Delorme, S. B. Dilton, C. Erickson-Miller, L. Giampa, Y. Huang, R. M. Keenan, P. Lamb, N. Liu, S. G. Miller, A. T. Price, J. Rosen, H. Smith, K. J. Wiggall, L. Zhang, J. I. Luengo, *J. Med. Chem.* **2002**, *45*, 3573.

[9] J. P. Scovill, D. L. Klayman, D. G. Franchino, *J. Med. Chem.* **1982**, *25*, 1261.

[10] (a) C. Navarro-Ranninger, I. Lopez-Solera, V. M. Gonzalez, J. M. Perez, J. H. Rodríguez, J. L. Garcia-Ruano, P. Raithby, J. R. Masaguer, C. Alonso, *J. Med. Chem.* **1993**, *36*, 3795; (b) C. Navarro-Ranninger, I. Lopez-Solera, V. M. Gonzalez, J. M. Perez, A. Alvarez-Valdes, A. Martin, P. Raithby, J. R. Masaguer, C. Alonso, *Inorg. Chem.* **1996**, *35*, 5181.

[11] A. Papageorgiou, A. Iadovidou, D. Mourelatos, E. Mioglou, L. Boutis, A. Kotsis, D. Kovala-Demertzi, A. Domopoulo, D. X. West, M. A. Demertzis, *Anticancer Res.* **1997**, *17*, 247.

[12] A. Gomez-Quiroga, C. Navarro-Ranninger, *Coord. Chem. Rev.* **2004**, *248*, 119.

[13] (a) M. Nonoyama, *Inorg. Chim. Acta* **1992**, *202*, 183; (b) H. Mizuo, M. Nonoyama, *Polyhedron* **1990**, *9*, 1287.

[14] E. C. Constable, R. P. G. Henney, T. A. Leese, *J. Organomet. Chem.* **1989**, *277*, 277.

[15] C. Anderson, M. Crespo, M. Font-Brdía, X. Soláns, *J. Organomet. Chem.* **2000**, *604*, 178.

[16] D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals, Butterworth-Heinemann*, London, 4th ed., **1996**.

[17] G. M. Sheldrick, SHELX-97, *An Integrated System for Solving and Refining Crystal Structures from Diffraction Data*, University of Göttingen, Germany, **1997**.

[18] (a) M. Onoue, I. Moritani, *J. Organomet. Chem.* **1972**, *43*, 431; (b) H. Onoue, K. Minami, K. Nakagawa, *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3480.

[19] Y. A. Ustinyuk, V. A. Chertov, I. V. Barinov, *J. Organomet. Chem.* **1971**, *29*, C53.

[20] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed. Wiley & Sons, New York, **1997**.

[21] J. M. Vila, M. Gayoso, M. T. Pereira, J. M. Ortigueira, M. López-Torres, A. Castiñeiras, A. Suárez, J. J. Fernández, A. Fernández, *J. Organomet. Chem.* **1997**, *547*, 297.

[22] P. S. Pregosin, R. W. Kuntz, *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*, P. Diehl, E. Fluck and R. Kosfeld, Springer, Berlin, **1979**, p.52.

[23] W. J. Geary, *Coord. Chem. Rev.* **1971**, *7*, 81.

[24] J. Albert, M. Gómez, J. Granell, J. Sales, *Organometallics* **1990**, *9*, 1405.

[25] R. Bosque, J. Granell, J. Sales, M. Font-Bardía, X. Soláns, *J. Organomet. Chem.* **1993**, *453*, 147.

[26] J. Albert, J. Granell, J. Sales, M. Font-Bardía, X. Soláns, *Organometallics* **1995**, *14*, 1393.

[27] The crystallographic and chemical notation differ slightly, for **4b** C(4) is C5 in Scheme 2, and for **4b′** C(4) is C2 and C(2) is C5 in Scheme 2.

[28] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, New York, **1960**.

[29] O. Clot, M. O. Wolf, B. O. Patrick, *J. Am. Chem. Soc.* **2001**, *123*, 9963.

[30] O. Clot, M. O. Wolf, B. O. Patrick, *J. Am. Chem. Soc.* **2000**, *122*, 10456.

[31] A. Fernández, D. Vázquez-García, J. J. Fernández, M. López-Torres, A. Suárez, S. Castro-Juiz, J. M. Vila, *Eur. J. Inorg. Chem.* **2002**, 2389.

[32] A. Fernández, D. Vázquez-García, J. J. Fernández, M. López-Torres, A. Suárez, S. Castro-Juiz, J. M. Vila, *New J. Chem.* **2002**, *26*, 398

[33] A. Fernández, M. López-Torres, A. Suárez, J. M. Ortigueira, T. Pereira, J. J. Fernández, H. Adams, J. M. Vila, *J. Organomet. Chem.* **2000**, *598*, 1.