Dalton Transactions

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Stepwise Cyclopalladation of 2-Phenacylthiopyridine to Give *C,C,N-pincer* Complexes

María-Teresa Chicote,*,[a] Concepción Rubio,[a] Delia Bautista[b] and José Vicente[a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Orthopalladation of the phenyl ring in the cyclopalladated complex [Pd{*C,N*-pyl-SCHC(O)Ph}(μ-X)]$_2$ (pyl = 2-pyridyl, X = Cl; **1·Cl**) occurs upon reacting it with AgOAc (1:2) in MeCN to give the pincer complex [Pd{*C,C,N*-pyl-SCHC(O)C$_6$H$_4$-2}(NCMe)] (**2**). The nature of the base and X, plays a key role because palladation neither occurs with other bases nor when X is AcO (**1·OAc**) or Br, in which case **1·OAc** is obtained. Complex **2** affords complexes [Pd{*C,C,N,S*-pyl-SCHC(O)C$_6$H$_4$-2}]$_n$, [Pd{*C,C,N*-pyl-SCHC(O)C$_6$H$_4$-2}L] (L = PPh$_3$, ^{t}BuNC, XyNC) or Me$_4$N[Pd{*C,C,N*-pyl-SCHC(O)C$_6$H$_4$-2}Cl] upon acetonitrile loss, or its replacement by neutral or anionic ligands, respectively. Some such complexes act as metallaligands towards AgClO$_4$ or [PdCl$_2$(NCPh)$_2$] giving rise to heterodinuclear [{Pd{*C,C,N*-pyl-SCHC(O)C$_6$H$_4$-2}(PPh$_3$)}{Ag(PPh$_3$)}]ClO$_4$ or homodinuclear [{Pd{*C,C,N*-pyl-SCHC(O)C$_6$H$_4$-2}(Cl)}{Pd(μ-Cl)}]$_2$, [{Pd{*C,C,N*-pyl-SCHC(O)C$_6$H$_4$-2}(Cl)}{Pd(Cl)(PPh$_3$}] complexes. Some derivatives of complexes **1** have also been obtained.

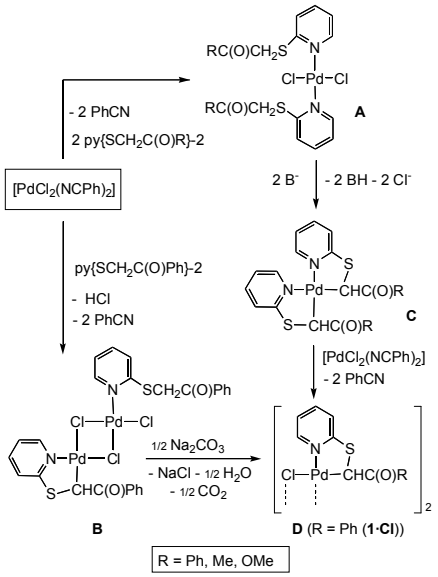
1. Introduction

Cyclopalladated complexes are increasingly important in organic synthesis.[1-3] Chiral cyclopalladated derivatives are being used both for optical resolution purposes[4] and for enantioselective catalysis[3,5] Many palladacycles have found use in the preparation of metallomesogens[6] and some show antitumor activity.[7] 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 in the minority,[2,8-12] those concerning a prochiral C(sp^3) atom being particularly rare.[11,12] We have previously reported the cyclopalladation[13] and cycloauration[14] of 2-R-carbonylmethylenethiopyridines pyl-SCH$_2$C(O)R (pyl = 2-pyridyl, R = Ph, Me, OMe). By reacting these ligands with [PdCl$_2$(NCPh)$_2$], or the coordination complexes [Pd{pyl-SCH$_2$C(O)R}$_2$Cl$_2$] (**A**, Scheme 1) with Na$_2$CO$_3$ or NaH, chiral complexes with one (**B**) or two (**C**) five-membered *C,N*-metallacycles were prepared (Scheme 1). Transmetalation reactions between **C** and [PdCl$_2$(NCPh)$_2$] or deprotonation of **B** with Na$_2$CO$_3$ allowed the syntheses of dinuclear complexes **D**. Reactions of complex **B** or **D** (R = Ph) with excess Na$_2$CO$_3$, which we carried out in an attempt to prepare pincer complexes resulting upon the additional cyclometalation of the phenyl group, were unsuccessful. This was not surprising because, although double C–H activation processes leading to various types of doubly cyclopalladated compounds are well known,[15] cyclometalation reactions involving two C–H bond activations per metal atom are very rare, not only for palladium[8,9,13] but also for any metal.[16] However, in this paper we report that by using AgOAc as a base it is possible to prepare, from complex **D** (R = Ph), pincer complexes bearing a dianionic *C*(sp^2),*C*(sp^3),*N*-donor ligand. Carbometalated pincer complexes were defined as "organometallic compounds bearing tridentate monocarbanionic ligands that coordinate metal in a η^3-mer fashion".[17] Most complexes included in this general definition display one Csp^2–M bond. However, only a few such complexes with a Pd–Csp^3 bond are known, some of which have been found to be more active catalysts than their Pd–C$_{sp}$^{2} counterparts.[8,18] On the other hand, as far as we are aware, very few palladium complexes with dianionic pincer ligands have been reported so far,[8,19] only one of them bearing a C,C,N-pincer ligand.[20] We have recently reported the synthesis of the first family of stable Pd(IV) pincer complexes[21,22] and the first generation of a coordinating side arm on a chelate complex giving rise to a pincer complex.[23] A few examples have been reported of chelate complexes converting into palladium pincer derivatives as a consequence of the chelating ligand bearing a pendant aryl group that palladates intramolecularly by heating or by adding a base (NaOAc).[24] However, in these cases the ligand to be palladated is a N^N neutral ligand while in the present work we report the palladation of the side arm of a cyclopalladated ligand, which is probably responsible for the difficulty of the palladation process, which does not occur upon heating. A relatively large number of cyclopalladated compounds containing a dianionic C,N,O-pincer ligand has been reported.[25]

2. Results and discussion

2.1 Synthesis

Scheme 1 shows the results, previously reported by us[13] on the reactivity of [PdCl$_2$(NCPh)$_2$] toward various 2-R-carbonylmethylenethiopyridines pyl-SCH$_2$C(O)R (pyl = 2-pyridyl, R = Ph, Me, OMe) including dehydrohalogenation reactions, spontaneous or induced by the use of a base such as Na$_2$CO$_3$ or NaH, to give palladacyclic complexes of the types **B** or **C**, respectively. However, further deprotonation of the methine proton or of the R group did not occur even when an excess of these bases was used.

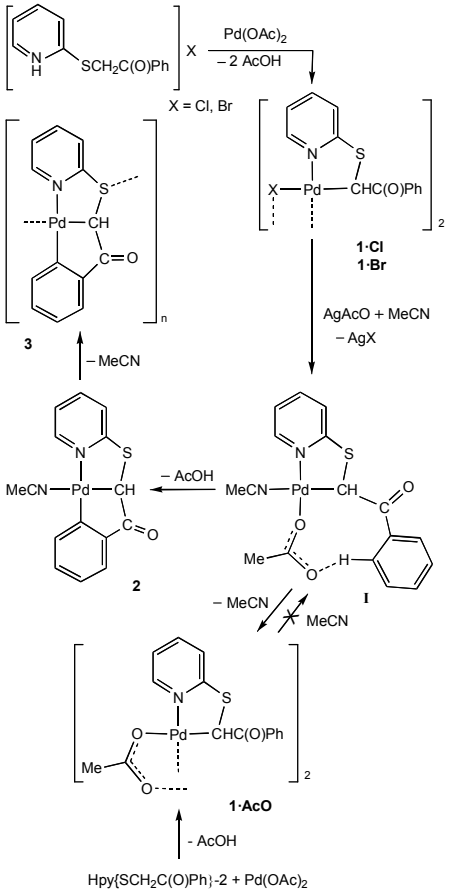


Scheme 1

With the purpose of further studying dehydrohalogenation reactions on complexes [Pd{*C,N*-pyl-SCHC(O)R}(μ-Cl)]$_2$ (**D** in Scheme 1) to give *C,C,N*-pincer complexes, we attempted an alternative synthesis of **1·Cl** (**D**, R = Ph) because the previous methods were rather cumbersome ([PdCl$_2$(NCPh)$_2$] → **B** → **D** or [PdCl$_2$(NCPh)$_2$] → **A** → **C** → **D**).[13] Thus, a double deprotonation of [Hpyl-SCH$_2$C(O)Ph]Cl (pyl- = 2-pyridyl),[26] with Pd(OAc)$_2$ (1:1, refluxing in acetone for 3h) gave 92% yield of **1·Cl** in a single step. Similarly, its homologous [Pd{*C,N*-pyl-SCHC(O)Ph}(μ-Br)]$_2$ (**1·Br**) was obtained in 83% yield from [pylH-SCH$_2$C(O)Ph]Br[26] and Pd(OAc)$_2$ (1:1, refluxing in acetone for 3 h). Complexes **1·Cl** and **1·Br** are obtained as a mixture of isomers (See Experimental Section) which can be explained by the fact that they bear two chiral CH^{Pd} carbon atoms and two palladacycles that can adopt mutual *cisoid*- or *transoid*-disposition.

Complex **1·Cl** was recovered unchanged after reacting it with K^{t}BuO (1:1, in CH_2Cl_2) at room temperature for 3 h or, by additionally refluxing the reaction mixture for 2 h. However, the same complex reacted with AgOAc to give, after 4 h refluxing in MeCN, the *C,C,N*-pincer complex [Pd{*C,C,N*-pyl-SCHC(O)C$_6$H$_4$-2}(NCMe)] (**2**). Although a small amount of colloidal palladium also formed, complex **2** could be isolated in 77% yield. The different behavior of AgOAc with respect to Na_2CO_3 or K^{t}BuO suggests that the driving force for this reaction is the formation of an intermediate (**I**, in Scheme 2) in which the acetato ligand interacts with the ortho hydrogen of the aryl group, as has been suggested previously.[27,28] This C–H activation is probably preferred to that of the CH group coordinated to Pd, in spite of its vicinity to the carbonyl group, because of the +I effect of the metallic moiety. This is confirmed by the shift of the ν(CO) frequency towards the low energy region in all *C,N*-cyclopalladated complexes compared to that in N-coordinated [Pd]-pyl-SCH$_2$C(O)Ph complexes.[13] In fact, we have failed other attempts to deprotonate the methine group (see below). In addition, an intermediate similar to **I** involving the methine proton would probably be less favored from a steric point of view.

Using **1·Br** instead of **1·Cl** in its reaction with AgOAc, under the same reaction conditions, gave instead a mixture containing, among other species, **1·Br** and the bridging acetato complex [Pd{*C,N*-pyl-SCHC(O)Ph}(μ-*O,O'*-OAc)]$_2$ (**1·OAc**) that we could not separate. When a dichlorometane solution of that mixture was layered with n-hexane, in an attempt to obtain **1·OAc**, crystals of **1·Br** grew instead, which were suitable for determining its crystal structure. However, pure **1·OAc** was obtained after refluxing in acetone for 1.5 h an equimolar mixture of pyl{SCH$_2$C(O)Ph}-2 and Pd(OAc)$_2$ in the presence of AcOH (1 equiv) The same result was obtained by using 0.5 equiv of AcOH and acetonitrile as solvent. In the absence of acid, some decomposition to Pd(0) was observed causing a yield decrease. **1·OAc** was also obtained as a mixture of isomers (See Experimental Section).



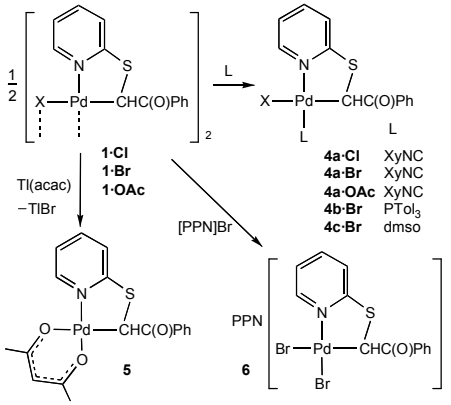
Scheme 2

Although we can not fully understand the different behavior of **1·Br** and **1·Cl** toward AgOAc it seems that the reaction starting from **1·Cl** favors the formation of the intermediate **I** while that from **1·Br** allows its irreversible conversion into **1·OAc** (Scheme 2). In fact, after stirring **1·OAc** (0.1mmol) with MeCN (5 mL) at room or refluxing temperature for 5 or 3 h, respectively, the formation of **2** could not be evidenced by ^{1}H NMR and **1·OAc** was recovered unchanged.

Complex **2** is soluble in MeCN and dmso and partially soluble in acetone. However it decomposed upon standing in CH_2Cl_2 or $CHCl_3$ solutions to give the insoluble complex [Pd{*C,C,S,N*-pyl-SCHC(O)C$_6$H$_4$-2}]$_n$ (**3**) (Scheme 2) along with a solution containing a mixture of products, likely to be oligomers that we

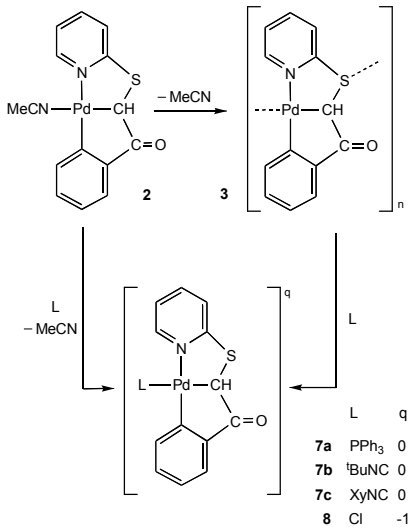
could not identify by ^{1}H-NMR spectroscopy. Complex **3** presumably forms because the sulfur atom is capable of replacing the labile MeCN ligand in **2** (see below).

Complexes **1-3** have been used as starting materials for the synthesis of related complexes. Thus, neutral complexes [Pd{*C,N*-pyl-SCHC(O)Ph}X(L)] (L = XyNC (Xy = $C_6H_3Me_2$-2,6), X = Cl, (**4a·Cl**), Br (**4a·Br**) AcO (**4a·OAc**), L = $PTol_3$ (Tol = C_6H_4Me-4), X = Br (**4b·Br**), L = dmso, X = Br (**4c·Br**)) and [Pd{*C,N*-pyl-SCHC(O)Ph}{*O,O'*-acac}] (acacH = acetylacetone, **5**) or anionic PPN[Pd{*C,N*-pyl-SCHC(O)Ph}Br_2] (**6**) (PPN = Ph_3P=N=PPh_3) were prepared in good yields by reacting the appropriate complex **1** with neutral monodentate ligands, with Tl(acac) or with [PPN]Br, respectively (Scheme 3). Complex **4c·Br** was obtained as a mixture of the *SP-4-3-* and *SP-4-4-* isomers (see NMR Discussion and Experimental Section).



Scheme 3

We attempted the synthesis of [Pd{*C,N*-pyl-SCHC(O)C_6H_4-2}(OAc){S(O)Me_2}] (**4c·OAc**, analogous to **4c·Br**) by reacting **1·OAc** with dmso under various reaction conditions (1:1 or 1:2, at room temperature or refluxing in chloroform for 3 h or, as for **4c·Br**, 1:9 in acetone at room temperature for 2 h or even after 3 h refluxing) in the hope that, if both of the possible isomers formed, the *SP-4-4-*one would be prone to form upon heating an intermediate similar to **I**, replacing MeCN by dmso, giving finally the pincer complex [Pd{*C,C,N*-pyl-SCHC(O)C_6H_4-2}(S(O)Me_2)] homologous of **2**. Unfortunately, from any of these reactions, neither the mononuclear dmso-complex **4c·OAc** nor the pincer complex could be detected by NMR. In fact, **1·OAc** was recovered almost quantitatively in all cases. Also, **1·OAc** was isolated in 70% yield from the reaction of **1·Cl** with AgOAc and dmso (1:1:2, refluxing in acetone for 2 h). The acetylatetonato complex **5** was recovered unchanged after refluxing it in MeCN for 4 h in an attempt to prepare **2** upon acetylacetone loss. Similarly, refluxing **6** in acetonitrile for 5 h did not give **2** or the anionic pincer PPN[Pd{*C,C,N*-pyl-SCHC(O)C_6H_4-2}Br] and **6** was also recovered unchanged. From complex **2**, neutral [Pd{*C,C,N*-pyl-SCHC(O)C_6H_4-2}L] (L = PPh_3 (**7a**), ^{t}BuNC (**7b**), XyNC (**7c**)) or anionic Me_4N[Pd{*C,C,N*-pyl-SCHC(O)C_6H_4-2}Cl] (**8**) complexes could be obtained upon replacement of the labile MeCN ligand by the appropriate ligands (Scheme 4). Complex **7a,** could be prepared using a 1:1 molar ratio of the reagents but it was best obtained by slow addition of solid complex **2** to a solution of PPh_3 in CH_2Cl_2 in order to minimize the formation of the polymer **3**. The yield of **7b** improved when an excess of the ligand (1:2) was used; otherwise some unidentified side-products also formed which we could not separate. In spite of the excess ^{t}BuNC in the reaction giving **7b**, neither insertion of the isocyanide into the Pd-C_{aryl} bond nor replacement of the pyridine moiety was observed. The reaction of **2** with pyridine gave a product the spectroscopic data of which suggest the formation of the corresponding neutral complex. However, its elemental analyses indicate some contamination,[29] probably with **3** that we could not resolve.

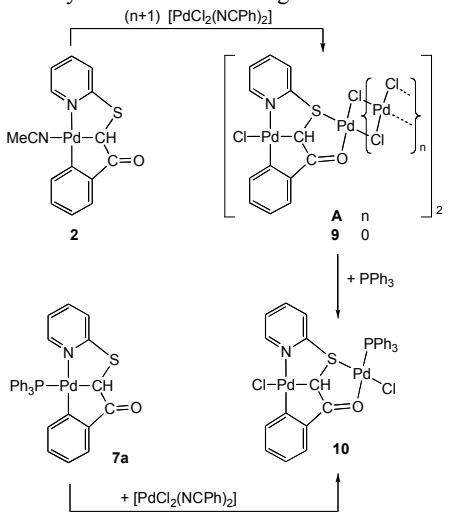


Scheme 4

Complexes **7a-c** could also be obtained by reacting **3** with the appropriate ligand, but since this complex is obtained in rather low yield, the former method was preferred. However, as an example of its use, we describe in the Experimental Section the synthesis of [Pd{*C,C,N*-pyl-SCHC(O)C_6H_4-2}(CNXy)] (**7c**) by slow addition of a CH_2Cl_2 solution of XyNC to a suspension containing the equimolar amount of **3** in the same solvent (40 min, 72%). No insertion of XyNC was observed either in the reaction of **3** with 3 equiv XyNC in $CHCl_3$ at room temperature or at 65 ºC in a Carius tube for 6 h, giving only **7c**.

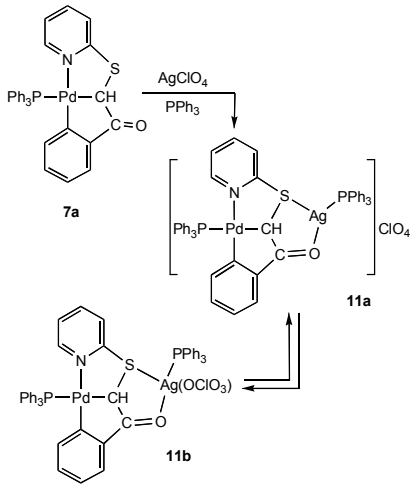
Since the sulfur and oxygen atoms in complexes **2** and **7** bear lone electron pairs we have explored their behavior as ligands towards palladium(II) and silver(I). The reaction of **2** with [$PdCl_2$($NCPh)_2$] in acetone gave different species depending on the molar ratio of reagents that can be considered derivatives of the anion of **8** acting as a ligand (Scheme 5). However, we have only been able to isolate pure the complex [*S,O*-{Pd{*C,C,N*-pyl-SCHC(O)C_6H_4-2}Cl}{Pd(μ-Cl)}]$_2$ (**9**) which immediately precipitates in the 1:1 reaction (Scheme 5). **9** results from the replacement of all the nitrile ligands, migration of one chloro ligand from [$PdCl_2$($NCPh)_2$] to **2** and the necessary dimerization in order to provide Pd(II) with its preferred square planar tetracoordination. When different **2**:[$PdCl_2$($NCPh)_2$] molar ratios were used, ranging from 1:2 to 1:4, precipitation of variable amounts of **9** occurred and, from the solutions, mixtures were obtained (by ^{1}H NMR) with elemental analyses approaching those for **A** with n = 1 (Scheme 5). The reaction of **2** with $PdCl_2$ (1:1 in acetone) intended to produce **9** gave instead a red insoluble compound with elemental analyses suitable for the stoichiometry of **A** with n = 2.5. These results suggest processes in which soluble species resulting from bridge splitting of complexes **A** by RCN (R = Me, Ph) or acetone could be involved,

giving rise to complexes with different stoichiometries depending on their solubility as well as on the reagents' molar ratio.



Scheme 5

The reaction of **9** with PPh_3 (acetone, 1:1), or better that of **7a** with $[PdCl_2(NCPh)_2]$ (CH_2Cl_2, 1:1), gave [*S,O*-{Pd{*C,C,N*-pyl-SCHC(O)C_6H_4-2}Cl}{Pd(Cl)PPh_3}] (**10**), which again is a derivative of the anionic metallaligand present in **8**. The former of these reactions produced bridge splitting and coordination of the neutral ligand while in the latter, the interchange of chloro and phosphine ligands provided a new example of PPh_3/carbon donor ligands transphobia.[13,30,31,32] The proposed geometry for **10** is based on those of related complexes in which P- and O-donor ligands as well as Cl and S-donor ligands are placed in trans.[33] The reaction of **2** with $(PPN)_2[Pd_2Cl_6]$ (acetone, 2:1) intended to produce the anionic dinuclear complex PPN[*S,O*-{Pd{*C,C,N*-pyl-SCHC(O)Ph}Cl}($PdCl_2$)], led instead to the precipitation of **9** while (PPN)Cl was recovered from the mother liquor.



Scheme 6

In turn, the reaction of **7a** with $AgClO_4$ and PPh_3 (acetone, 1:1:1) produced a white suspension of **11** (57%, Scheme 6) shown by ^{31}P NMR to be an equilibrium mixture of complexes [*S,O*-{Pd{*C,C,N*-pyl-SCHC(O)C_6H_4-2}PPh_3}($AgPPh_3$)]ClO_4 (**11a**) and [*S,O*-{Pd{*C,C,N*-pyl-SCHC(O)C_6H_4-2}PPh_3}{Ag($OClO_3$)PPh_3}] (**11b**) (see below).

Attempts to deprotonate the CH^{Pd} group by reacting **2** with AgOAc (acetone, 1:1) or **7a** or **8** with [Ag(acac)(PPh_3)](acetone, 1:1)[34] failed and the starting materials were recovered in all cases. We have also reacted **7a** or **8** with an excess of Cl_2 in CCl_4 or with the stoichiometric amount of Cl_2IPh, respectively, in an attempt to produce Pd(IV) complexes, as we have reported with other pincer complexes,[22] or, more likely, according to previous experiences in similar systems,[12,22] the C–Pd bond cleavage to form C–Cl + Pd–Cl bonds. However, complex mixtures were obtained in the reactions with Cl_2 and no reaction was observed in those with Cl_2IPh.

2.2. X-ray crystal structures

The crystal structures of complexes **1·Br**·$CHCl_3$ (Figure 1), **1·AcO** (Figure 2) and **7c** (Figure 3) have been determined by X-ray diffraction studies. Details on crystal data, data collection, and refinements are summarized in the Supporting Information. The crystal structure of **1·Br**·$CHCl_3$ corresponds to the *RS-transoid* isomer and is centrosymetric while that of **1·OAc** corresponds to the the *RR-cisoid* isomer, the *SS*-one being also present in the centrosymetric unit cell. All the structures display some common features. Thus, in all cases, the Pd atom is in a distorted square-planar environment, the mean deviation from planarity for the Pd atom and its four immediate neighbors being ≤0.05 Å, except for Pd1 in **1·OAc** (0.08Å). The five membered C-Pd-N ring adopts in complexes **1·Br** and **1·OAc** an envelope conformation. However in **7c** it is nearly planar (mean deviation from planarity 0.065 Å, being the C1 atom the most deviated, +0.0833 Å) while the other five membered C-Pd-C palladacycle adopts an envelope conformation. In **1·OAc** the two acetato ligands substend an angle of 91.7º. The Pd−C(sp^3) bond distances (similar in all complexes: 2.042(6) Å in **1·Br**, 2.027(3) and 2.035(3) Å in **1·OAc,** 2.049(4) Å in **7c**) are longer than the Pd-C(sp^2) and Pd-C(sp) bond distances in **7c** (2.0072(17) and 1.9904(16) Å, resectively). The *trans* influence sequence C > Br > O is responsible for the slightly different Pd−N bond distances in these complexes (2.1080(16) (**7c**) > 2.036(5) (**1·Br**) > 2.012(3), 2.007(3) Å (**1·OAc**)). All other structural parameters are unremarkable. The bite angles of the *N,C*-chelating ligand in **1·Br** and **1·OAc** (N(1)-Pd-C(6), 85.5(2) and 85.39(12)º, respectively) are similar while in the pincer complex **7c** the homologous N(1)-Pd(1)-C(1) bond angle is similar (86.47(6)º) and the C(1)-Pd(1)-C(31) one rather narrower (80.98(7)°). Intermolecular hydrogen bonds are present in all the structures. In **1·Br** and **7c**, chains parallel to the *a* axis form through C-H···O bonds with participation of the carbonyl oxygen and the *ortho*-CH(phenyl) (**1·Br)** or the *ortho*-CH(phenyl) plus one CH in the Me (xylyl) fragment. In **1·AcO** a 3D net forms through various C-H···O hydrogen bonds with participation of CH groups in the pyridine, phenyl and methyl fragments and both, acetato and phenacyl oxygen atoms.

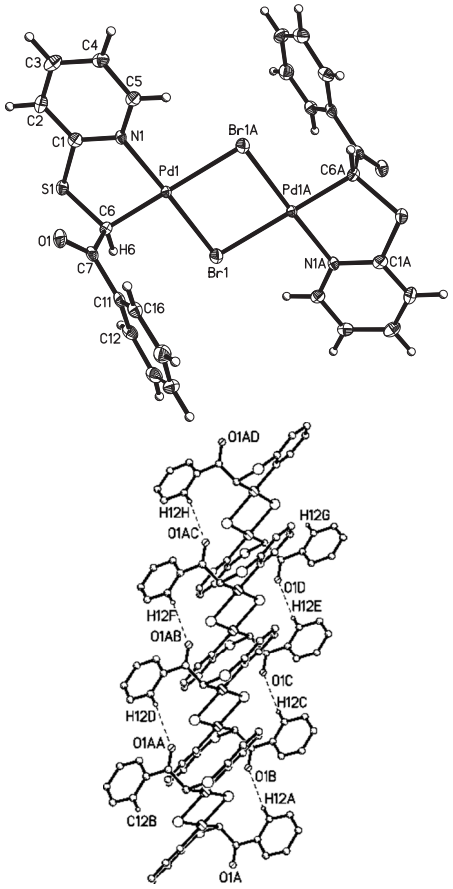


Figure 1. Thermal ellipsoid representation plot (50% probability) of compound **1·Br**. Selected bond lengths (Å) and angles (deg): Pd(1)–N(1) 2.036(5), Pd(1)–C(6) 2.042(6), Pd(1)–Br(1) 2.4351(8), Pd(1)–Br(1A) 2.5266(8), N(1)–C(1) 1.354(8), C(1)–S(1) 1.740(6), C(6)–S(1) 1.811(6), C(7)–O(1) 1.225(7); N(1)–Pd(1)–C(6) 85.5(2), C(6)–Pd(1)–Br(1) 92.41(16), N(1)–Pd(1)–Br(1A) 95.36(13), Br(1)–Pd(1)–Br(1A) 86.63(3), C(1)–S(1)–C(6) 98.5(3), S(1)–C(6)–Pd(1) 108.3(3), O(1)–C(7)–C(6) 123.2(6), O(1)–C(7)–C(11) 119.7(5).

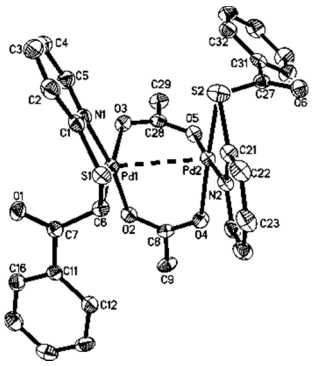


Figure 2. Thermal ellipsoid representation plot (50% probability) of compound 1·AcO. Selected bond lengths (Å) and angles (deg): Pd(1)–N(1) 2.012(3), Pd(1)–C(6) 2.027(3), Pd(1)–O(2) 2.033(2), Pd(1)–O(3) 2.134(2), N(1)–C(1) 1.358(4), C(1)–S(1) 1.735(3), C(6)–S(1) 1.811(3), C(7)–O(1) 1.229(4); N(1)–Pd(1)–C(6) 85.39(12), C(6)–Pd(1)–O(2) 92.99(11), N(1)–Pd(1)–O(3) 93.44(10), O(2)-Pd(1)-O(3) 88.33(9), C(1)–S(1)–C(6) 98.05(15), S(1)–C(6)–Pd(1) 109.07(16), O(1)–C(7)–C(6) 122.0(3), O(1)–C(7)–C(11) 119.3(3).

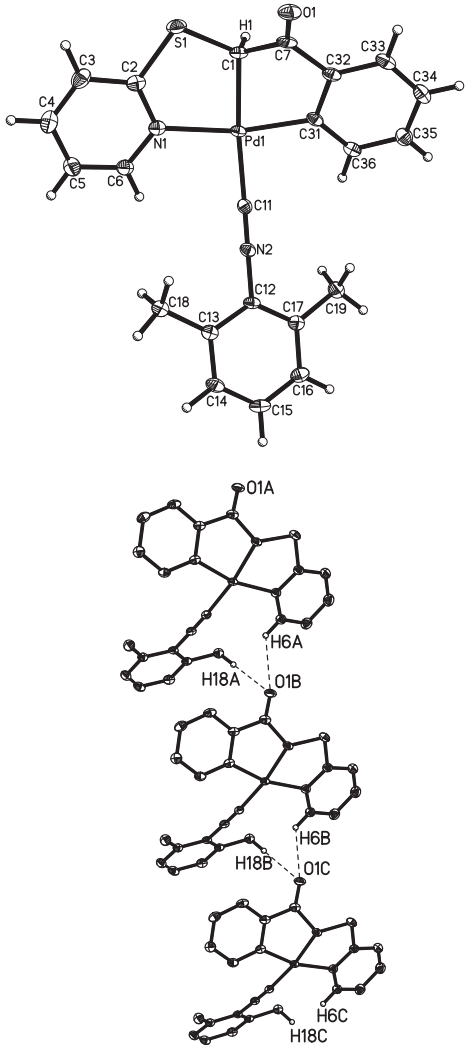


Figure 3. Above: Thermal ellipsoid representation plot (50% probability) of compound **7c**. Selected bond lengths (Å) and angles (deg): Pd(1)–C(11) 1.9904(16), Pd(1)–C(31) 2.0072(17), Pd(1)–C(1) 2.0494(16), Pd(1)–N(1) 2.1080(16), C(1)–S(1) 1.7971(18), C(1)–C(7) 1.493(2), C(11)–N(2) 1.154(2); C(11)–Pd(1)–C(31) 94.10(7), C(31)–Pd(1)–C(1) 80.98(7), C(1)–Pd(1)–N(1) 86.47(6), C(11)–Pd(1)–N(1) 97.63(6), C(2)–S(1)–C(1) 101.44(7), S(1)–C(1)–Pd(1) 113.45(8), C(7)–C(1)–Pd(1) 104.65(10), C(32)–C(7)–C(1) 109.42(13). Below: Chain parallel to axis *a* formed in **7c** through C–H···O hydrogen bonds. Hydrogens omitted except those involved in these bonds.

2.3. NMR spectra

The NMR spectra of complexes **1·OAc**, **4-8**, **10** and **12**-were measured in $CDCl_3$, (**1·Br** also in dmso-d_6) while the instability (**2**, **4c·Br**) or the insolubility of the other complexes in non-donor solvents required the use of CD_3CN (**2**) or dmso-d_6 (**3**, **4c·Br**, **9** and **11**), which means that the NMR spectra of the latter probably correspond to species resulting from solvent coordination. As mentioned above, various isomeric forms are possible for complexes **1·Cl**, **1·Br** and **1·OAc.** The presence in their ^{1}H NMR spectra, measured in $CDCl_3$, of various CH^{Pd} resonances at 5.22, 5.58, 5.64 (**1·Cl**, relative intensities 1:1:0.5), 5.24, 5.62, 5.66 (**1·Br**, relative intensities 1:1:0.5) and 4.78, 4.86, 5.90, 6.20, 6.34

(**1·OAc**, relative intensities 0.16:1:0.21:0.11:0.18) as well as various *Me*CO_2 resonances in **1·OAc** at 1.13, 1.48, 1.74, 1.77, 1.95 ppm (relative intensities 0.16:0.11:1:0.18:0.21) is indicative of the presence of different isomers in solution. Supporting that these extra resonances are no arising from impurities, only one set of resonances is observed for the *R* + *S* enantiomers in the NMR spectra of their mononuclear derivatives, except in the case of **4c·Br**. Its ^{1}H NMR spectrum, which coincides with that of **1·Br** in dmso-d_6, shows two CH^{Pd} resonances at 5.33 and 5.56 ppm that we attribute to the *SP-4-3-* and *SP-4-4-* isomers. The same occurs in the ^{1}H NMR spectrum of **9** in dmso-d_6. We assume the geometry of the remaining complexes **4** to be that with the neutral ligand disposed *trans* to nitrogen in order to avoid the high *transphobia* of the C/C and C/P couples.[13,30,31,32]

The room temperature $^{31}P\{^1H\}$-NMR spectrum of **11** in $CDCl_3$ shows a singlet at 31.04 ppm, assignable to the phosphine ligand coordinated to palladium and two broad resonances centered at 15.5 and 11.5 ppm, with relative intensities 1:3, attributable to PPh_3 coordinated to silver. At –60 ºC the resonance at higher frequency splits into two singlets at 32.6 and 34.0 ppm, with relative intensities 3:1 while that at 15.5 ppm splits into two broad peaks at 18.1 and 12.7 ppm (separated 660 Hz approx.) and that at 11.5 resolves into two doublets centered at 12.0 ppm (due to coupling to ^{109}Ag and ^{107}Ag; J_{AgP} = 564 and 489 Hz, respectively). These data support the existence of two isomeric species in solution (**11a** and **11b**) and, as bigger J values correspond to larger s-character of the hybrid orbital involved and thus to smaller coordination numbers, Ag(I) should be tricoordinate in the less abundant species (δ = 15.5) in solution (structure **11a**) while the most abundant one (δ = 11.5) should contain tetracoordinate Ag(I) (structure **11b**).

The $^{13}C\{^1H\}$-NMR spectrum of complex **9** could not be measured because its dmso solution is not stable long enough. In the remaining complexes, the CH^{Pd} carbon resonance appears in the ranges of 39.8–45.6 or 55.2–67.4 ppm for quelate or pincer complexes, respectively, while the CS and CO resonances (in the ranges 171.22-178.00 and 187.02-199.55 ppm, respectively) do not show noticiable differences among both types of complexes.[13]

The IR spectra of pincer complexes show one CO band in the 1634-1658 cm^{-1} range, at lower energy than that of the 2-(phenacylthio)pyridine ligand (1678 cm^{-1}) and similar to that in the cyclometallated complexes *C,N*-Pd{pyl-SCHC(O)Ph}here or previously reported,[13] in the range 1623-1652 cm^{-1}. Coordination of Ag(I) or Pd(II) to the carbonyl group in complexes **9-11** must be weak as it does not affect significantly the energy of the ν(CO) band. Weak to medium bands in the 1540-1590 cm^{-1} region can be assigned to ν(CC) and ν(CN) from the aryl and pyridyl rings.[35] The chloro complexes show, one (**4a·Cl**, 267; **8**, 293 cm^{-1}), or two (**9**, 322, 265; **10**, 355, 255 cm^{-1}) ν(PdCl) bands. We assign those below 300 cm^{-1} to ν(PdCl) *trans* to carbon because of its higher *trans* influence. Complexes bearing an isocyanide ligand display an intense ν(C≡N) absorption in the 2179-2209 cm^{-1} range. The presence of an strong ν(S=O) band at 1117 cm^{-1} in the spectrum of **4c·Br** is indicative of the S-coordination of the dmso ligand.[36] The IR spectrum of **11** shows strong perchlorate bands at around 1100 and 620 cm^{-1}. Both bands are narrow pointing to a species with tricoordinate silver (structure **11a**). The molar conductivity of **11** in acetone solution corresponds to that of an 1:1 electrolyte (118 $\Omega^{-1}cm^2\ mol^{-1}$).[37]

The FAB^+-MS of complexes **7a-c** show the M^+ ion at m/z 595.89 (**7a**), and 416.85 (**7b**), respectively. Additionally, the molecular weight of **7a** measured in chloroform by vapor-pressure osmometry (560) demonstrates the mononuclear nature of this complex in solution. The spectra of **7b** (as well as that of **8**) show also a peak at m/z 333.8 corresponding to the fragment "Pd{pyl-{SCHC(O)C_6H_4-2}". The spectrum of complex **11** shows peaks corresponding to M^+-ClO_4 and M^+-$AgClO_4$-PPh_3, which support the structure proposed. In the spectra of complexes **2**, **3**, **9** and **10**, only peaks of the matrix were observed.

4. Conclusion

We report the synthesis of a family of palladium *C,C,N*-pincer complexes derived from 2-phenacylthiopyridine obtained by an unprecedented stepwise double cyclopalladation process. The second step was successful by using AgAcO as the base and dehalogenating reagent. Other attempts with various bases or monocyclopalladated precursors, some here reported for the first time, were unsuccessful. We have shown that the pincer complex containing MeCN as ligand polymerizes, most likely because the sulfur and carbonyl oxygen atoms make the pincer moiety a chelating metallaligand. We have supported this idea by reacting it with neutral ligands and by preparing Ag(I) and Pd(II) derivatives of such ligand.

3. Experimental Section

The IR spectra, elemental analyses, conductance measurements in acetone and melting point determinations were carried out as described earlier.[38] The neutral complexes **2**, **4a-d**, and **9** are non-conducting in acetone. The molar conductivities of complexes **3**, **6** and **8** could not be measured because of their very low solubility in acetone. Unless otherwise stated the reactions were carried out at room temperature without special precautions against moisture. The ^{1}H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded with a Varian Unity-300 spectrometer in $CDCl_3$ solution and chemical shifts are referred to TMS [^{1}H, $^{13}C\{^1H\}$] or H_3PO_4 [$^{31}P\{^1H\}$]. Mass spectra (FAB+) were measured with a Fisons VG-Autospec spectrometer using 3-nitrobenzyl alcohol as the dispersing matrix. The molecular weight was determined with a vapor-pressure osmometer. The synthesis of **6** required the use of [PPN]Br which we prepared as a dichloromethane solvate from the commercial chloride and excess NaBr (1:3, in acetone, 4 h). The suspension was concentrated to dryness, the residue was stirred with CH_2Cl_2, and the suspension was filtered through a short pad of Celite. The solution was concentrated (1 mL) and Et_2O (15 mL) was added. The suspension was filtered and the solid collected was recrystallized from CH_2Cl_2 and Et_2O and dried, first by suction and then in an oven at 70 ºC for 2 h to give [PPN]Br·CH_2Cl_2 as a white solid. Yield: 84%. Mp: 252 ºC. Anal. Calcd for $C_{37}H_{32}Cl_2BrNP_2$: C, 63.17; H, 4.58; N, 1.99. Found: C, 62.86; H, 4.59; N, 2.04. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.30 (s, 2 H, CH_2Cl_2), 7.30-7.50 (various m, 24 H, *orto-* + *meta*-Ph), 7.65 (tdd, 6 H, *para*-Ph, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ 126.8 (d, *ipso*-C, $^1J_{CP}$ = 108 Hz), 129.5

(m, *meta*-CH), 132.0 (m, *ortho*-CH), 133.9 (*para*-CH). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 21.11 (s).

Single-Crystal X-ray Structure Determinations: Crystals suitable for X-ray diffraction of compounds **1·Br**·$CHCl_3$, **1·OAc** and **7c** were mounted in inert oil on a loop and transferred to a Bruker D8 Quest diffractometer. Data were recorded at 100(2) K using multilayer-monochromated Mo Kα radiation (λ = 0.71073 Å) and ω-scan mode. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the multi-scan method (SADABS).

Solution and Refinements: Crystal structures were solved by direct method and all non-hydrogen atoms refined anisotropically on F^2 using the program SHELXL-97[39] for **1·Br**·$CHCl_3$ and **7c** and SHELXTL-2013[40] for **1·OAc**. The methyl groups were refined using rigid groups (AFIX 137), and the other hydrogens were refined using a riding model.

Synthesis of [Pd{*C,N*-pyl-SCHC(O)Ph}(μ-Br)]$_2$ (1·X) (X = Cl (**1·Cl**), Br (**1·Br**)). A suspension containing $Pd(OAc)_2$ (for **1·Cl**, 298 mg, 1.33 mmol; for **1·Br**, 387 mg, 1.72 mmol) and the appropriate [Hpyl-$SCH_2C(O)Ph$]X (X = Cl, 353 mg, 1.33 mmol; Br, 535 mg, 1.72 mmol) in acetone (30 mL) was refluxed for 4 h. During that time a solution initially formed which gradually transformed into a suspension. After allowing the suspension to cool at room temperature, it was filtered and the solid collected was washed with acetone (5 mL) and Et_2O (2 x5 mL) and dried, first by suction and then in an oven at 75 ºC for 4 h to give a yellow (**1·Cl**) or orange (**1·Br**) solid.

1·Cl: Yield 436 mg, 1.18 mmol, 89%). Mp: 225 ºC. Anal. Calcd for $C_{13}H_{10}ClNOPdS$: 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(C=C), (C=N), 1590, 1552. ^1H NMR (300 MHz, dmso-d_6): δ 5.20, (s, 1H, CH^{Pd}), 7.27 (ddd, 1 H, H5, pyl, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz), 7.37-7.96 (various m, 7 H, H3 + H4, pyl + Ph), 8.57 (dd, 1 H, H6, pyl, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz). Resonances for the minor isomer (21% with respect to the major one, see Discussion) are also observed. Most of them are obscured in part by those of the major isomer, except those at δ 5.52 (s, 1 H, CH^{Pd}), 7.18 (ddd, 1 H, H5$^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz). In $CDCl_3$ (200 MHz) three CH^{Pd} resonances appear at 5.22, 5.58 and 5.64 ppm with relative intensities 1:1:0.5 while the aromatic region is poorly resolved (See Discussion).

1·Br: Yield, 584 mg, 1.41 mmol, 82%. Mp: 206 ºC. Anal. Calcd for $C_{13}H_{10}BrNOPdS$: C, 37.61; H, 2.60; N, 3.38, S, 7.73. Found: C, 37.75; H, 2.54; N, 3.45, S, 7.44. IR(cm^{-1}): ν(C=O), 1641; ν(C=C), (C=N), 1588, 1553. ^1H NMR (300 MHz, dmso-d_6): δ 5.33, (s, 1H, CH^{Pd}), 7.27 (ddd, 1 H, H5, pyl, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.47 ("t", 2 H, Ph, $^3J_{HH}$ = 7 Hz), 7.58 ("t", 1 H, Ph, $^3J_{HH}$= 7 Hz), 7.73-7.84 (m, 3 H, H3, pyl + Ph), 7.86 (td, 1 H, H4, pyl, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 8.78 (dd, 1 H, H6, pyl, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz). Resonances for the minor isomer (36% with respect to the major one, see Discussion) are also observed at δ 5.56 (s, 1 H, CH^{Pd}). 7.21 ("t", 1H, H5, pyl, $^3J_{HH}$ = 6 Hz), 7.39 ("t", 2 H, Ph, $^3J_{HH}$ = 7 Hz), 7.51 (t, 1 H, Ph, $^3J_{HH}$ = 7 Hz), 7.74 ("d", 1 H, H3, pyl, $^3J_{HH}$ = 8 Hz), 7.92 (m, 3 H, H4, pyl +Ph, $^3J_{HH}$ = 7 Hz), 8.00 (d, br, H6, pyl, $^4J_{HH}$ = 5 Hz). In $CDCl_3$ (300 MHz) three CH^{Pd} resonances appear at 5.24, 5.62 and 5.66 ppm with relative intensities 1:1:0.5 while the aromatic region is poorly resolved (See Discussion).

Crystals of **1·Br** suitable for an X ray diffraction study were obtained by the slow diffusion of n-hexane in a dichlorometane solution of a mixture obtained in the reaction of **1·Br** with AgOAc (see Discussion).

Synthesis of [Pd{*C,N*-pyl-SCHC(O)Ph}(μ-OAc)]$_2$ (1·OAc). $Pd(OAc)_2$ (248 mg, 1.10 mmol) and AcOH (0.1 mL, 1.2 mmol) were added to a solution of pyl-$SCH_2C(O)Ph$ (253 mg, 1.10 mmol) in acetone (15 mL). After refluxing the reaction mixture for 1.5 h, the solution was concentrated under vacuum to 1 mL and the suspension formed was filtered. The solid collected was washed with acetone (2 mL) and Et_2O (3 x 5 mL) and dried, first by suction and then in an oven at 70 ºC for 2h, to give **1·OAc** as an orange/red solid. Yield, 365 mg, 0.93 mmol, 84%. Mp: 242 (decomp) ºC. Anal. Calcd for $C_{15}H_{13}NO_3PdS$: C, 45.76; H, 3.33; N, 3.56, S, 8.14. Found: C, 46.03; H, 3.12; N, 3.51, S, 8.41. IR(cm^{-1}): ν (C=O), 1653; ν_{asym} (CO_2), 1562 ν(C=C), (C=N), 1590, 1551. ^1H NMR (400 MHz, $CDCl_3$): δ 1.74 (s, 3 H, Me, AcO), 4.86 (s, 1 H, CH^{Pd}), 7.03 (ddd, 1 H, H5, pyl, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.36 (m, 2 H, *meta*-Ph), 7.43-7.47 (m, 2 H, *para*-Ph + H3, pyl), 7.63 (ddd, 1 H, H4, pyl, $^3J_{HH}$ = 9 Hz, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.77 (m, 2 H, *ortho*-Ph), 8.13 (dm, 1 H, H6, pyl, $^3J_{HH}$ = 6 Hz). Various other minor resonances are also found at 1.13, 1.49, 1,77, 1.96 ppm (Me, OAc, relative intensities 0.16, 0.11, 0.18 and 0.21 with respect to that at 1.74 ppm) and at 4.78, 5.90, 6.20, 6.34 ppm (CH^{Pd}, relative intensities 0.16, 0.21, 0.11 and 0.18 with respect to that at 4.86 ppm) which indicate the presence of four other isomers (see Discussion). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 23.9 (Me, AcO), 39.8 (CH^{Pd}), 119.4 (CH5, py), 120.8 (CH3, py), 127.9 (*ortho*-CH, Ph), 128.4 (*meta*-CH, Ph), 131.9 (*para*-CH, Ph), 137.6 (CH4, py), 138.0 (*ipso*-C, Ph), 149.8 (CH6, py), 176.9 (CS), 182.5 (CO_2, AcO), 196.8 (*C*=O). Crystals suitable for an X ray diffraction study were obtained by the slow diffusion of Et_2O into a $CDCl_3$ solution of **1·OAc** .

Synthesis of [Pd{*C,C,N*-pyl-SCHC(O)C_6H_4-2}(NCMe)] (2). To a suspension of **1·Cl** (215 mg, 0.29 mmol) in MeCN (20 mL) solid AgOAc (97 mg, 0.58 mmol) was added and the mixture was refluxed for 4 h. The suspension was filtered through anhydrous $MgSO_4$ to remove AgCl and a small amount of palladium, the resulting brown solution was concentrated to *ca* 1 mL, and Et_2O (15 mL) was added. The suspension was filtered and the solid was dried, by sucction to give **2** as a brown solid. Yield, 138 mg, 0.37 mmol, 63%. Mp: 215 °C (decomp). Anal. Calcd for $C_{15}H_{12}N_2OPdS$: C, 48.08; H, 3.23; N, 7.48, S, 8.56. Found: C, 47.98; H, 2.91; N, 7.27, S, 8.44 . IR (cm^{-1}): ν(C=O), 1644; ν(C=C), (C=N), 1588, 1574, 1550. ^1H NMR (200 MHz, CD_3CN): δ 1.97 (m, Me + solvent), 5.71 (s, 1 H, CH^{Pd}), 7.03-7.09 (m, 2 H, C_6H_4), 7.12 (ddd, 1 H, H5, pyl, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.28 (ddd, 1 H, H3, pyl, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, $^5J_{HH}$ = 0.4 Hz)), 7.42 (dm, 1 H, H4, pyl, $^3J_{HH}$ = 8 Hz), 7.55-7.65 (m, 2 H, C_6H_4), 8.35 (dm, 1 H, H6, pyl, $^3J_{HH}$ = 6 Hz). $^{13}C\{^1H\}$ NMR (50 MHz, CD_3CN): δ 57.1 (CH^{Pd}), 119.6 (CH), 121.8 (CH), 124.68 (CH), 124.8 (CH), 128.8 (C), 130.2 (CH), 131.5 (C), 136.1 (CH), 137.9, (CH) 150.0 (CH), 173.2 (CS), 199.7 (CO).

Synthesis of [Pd{*N,C,C,S*-pyl-SCHC(O)C_6H_4-2}]$_n$ (3). A solution of **2** (84 mg, 0.22 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 1h during which time a white suspension formed which was allowed to stir for 24 h and then filtered. The

solid was washed with CH_2Cl_2 (3 x 5 mL) and air-dried to give **3** as a white solid. Yield, 29 mg, 0.09 mmol, 39%. Mp: 248 °C. Anal. Calcd for $C_{13}H_9NOPdS$: C, 46.79; H, 2.72; N, 4.20, S, 9.61. Found: C, 46.56; H, 2.56; N, 4.36, S, 9.31. IR (cm^{-1}): ν(C=O), 1658, ν(C=C), (C=N), 1590, 1580, 1556. ^{1}H NMR (300 MHz, dmso-d_6): δ 5.68 (s, 1 H, CH^{Pd}), 6.98-7.19 (m, 4 H, pyl + C_6H_4), 7.49 ("d", 2H, C_6H_4, $^3J_{HH}$ = 9 Hz), 7.70 ("t", 1 H, pyl, $^3J_{HH}$ = 8 Hz), 8.29 ("d", 1H, H6, pyl, $^6J_{HH}$ = 6 Hz). $^{13}C\{^1H\}$ NMR (50 MHz, dmso-d_6): δ 55.2 (CH), 119.3 (CH), 121.4 (CH), 123.8 (CH), 123.9 (CH), 129.3 (CH), 134.2 (CH), 137.8 (CH), 146.5 (C), 148.8 (CH), 152.1 (C), 171.2 (CS), 199.1 (CO).

Synthesis of [Pd{*N,C*-pyl-SCHC(O)Ph}X(L)] (L = CNXy, Xy = $C_6H_3Me_2$-2,6, X = Cl (4a·Cl), Br (4a·Br), AcO (4a·OAc); L = $PTol_3$, Tol = C_6H_4Me-4, X = Br (4b·Br). A solution containing the appropriate complex **1** (for **4a·Cl**, **1·Cl**, 53 mg, 0.07 mmol; for **4a·Br** or **4b·Br**, **1·Br**, 82 mg, 0.1 mmol or 100 mg, 0.12 mmol, respectively; for **4a·OAc**, **1·OAc**, 100 mg, 0.25 mmol) and ligand (for **4a·Cl** or **4a·Br** or **4a·OAc**, XyNC, 18.8 mg, 0.14 mmol, 26 mg, 0.2 mmol, or 33.3 mg, 0.25 mmol, respectively; for **4b·Br**, $PTol_3$, 110 mg, 0.36 mmol) in CH_2Cl_2 (10 mL) was stirred for 1 h or 30 min (**4a·OAc**, **4b·Br**, respectively**)**, filtered through a short pad of Celite and concentrated under vacuum (1 mL). Upon the addition of Et_2O (15 mL) or pentane (**4a·OAc**) a suspension formed which was filtered and the yellow or pale tan (**4a·OAc**) solid collected was washed with Et_2O (2 x 2 mL) or pentane (**4a·OAc**, 2 x 3 mL) and dried by suction. In the case of **4a·Br**, a second crop precipitated when n-hexane (15 mL) was added to the concentrated filtrate. **4b·Br** was recrystallized from CH_2Cl_2/Et_2O.

4a·Cl: Yield, 55 mg, 0.11 mmol, 78%. Mp: 160 ºC. Anal. Calcd for $C_{22}H_{19}ClN_2OPdS$: C, 52.71; H, 3.82; N, 5.59, S, 6.40. Found: C, 52.79; H, 3.75; N, 5.52, S, 6.31. IR(cm^{-1}): ν(C≡N), 2199; ν(C=O), 1650; ν(C=C), ν(C=N), 1591, 1578, 1555; ν(PdCl), 267. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.21 (s, 6 H, Me, Xy), 5.73 (s, 1H, CH^{Pd}), 7.03 (d, 2 H, *meta*-CH, Xy), 7.11 (ddd, 1H, H5, pyl,$^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.17-7.21 (m, 3 H, *meta*-CH, Ph + *para*-CH, Xy), 7.24 (m, 1 H, *para*-Ph), 7.57 (d, 1H, H3, pyl, $^3J_{HH}$ = 9 Hz), 7.65 (ddd, 1 H, H4, pyl, $^3J_{HH}$ = 9 Hz, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.90 (m, 2 H, *ortho*-Ph), 9.04 (dm, 1 H, H6, pyl, $^3J_{HH}$ = 6 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 18.5 (Me, Xy), 45.6 (CH^{Pd}), 119.9 (CH5, pyl), 120.3 (CH3, pyl), 127.7 (*ortho*-CH, Ph), 127.8 (*meta*-CH, Xy), 128.1 (*meta*-CH, Ph), 129.9 (*para*-CH, Xy), 131.9 (*para*-CH, Ph), 135.5 (*ortho*-C, Xy), 137.5 (*ipso*-C, Ph), 138.4 (CH4, pyl), 151.0 (CH6, pyl), 173.0 (CS), 196.5 (C=O).

4a·Br: Yield, 95 mg, 0.17 mmol, 87%. Mp: 159 ºC. Anal. Calcd for $C_{22}H_{19}BrN_2OPdS$: C, 48.42; H, 3.51; N, 5.13, S, 5.87. Found: C, 48.35; H, 3.28; N, 5.12, S, 5.72. IR(cm^{-1}): ν(C≡N), 2196; ν(C=O), 1648; ν(C=C), ν(C=N), 1591, 1578, 1555. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.22 (s, 6 H, Me, Xy), 5.80 (s, 1H, CH^{Pd}), 7.03 (d, 2 H, *meta*-CH, Xy, $^2J_{HH}$ = 8 Hz), 7.10 (ddd, 1H, H5, pyl, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.15-7.25 (various m, 4 H, *meta*-CH, Ph + *para*-CH, Ph + *para*-CH, Xy), 7.58 (dm, 1H, H3, pyl, $^3J_{HH}$ = 7 Hz), 7.64 (ddd, 1 H, H4, pyl, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.89 (m, 2 H, *ortho*-Ph), 9.24 (dm, 1 H, H6, pyl, $^3J_{HH}$ = 6 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 18.6 (Me, Xy), 47.3 (CH^{Pd}), 120.2 (CH5, pyl), 120.4 (CH3, pyl), 127.7 (*ortho*-CH, Ph), 127.8 (*meta*-CH, Xy), 128.2 (*meta*-CH, Ph), 129.9 (*para*-CH, Xy), 131.9 (*para*-CH, Ph), 135.5 (*ortho*-C, Xy), 137.7 (*ipso*-C, Ph), 138.4 (CH4, pyl), 152.5 (CH6, pyl), 172.8 (CS), 196.1 (CO).

4a·OAc: Yield, 98 mg, 0.19 mmol, 75%. Mp: 145 ºC. Anal. Calcd for $C_{24}H_{22}N_2O_3PdS$: C, 54.92; H, 4.22; N, 5.34, S, 6.11. Found: C, 54.71; H, 3.91; N, 5.31, S, 5.99. IR(cm^{-1}): ν(C≡N), 2209; ν(C=O), 1642; $\nu_{asym}(CO_2)$, 1620; ν(C=C), ν(C=N), 1591, 1553. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.04 (s, 3 H, Me, OAc), 2.19 (s, 6 H, Me, Xy), 5.51 (s, 1H, CH^{Pd}), 7.00 (d, 2 H, *meta*-CH, Xy, $^3J_{HH}$ = 7 Hz), 7.08 (ddd, 1H, H5, pyl, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.14-7.17 (various m, 3 H, *meta*-CH, Ph + *para*-CH, Ph), 7.21 (d, 1 H, *para*-CH, Xy, $^3J_{HH}$ = 7 Hz), 7.53 (d, 1H, H3, pyl, $^3J_{HH}$ = 8 Hz), 7.64 (ddd, 1 H, H4, pyl, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.90 (m, 2 H, *ortho*-Ph), 8.36 (dm, 1 H, H6, pyl, $^3J_{HH}$ = 6 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 18.4 (Me, Xy), 23.8 (Me, OAc), 41.7 (CH^{Pd}), 119.4 (CH5, pyl), 120.3 (CH3, pyl), 127.7 (*ortho*-CH, Ph), 127.8 (*meta*-CH, Xy), 128.1 (*meta*-CH, Ph), 129.7 (*para*-CH, Xy), 131.8 (*para*-CH, Ph), 135.6 (*ortho*-C, Xy), 137.7 (*ipso*-C, Ph), 138.4 (CH4, pyl), 149.3 (CH6, pyl), 173.8 (CS), 176.4 (*C*O_2, OAc), 198.1 (CO).

4b·Br: Yield, 202 mg, 0.28 mmol, 78%. Mp: 232 ºC (decomp). Anal. Calcd for $C_{34}H_{31}BrNOPPdS$: C, 56.80; H, 4.35; N, 1.95: S, 4.46. Found: C, 56.56; H, 4.35; N, 1.92; S, 4.19. IR (cm^{-1}): ν(C=O), 1644; ν(C=C), ν(C=N), 1588, 1555. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.35 (s, 9 H, Me, Tol), 4.48 (d, 1 H, CH^{Pd}, $^3J_{HP}$ = 3 Hz), 7.07-7.13 (m, 12 H, Tol + Ph + pyl), 7.30-7.37 (m, 6 H, Tol), 7.54 (t, br, 1 H, pyl,$^3J_{HH}$ = 8 Hz), 7.60 (td, 1 H, pyl, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 9.25 (m, 1 H, H6, pyl, $^3J_{HH}$ = 6 Hz). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 26.4. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 21.3 (Me, Tol), 51.3 (CH^{Pd})**,** 120.21 (CH5, pyl), 120.23 (CH3, pyl), 127.6 (*ortho*-CH, Ph), 128.0 (*meta*-CH, Ph), 128.2 (d, *ipso*-C, Tol, $^1J_{CP}$ = 46 Hz), 128.9 (d, *meta*-CH, Tol, $^3J_{CP}$ = 12 Hz), 131.1 (*para*-CH, Ph), 134.6 (d, *ortho*-CH, Tol, $^2J_{CP}$ = 12 Hz), 137.5 (CH4, pyl), 139.1 (*ipso*-C, Ph), 140.7 (d, *para*-CH, Tol, $^4J_{CP}$ = 2 Hz), 152.2 (CH6, pyl), 170.4 (CS), 196.8.1 (C=O).

Synthesis of [Pd{*N,C*-pyl-SCHC(O)Ph}Br(dmso)] (4c·Br). To a suspension containing **1·Br** (100 mg, 0.24 mmol) in acetone (5 mL) was added dmso (0.15 mL, 2.11 mmol). After 2h, of stirring, the resulting solution was concentrated under vacuum to 2 mL and Et_2O (20 mL) was added. Partial evaporation of the solvents' mixture under vacuum, and the concomitant cooling, caused the precipitation of a yellow solid which was filtered, washed with Et_2O (2 mL) and dried by suction to give **4c·Br**. Yield, 95 mg, 0.19 mmol, 80%. Mp: 138 ºC. Anal. Calcd for $C_{15}H_{16}BrNO_2S_2Pd$: C: 36,56; H: 3.27; N, 2.84; S: 13.01. Found: C: 36,63; H: 3.47; N, 2.92; S: 12.98. IR (cm^{-1}): ν(C=O), 1643; ν(C=C), ν(C=N), 1588, 1577; ν(S=O), 1117. The ^{1}H NMR spectrum of **4c·Br** in dmso-d_6 is identical to that of **1·Br** in the same solvent.

Synthesis of [Pd{*C,N*-pyl-SCHC(O)Ph}(*O,O'*-acac)] (5). To a suspension of **1·Br** (106 mg, 0.26 mmol) in CH_2Cl_2 (15 mL) was added Tl(acac) (77.6 mg, 0.26 mmol). A yellow suspension immediately formed which was stirred for 1 h and then filtered. The solution was concentrated under vacuum to *ca* 2 mL and n-hexane (20 mL) was added. The resulting suspension was filtered, and the solid collected was washed with n-hexane 2 mL and dried, first by suction and then in an oven at 70 ºC for 2 h to give **5** as a yellow solid. Yield, 89 mg, 0.20 mmol, 80%. Mp: 188

ºC (decomp). Anal. Calcd for $C_{18}H_{17}NO_3PdS$: C, 49.84; H, 3.95; N, 3.23, S, 7.39. Found: C, 49.56; H, 3.80; N, 3.27, S, 7.36. IR (cm^{-1}): ν(C=O), 1637; ν(C=C), (C=N), 1578, 1557. ^1H NMR (200 MHz, $CDCl_3$): δ 1.67 (s, Me, acac), 1.95 (s, Me, acac), 5.20 (s, 1 H, CH^{Pd}), 5.53 (s, 1 H, CH, acac), 6.93 (ddd, 1 H, H5, pyl, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.31-7.59 (various m, 5 H, pyl + Ph), 8.05 (m, 2 H, *ortho*-Ph), 8.24 (dm, 1 H, H6, pyl, $^3J_{HH}$ = 6 Hz). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 26.2 (Me, acac), 27.4 (Me, acac), 41.7 (CH^{Pd}), 100.1 (CH, acac), 118.8 (CH5, pyl), 120.7 (CH3, pyl), 127.2 (*ortho*-CH, Ph), 128.9 (*meta*-CH, Ph), 131.6 (*para*-CH, Ph), 137.4 (CH4, pyl), 137.9 (*ipso*-C, Ph), 148.8 (CH6, pyl), 176.9 (CS), 185.334 (CO, acac), 187.2 (CO, acac), 197.1 (C=O).

Synthesis of PPN[Pd{*C,N*-pyl-SCHC(O)Ph}Br_2] (6). To a suspension of **1·Br** (62 mg, 0.15 mmol) in CH_2Cl_2 (10 mL) was added [PPN]Br·CH_2Cl_2 (105.2 mg, 0.15 mmol). The resulting solution was stirred for 30 min, filtered through a short pad of Celite and concentrated under vacuum (1 mL). Upon the addition of Et_2O a suspension formed which was filtered. The solid collected was recrystallized from CH_2Cl_2 and Et_2O to give **6** as an orange solid. Yield, 135 mg, 0.13 mmol, 87% Mp: 97 ºC. Anal. Calcd for $C_{49}H_{40}Br_2N_2OP_2PdS$: C, 56.97; H, 3.90; N, 2.71; S, 3.10. Found: C, 56.90; H, 3.91; N, 2.87; S, 3.07. IR (cm^{-1}): ν(C=O), 1630; ν(C=C), (C=N), 1586, 1575, 1552. ^1H NMR (200 MHz, $CDCl_3$): δ 5.71 (s, 1 H, CH^{Pd}), 6.81 (m, 1 H, H4, pyl), 7.27-7.44 (various m, 7 H, H3 + H5, pyl, +Ph), 7.48 (m, 24 H, PPN), 7.67 (m, 6 H, PPN), 8.17 (d, 1 H, H6, pyl, $^3J_{HH}$ = 7 Hz). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 21.2. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 42.9 (CH^{Pd}), 119.2 (CH5, pyl), 120.2 (CH3, pyl), 127.2 (*ortho*-CH, Ph), 127.9 (*ipso*-C, PPN), 129.4 (*meta*-CH, Ph), 129.6 (*meta*-CH, PPN), 130.9 (*para*-CH, Ph), 132.0 (*ortho*-PPN), 133.8 (*para*-PPN), 136.2 (CH^4, pyl), 137.9 (*ipso*-C, Ph), 144.2 (CH6, pyl), CS, C=O not observed.

Synthesis of [Pd{*C,C,N*-pyl-SCHC(O)Ph}(PPh_3)] (7a). To a solution of PPh_3 (95 mg, 0.36 mmol) in CH_2Cl_2 (20 mL) was added complex **2** (136 mg, 0.36 mmol). The resulting brown-orange solution was stirred for 1h, concentrated to *ca.* 2 mL and Et_2O (20 mL) was added to give a solid which was recrystallized from CH_2Cl_2 and Et_2O to give **7a** as a pale brown solid. Yield, 181 mg, 0.31 mmol, 85%. Mp: 205 °C. Anal. Calcd for $C_{31}H_{24}NOPPdS$: C, 62.48; H, 4.06; N, 2.35; S, 5.38. Found: C, 62.53; H, 4.18; N, 2.59, S, 5.86. IR (cm^{-1}): ν(C=O), 1634; ν(C=C), ν(C=N), 1588, 1576, 1548. ^1H NMR (300 MHz, $CDCl_3$): δ 5.92 (d, 1 H, CH^{Pd}, $^3J_{HP}$ = 12 Hz), 6.15-6.19 (m, 1 H), 6.51-6.53 (m, 1 H), 6.90-6.95 (m, 1 H), 6.99-7.01 (m, 1 H), 7.21-7.26 (m, 14 H), 7.59-7.65 (m, 5 H). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 67.4 (d, CH^{Pd}, $^2J_{CP}$ = 72 Hz), 117.3 (CH), 121.5 (CH), 123.9 (CH), 124.3 (CH), 128.0 (d, CH, $^2J_{CP}$ = 2 Hz), 128.5 (d, CH, $^2J_{CP}$ = 10 Hz), 130.3 (d, CH $^2J_{CP}$ = 2 Hz), 131.4 (C), 132.1 (C), 134.8 (d, CH, J_{CP} = 14 Hz), 135.8 (CH), 136.9 (d, CH, J_{CP} = 12 Hz), 147.2 (d, C, J_{CP} = 9 Hz), 147.6 (C), 151.2 (d, CH, $^2J_{CP}$ = 2.82 Hz), 177.4 (CS), 195.8 (d, CO, J_{CP} = 6 Hz)**.** $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 27.8 (s). Mass spectrum (FAB^+) *m/z* (% abundance) 595.89 (M^+, 10.43%). Molecular weight in chloroform, 560.

Synthesis of [Pd{*C,C,N*-pyl-SCHC(O)C_6H_4-2}(^{t}BuNC)] (7b). To a suspension of **2** (*ca.* 0.1-0.5 mmol) in acetone (10-20 mL) one equivalent of ^{t}BuNC was added. The resulting red brown solution was stirred for 1 h, concentrated (2 mL) and n-hexane (15 mL) added to precipitate a dark red solid which was filtered and air dried. Yield, 204 mg, 0.49 mmol, 92%. Mp: 158 ºC. Anal Calcd for $C_{18}H_{18}N_2OPdS$: C, 51.87; H, 4.35; N, 6.72; S, 7.69%. Found: C, 51.65; H, 4.76; N, 7.12, S, 7.38. IR (cm^{-1}): ν(C≡N), 2179; ν(C=O), 1636; ν(C=C), ν(C=N), 1583, 1568, 1546. ^1H NMR (300 MHz, $CDCl_3$): δ 1.65 (s, 9 H, Me, ^{t}Bu), 5.57 (s, 1 H, CH^{Pd}), 6.87 (m, 1 H, H5, pyl), 7.10-7.14 (m, 2 H, C_6H_4), 7.27-7.54 (m, 4 H, pyl + C_6H_4), 8.24 (d, 1 H, H6, pyl, $^3J_{HH}$ = 5 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 30.4 (Me, ^{t}Bu), 57.6 (CMe_3), 61.7 (CH^{Pd}), 118.5 (CH5, pyl), 121.7 (CH4, pyl), 124.6 (CH, C_6H_4), 125.3 (CH, C_6H_4), 128.3 (C), 129.7 (CH, C_6H_4), 136.3 (CH3, pyl), 137.5 (CH, C_6H_4), 147.8 (Pd-*C*, C_6H_4), 148.4 (C(O)*C*-C_6H_4), 150.5 (CH6, pyl), 177.0 (CS), 196.7 (CO). Mass spectrum (FAB^+) *m/z* (% abundance) 416.86 (M^+, 27.34%), 333.77 (M^+ - ^{t}BuNC, 16.38%).

Synthesis of [Pd{*C,C,N*-pyl-SCHC(O)C_6H_4-2}(CNXy)] (7c). To a suspension of complex **3** (51 mg, 0.15 mmol) in CH_2Cl_2 (2 mL) was added dropwise a solution of XyNC (20.1 mg, 0.15 mmol) in the same solvent (5 mL). After 1 h of stirring, the resulting solution was filtered through a short pad of Celite, concentrated to 1 mL and Et_2O (10 mL) was added. The suspension was filtered and the solid collected was recrystallized from CH_2Cl_2 and Et_2O to give **7c** (52 mg, 0.11 mmol) as an off white solid which was dried by suction. Yield, 52 mg, 0.11 mmol, 72%. Mp: 160 ºC. Anal Calcd for $C_{22}H_{19}ClN_2OPdS$ C, 52.71; H, 3.82; N, 5.69; S, 6.40. Found: C, 52.79 ; H, 3.75; N, 5.52, S, 6.31. IR(cm^{-1}): ν(C≡N), 2199; (C=O), 1650; ν(C=C), ν(C=N), 1591, 1578, 1555. ^1H NMR (300 MHz, $CDCl_3$): δ 2.53 (s, 6 H, Me, Xy), 5.70 (s, 1 H, CH^{Pd}), 6.87 (ddd, 1 H, H5, pyl, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.11 (m, 2 H, C_6H_4), 7.20 (d, 2 H, *meta*-Xy, $^3J_{HH}$ = 8 Hz), 7.32 (dd, 1 H, *para*-Xy, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7 Hz), 7.39 (d, 1 H, H3, pyl, $^3J_{HH}$ = 8 Hz), 7.48 (ddd, 1 H, H4, pyl, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 7.55 (m, 2H, C_6H_4), 8.43 (d, 1 H, H6, pyl, $^3J_{HH}$ = 6 Hz) . $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 19.1 (Me, Xy), 62.5 (CH^{Pd}), 118.6 (CH5, pyl), 121.9 (CH3, pyl), 124.8 (CH, C_6H_4), 125.5 (CH, C_6H_4), 126.1 (*ipso*-C, Xy), 128.5 (*meta*-CH, Xy), 129.8 (CH, C_6H_4), 129.9 (*para*-CH, Xy), 135.5 (*ortho*-C, Xy), 136.5 (CH4, pyl), 147.7 (Pd-*C,* C_6H_4), 148.5 (C(O)*C*, C_6H_4), 150.8 (CH6, py), 177.0 (*C*S), 196.8 (*C*O). Crystals of **7c** suitable for an X ray diffraction study were obtained by the liquid diffusion method from CH_2Cl_2/Et_2O.

Synthesis of Me_4N[Pd{*C,C,N*-pyl-SCHC(O)C_6H_4-2}Cl] (8). To a suspension of **2** (144 mg, 0.38 mmol) in acetone (20 mL), solid Me_4NCl (42 mg, 0.38 mmol) was added. The resulting suspension was stirred for 7 h, the solvent was then removed under vacuum and the residue extracted with CH_2Cl_2 (3 x 5 mL). The combined extracts were filtered through Celite. Concentration of the brown-orange solution under vacuum (to *ca*. 2 mL) and addition of Et_2O (15 mL) gave a solid that was filtered and dried in an oven at 80 ºC overnight to give **8** as an orange-brown solid. Yield 159 mg, 0.36 mmol, 94%. Mp: 178 ºC. Anal Calcd for $C_{17}H_{21}ClN_2OPdS$: C, 46.06; H, 4.78; N, 6.32; S, 7.23. Found: C, 46.15; H, 5.08; N, 6.50; S, 6.97. IR (cm^{-1}): ν(C=O), 1637; ν(C=C), ν(C=N), 1582, 1568, 1547; ν(PdCl), 293. Λ_M, 61 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.15 (s, 12 H, NMe_4), 5.83 (s, 1 H, CH^{Pd}), 6.85 (ddd, 1 H, H5, pyl, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 6.97 (m, 2 H, C_6H_4) , 7.26-7.30 (m, 1

H, H3, pyl), 7.33-7.53 (m, 3 H, pyl + C_6H_4), 7.90 (d, 1 H, C_6H_4, $^3J_{HH}$ = 8 Hz), 8.90 (dm, 1 H, H6, pyl, $^3J_{HH}$ = 6 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 55.9 (t, NMe_4, $^1J_{CN}$ = 4 Hz), 58.2 (s, CH^{Pd}), 118.4 (CH5, pyl), 120.8 (CH3, pyl), 123.8 (CH, C_6H_4), 127.7 (CH, C_6H_4), 128.9 (CH, C_6H_4), 136.2 (CH4, pyl), 136.8 (CH), 147.4 (Pd-*C,* C_6H_4), 150.0 (CH6, pyl), 151.1 (C(O)*C*, C_6H_4), 174.1 (CS), 198.6 (s, CO). Mass spectrum (FAB^+) *m/z* (% abundance): 333.81 (M^+ - NMe_4Cl, 7.25%).

Synthesis of [*S,O*-{Pd{*C,C,N*-pyl-SCHC(O)C_6H_4-2}Cl}{Pd(μ-Cl)}]$_2$ (9). To a suspension of **2** (203 mg, 0.54 mmol) in acetone (20 mL) was added solid [$PdCl_2(NCPh)_2$] (208 mg, 0.54 mmol). Immediately an orange suspension formed which was stirred for 1h. It was then filtered and the solid washed with acetone (3 x 5 mL) to give a solid. A second crop was obtained upon concentration of the mother liquor. Complex **9** was obtained as an orange solid by treating both samples in an oven at 80 ºC overnight. Yield 267 mg, 0.26 mmol, 97%. Mp: 267 ºC**.** Anal Calcd for $C_{26}H_{18}Cl_4N_2O_2Pd_4S_2$: C, 30.56; H, 1.78; N, 2.74; S, 6.27. Found: C, 31.06; H, 2.00; N, 2.80; S, 6.06. IR (cm^{-1}): ν(C=O), 1638; ν(C=C), (C=N), 1587, 1569, 1541; ν(PdCl), 322 , 265. ^1H NMR (200 MHz, dmso-d_6): δ 4.62 (s, br, 1 H, CH^{Pd}), 6.8-8.1 (various overlapping multiplets, 4 H, pyl + C_6H_4), 8.55 (d, 1 H, H6, py, $^2J_{HH}$ = 6 Hz). Minor resonances are observed for another isomer at 5.64 (s, 0.2 H, CH^{Pd}), 8.50 (m, br, 0.2 H, H6, pyl)). The remaining resonances are obscured by those of the major isomer.

Synthesis of [*S,O*-{Pd{*C,C,N*-pyl-SCHC(O)C_6H_4-2}Cl}{Pd(Cl)(PPh_3)}] (10). To a solution of **7a** (80 mg, 0.13 mmol) in CH_2Cl_2 (15 mL) solid [$PdCl_2(NCPh)_2$] (52 mg, 0.13 mmol) was added. An orange color developed immediately and the solution was stirred for 20 h. It was filtered through anhydrous $MgSO_4$, concentrated under vacuum (to *ca.* 2mL) and Et_2O (15 mL) added to give **10** as a yellow solid. Yield 63 mg, 0.26 mmol, 61%. Mp: 210 ºC. Anal Calcd for $C_{31}H_{24}Cl_2NOPPd_2S$: 48.15; H, 3.13; N, 1.81; S, 4.15. Found: C, 47.96; H, 3.03; N, 1.85, S, 3.98. IR (cm^{-1}): ν(C=O), 1634; ν(C=C), ν(C=N), 1583, 1565, 1546; ν(PdCl), 355, 255. ^1H NMR (300 MHz, $CDCl_3$): δ 3.75 (s, br, 1 H, CH^{Pd}), 6.81 (m, 1 H, H5, pyl), 7.03 (m, 1 H, C_6H_4), 7.27 (m, 1 H, pyl), 7.30-7.65 (m, 14 H, C_6H_4 + ortho- + *meta*-PPh_3) 7.92 (m, 4 H, C_6H_4 + *para*-PPh_3), 8.21 (d, 1 H, pyl, $^3J_{HH}$ = 8 Hz), 8.92 (m, 1 H, H6, pyl). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 45.9 (CH^{Pd}), 122.9 (CH), 124.89 (CH), 125.25 (CH), 128.44 (CH, PPh_3), 128.66 (CH), 129.58 (C), 130.43 (C), 130.68 (CH, PPh_3), 131.13 (d, *ortho*-CH, PPh_3, $^3J_{CP}$ = 1 Hz), 134.81 (CH), 135.03 (CH, PPh_3), 138.64 (CH), 140.00 (C), 150.5 (CH6, pyl), 175.2 (CS), 187.0 (CO). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 29.79 (s).

Synthesis of [*S,O*-{Pd{*C,C,N*-pyl-SCHC(O)C_6H_4-2}(PPh_3)}Ag(PPh_3)ClO_4] (11). To a suspension of **7a** (115 mg, 0.19 mmol) in acetone (20 mL) solid $AgClO_4$ (40 mg, 0.19 mmol) was added. After 10 min of stirring a solution of PPh_3 (101 mg, 0.39 mmol) in acetone (20 mL) was added and the resulting suspension was stirred for 24 h. It was filtered through Celite, the pale orange solution was concentrated under vacuum (to *ca.* 2 mL) and Et_2O (20 mL) was added to give a solid which was recrystallized from $CHCl_3$ and Et_2O and dried in an oven at 80 ºC overnight to give **11** as a pale brown solid. Yield 119 mg, 0.11 mmol, 59%. Mp: 154 ºC. Anal Calcd for $C_{49}H_{39}AgClNO_5P_2PdS$: C, 55.23; H, 3.69; N, 1.31; S, 3.01. Found: C, 54.88; H, 3.68; N, 1.13; S, 2.78. IR (cm^{-1}): ν(C=O), 1652; ν(C=C), ν(C=N), 1586, 1573, 1558, ClO_4, 1190, 622. Λ_M (acetone) = 118 Ω^{-1} cm^2 mol^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.74 (d, 1 H, CH^{Pd}, $^3J_{HP}$ = 10.2 Hz), 6.41-6.54 (m, 1 H, H4, py), 7.68-7.16 (m, 37 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 62.4 (CH^{Pd}), 119.7 (CH), 122.3 (CH), 124.3 (CH), 124.6 (CH), 129.2 (CH), 130.2 (C), 130.7 (C), 130.9 (CH), 131.00 (CH), 132.0 (CH), 132.1 (CH), 133.8 (CH), 134.9 (CH), 135.0 (CH), 137.8 (CH), 147.3 (C), 151.6 (CH), 174.2 (CS), 194.6 (CO). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, see Discussion): δ (20 ºC) 11.5 (v br, $AgPPh_3$), 15.5 (v br, $AgPPh_3$), 31.0 (s, $PdPPh_3$); (–60 ºC) δ 12.0 [two d, $AgPPh_3$, J($^{109}Ag^{31}P$) = 564 Hz, J($^{107}Ag^{31}P$) = 489 Hz], 12.7 (br, $AgPPh_3$), 18.1 (br, $AgPPh_3$), 32.6 (s, $PdPPh_3$), 34.0 (s, $PdPPh_3$). Mass spectrum (FAB^+) *m/z* (% abundance): 966 (M^+-ClO_4, 5.34%); 595.97 (M^+-$AgClO_4$ - PPh_3).

Acknowledgments

We thank Ministerio de Educación y Ciencia (Spain), FEDER (CTQ2011-24016) and Fundación Séneca (04539/GERM/06 and 03059/PI/05) for financial support.

[a] *Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Apartado 4021, 30071 Murcia, Spain; E-mail: mch@um.es, jvs1@um.es*
[b] *SAI, Universidad de Murcia, Apartado 4021, 30071 Murcia, Spain; E-mail: dbc@um.es*

† Electronic Supplementary Information (ESI) available: Crystallographic data for compounds **1·Br**·$CHCl_3$, **1·AcO** and **7c**. CCDC 1001641 for **1·Br**·$CHCl_3$; 1001642 for **1·AcO**; 1001640 for **7c**. For ESI and crystallographic data in CIF format see DOI: 10.1039/b000000x/

Notes and references

1 L. A. Hegedus, *Tetrahedron*, 1984, **40**, 2415; R. D. O'Sullivan and A. W. Parkins, *J. Chem. Soc., Chem. Commun.*, 1984, 1165; A. D. Ryabov, *Synthesis*, 1985, 233; I. R. Girling and D. A. Widdowson, *J. Chem. Soc. Perkin Trans 1,* , 1988, 1317; M. Pfeffer, *Recl. Trav. Chim. Pays-Bas*, 1990, **109**, 567; M. Pfeffer, *Pure Appl. Chem.*, 1992, **64**, 335; J. Vicente, J.-A. Abad and J. Gil-Rubio, *J. Organomet. Chem.*, 1992, **436**, C9; P. Ballester, M. Capo, X. Garcias and J. M. Saa, *J. Org. Chem.*, 1993, **58**, 328; J. Vicente, J. A. Abad, J. Gil-Rubio and P. G. Jones, *Organometallics*, 1995, **14**, 2677; J. Vicente, J. A. Abad and J. Gil-Rubio, *Organometallics*, 1996, **15**, 3509; M. A. Stark and C. J. Richards, *Tetrahedron Lett.*, 1997, **38**, 5881; S. E. Denmark, R. A. Stavenger, A. M. Faucher and J. P. Edwards, *J. Org. Chem.*, 1997, **62**, 3375; M. Ohff, A. Ohff, M. E. van der Boom and D. Milstein, *J. Am. Chem. Soc.*, 1997, **119**, 11687; P. Steenwinkel, R. A. Gossage and G. van Koten, *Chem. Eur. J.*, 1998, **4**, 759; J. Vicente, J.-A. Abad, J. Lopez-Serrano, P. G. Jones, C. Najera and L. Botella-Segura, *Organometallics*, 2005, **24**, 5044; K. Godula and D. Sames, *Science*, 2006, **312**, 67; J. Vicente, I. Saura-Llamas, J.-A. Garcia-Lopez, B. Calmuschi-Cula and D. Bautista, *Organometallics*, 2007, **26**, 2768; K.-E. Lee, H.-T. Jeon, S.-Y.

Han, J. Ham, Y.-J. Kim and S. W. Lee, *Dalton*, 2009; X. Chen, K. M. Engle, D.-H. Wang and J.-Q. Yu, *Angew. Chem., Int. Ed. Engl.*, 2009, **48**, 5094; B. Xiao, T.-J. Gong, J. Xu, Z.-J. Liu and L. Liu, *J. Am. Chem. Soc.*, 2011, **133**, 1466; J.-A. Garcia-Lopez, M.-J. Oliva-Madrid, I. Saura-Llamas, D. Bautista and J. Vicente, *Chem. Commun.*, 2012, **48**, 6744.

2 W. A. Herrmann, C. Brossmer, K. Ofele, C. P. Reisinger, T. Priermeier, M. Beller and H. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1844.

3 T. W. Lyons and M. S. Sanford, *Chem. Rev.*, 2010, 1147.

4 M. Chiang, Y. Li, K. Deepa, S. Pulllarkat, K. H. Ng and P.-H. Leung, *Eur. J. Inorg. Chem.*, 2010, 1413; Y. Ding, M. Chiang, S. A. Pulllarkat, Y. Li and P.-H. Leung, *Organometallics*, 2009, **28**, 4358; M. Ogasawara, S. Arae, S. Watanabe, V. Subbarayan, H. Sato and T. Takahasi, *Organometallics*, 2013, **32**, 4997; C. E. Barday, G. Deeble, R. J. Doyle, S. A. Elix, G. Salem, T. L. Jones, S. B. Wild and A. C. Willis, *J. Chem. Soc., Dalton Trans.*, 1995, 57; M. Pabel, A. C. Willis and S. B. Wild, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1835; S. B. Wild, *Coord. Chem. Rev.*, 1997, **166**, 291; V. V. Dunina, L. G. Kuzmina, M. Y. Kazakova, Y. K. Grishin, Y. A. Veits and E. I. Kazakova, *Tetrahedron: Asymmetry*, 1997, **8**, 2537; J. Albert, J. M. Cadena and J. Granell, *Tetrahedron: Asymmetry*, 1997, **8**, 991; J. Spencer, F. Maassarani, M. Pfeffer, A. Decian and J. Fischer, *Tetrahedron: Asymmetry*, 1994, **5**, 321.

5 C. Chen, E. Zhan, Y. Li and W. Shen, *J. Mol. Catal.*, 2013, **379**, 117; Q. Liu, Y.-A. Zhanng, P. Xu and Y. Jia, *J. Org. Chem.*, 2013, **78**, 10885; L. Chu, X.-C. Wang, C. E. Moore, A. L. Rheingold and Y. J.-Q., *J. Am. Chem. Soc.*, 2013, **135**, 16344; T. K. Hollis and L. E. Overman, *Tetrahedron Lett.*, 1997, **38**, 8837.

6 N. Usol'tseva, P. Espinet, J. Buey and J. L. Serrano, *J. Mater. Chem.*, 1997, **7**, 215; J. L. Serrano, 'Metallomesogens', VCH, 1996; N. J. Thompson, J. L. Serrano, M. J. Baena and P. Espinet, *Chem. Eur. J.*, 1996, 214; D. P. Lydon and J. P. Rourke, *Chem. Commun.*, 1997, 1741; F. Neve, M. Ghedini and A. Crispini, *Chem. Commun.*, 1996, 2463; J. Barberá, P. Espinet, E. Lalinde, M. Marcos and J. L. Serrano, *Liq. Cryst.*, 1987, **2**, 833; P. Espinet, E. Lalinde, M. Marcos, J. Pérez and J. L. Serrano, *Organometallics*, 1990, **9**, 555; P. Espinet, J. Pérez, M. Marcos, M. B. Ros, J. L. Serrano, J. Barberá and A. M. Levelut, *Organometallics*, 1990, **9**, 2028; P. Espinet, J. Etxebarría, M. Marcos, J. Pérez, A. Remón and J. L. Serrano, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1065; A. El-ghayoury, L. Douce, A. Skoulios and R. Ziessel, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 1255; B. Neumann, T. Hegmann, R. Wolf and C. Tschierske, *Chem. Comunn.*, 1998, 105.

7 C. Bincoletto, I. L. S. Tersariol, C. R. Oliveira, S. Dreher, D. M. Fausto, M. A. Soufen, F. D. Nascimento and A. C. F. Caires, *Bioorg. Med.Chem.* , 2005, **13**, 3047; D. Pucci, V. Albertini, R. Bloise, A. Bellusci, A. Cataldi, C. V. Catapano, M. Ghedini and A. Crispini, *J. Inorg. Biochem.*, 2006, **100**; A. I. Matesanz and P. Souza, *J. Inorg. Biochem.*, 2007, **101**; A. C. Moro, A. E. Mauro, A. V. G. Netto, S. R. Ananias, M. B. Quilles, I. Z. Carlos, F. R. Pavan, C. Q. F. Leite and M. D. Hörner, *Eur. J. Med. Chem.*, 2009, **44**, 4611; C. Navarro-Ranninger, I. López-Solera, V. M. González, J. M. Pérez, A. Alvarez-Valdés, A. Martín, P. Raithby, J. R. Masaguer and C. Alonso, *Inorg. Chem.*, 1996, **35**, 5181; A. G. Quiroga, J. M. Perez, I. Lopez-Solera, J. R. Masaguer, A. Luque, P. Román, A. Edwards, C. Alonso and C. Navarro-Ranninger, *J. Med. Chem.*, 1998, **41**, 1399.

8 N. Nebra, J. Lisena, N. Saffon, L. Maron, B. Martin-Vaca and D. Bourissou, *Dalton Trans.,*, 2011, **40**, 8912.

9 G. R. Newkome, T. Kawato, D. K. Kohli, W. E. Puckett, B. D. Oliver, G. Chiari, F. R. Fronczek and W. A. Deutsch, *J. Am. Chem. Soc.*, 1981, **103**, 3423; G. R. Newkome, W. E. Puckett, G. E. Kiefer, V. K. Gupta, F. R. Fronczek, D. C. Pantaleo, G. L. McClure, J. B. Simpson and W. A. Deutsch, *Inorg. Chem.*, 1985, **24**, 811.

10 G. R. Newkome, V. K. Gupta and F. R. Fronczek, *Organometallics*, 1982, **1**, 907; G. R. Newkome, W. E. Puckett, V. K. Gupta and F. R. Fronczek, *Organometallics*, 1983, **2**, 1247; Y. Nojima, M. Nonoyama and K. Nakajima, *Polyhedron*, 1996, **15**, 3795; G. De Munno, M. Ghedini and F. Neve, *Inorg. Chim. Acta*, 1995, **239**, 155; B. Galli, F. Gasparrini, L. Maresca, G. Natile and G. Palimieri, *J. Chem. Soc., Dalton Trans.*, 1983, 1483; J. Forniés, R. Navarro, V. Sicilia and M. Tomas, *Inorg. Chem.*, 1993, **32**, 3675; A. D. Ryabov and A. K. Yatsimirsky, *Inorg. Chem.*, 1984, **23**, 789; A. G. Constable, W. S. McDonald, L. C. Sawkins and B. L. Shaw, *J. Chem. Soc. Dalton Trans.,*, 1980, 1992; J. E. Baldwin, R. H. Jones, C. Nájera and M. Yus, *Tetrahedron*, 1985, **41**, 699.

11 J. Dupont, R. A. P. Halfen, R. Schenato, A. Berger, M. Horner, A. Bortoluzzi and C. Maichlemossmer, *Polyhedron*, 1996, **15**, 3465; A. Yoneda, T. Hakushi, G. R. Newcome and F. R. Fronczek, *Organometallics*, 1994, **13**, 4912.

12 J. Vicente, M. T. Chicote, M. C. Lagunas, P. G. Jones and E. Bembenek, *Organometallics*, 1994, **13**, 1243.

13 J. Vicente, M. T. Chicote, C. Rubio, M. C. Ramírez de Arellano and P. G. Jones, *Organometallics*, 1999, **18**, 2750.

14 J. Vicente, M. T. Chicote, M. I. Lozano and S. Huertas, *Organometallics*, 1999, **18**, 753.

15 M. T. Chicote, I. Vicente-Hernández, P. G. Jones and J. Vicente, *Organometallics*, 2012, **31**, 6252; B. J. O'Keefe and P. J. Steel, *Organometallics*, 1998, **17**, 3621; K. Hamamura, M. Kita, M. Nonoyama and J. Fujita, *J. Organomet. Chem.*, 1993, **463**, 169; I. G. Phillipps and P. J. Steel, *J. Organomet. Chem.*, 1991, **410**, 247; G. B. Caygill and P. J. Steel, *J. Organomet. Chem.*, 1990, **395**, 375; B. J. O'Keefe and P. J. Steel, *Organometallics*, 2003, **22**, 1281; V. I. Sokolov, L. L. Troitskaya and V. L. Bondareva-Don, *Molecules*, 2005, **10**; M. Mariño, J. Martínez, M. Caamaño, M. T. Pereira, J. M. Ortigueira, E. Gayoso, A. Fernández and J. M. Vila, *Organometallics*, 2012, **31**, 890; D. J. Geest and S. P. J., *Inorg. Chem. Commun.*, 1998, **1**; S. Chakladar, P. Paul, A. K. Mukherjee, S. K. Dutta, K. K. Nanda, D. Podderb and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1992, 3119.

16 D.-H. Lee, J. Chen, J. W. Faller and R. H. Crabtree, *Chem. Commun.*, 2001, 213.

17 S. Musa, A. Shpruhman and D. Gelman, *J. Organomet. Chem.*, 2012, **699**, 92.

18 W. Weng, C.-H. Chen, B. M. Foxman and O. V. Ozerov, *Organometallics*, 2007, **26**, 3315; S. Sjövall, O. F. Wendt and C. Andersson, *J. Chem. Soc., Dalton Trans.*, 2002, 1396; R. Gerber, O. Blacque and C. M. Frech, *ChemCatChem.*, 2009, **1**, 393; M. Ciclosi, J. Lloret, F. Estevan, P. Lahuerta, M. Sanaú and J. Perez-Prieto, *Angew. Chem., Int. Ed. Engl.*, 2006, **45**, 6741.

19 P. Oulié, N. Nebra, S. Ladeira, B. Martin-Vaca and D. Bourissou, *Organometallics*, 2011, **30**, 6416.

20 D. Solé, X. Solans and M. Font-Bardia, *Dalton Trans.*, 2007, 4286.

21 J. Vicente, A. Arcas, F. Julia-Hernandez and D. Bautista, *Angew. Chem., Int. Ed. Engl.*, 2011, **50**, 6896; J. Vicente, A. Arcas, F. Julia-Hernandez and D. Bautista, *Inorg. Chem.*, 2011, **50**, 5339; F. Juliá-Hernández, A. Arcas and J. Vicente, *Chem. Eur. J.*, 2012, **18**, 7780.

22 J. Vicente, A. Arcas, F. Julia-Hernandez and D. Bautista, *Chem. Commun.*, 2010, **46**, 7253.

23 A. Abellan-Lopez, M. T. Chicote, D. Bautista and J. Vicente, *Organometallics*, 2012, **31**, 7434.

24 G. Aragay, J. Pons, J. García-Antón, X. Solans, M. Font-Bardía and J. Ros, *J. Organomet. Chem.*, 2008, **693**, 3396; C. J. Wallis, I. L. Kraft, J. N. Murphy, B. O. Patrick and P. Mehrkhodavandi, *Organometallics*, 2009, **28**, 3889.

25 J. Albert, M. Crespo, J. Granell, J. Rodriguez, J. Zafrilla, T. Calvet, M. Font-Bardia and X. Solans, *Organometallics*, 2010, **29**, 214; A. Bohm and W. Beck, *J. Organomet. Chem.*, 1999, **588**, 247; C. L. Chen, Y. H. Liu, S. M. Peng and S. T. Liu, *J. Organomet. Chem.*, 2004, **689**, 1806; S. Das and S. Pal, *J. Organomet. Chem.*, 2006, **691**, 2575; A. Fernandez, D. Vazquez-Garcia, J. J. Fernandez, M. Lopez-Torres, A. Suarez, S. Castro-Juiz and J. M. Vila, *New J. Chem.*, 2002, **26**, 398; R. Grigg and J. Devlin, *J. Chem. Soc., Chem. Commun.*, 1986, 631; K. Hiraki, S. Ibaraki, M. Onishi, Y. Ono, J. K. Kawashima and M. Ando, *J. Organomet. Chem.*, 1997, **547**, 199; Y. Hu, M. A. Khan and K. M. Nicholas, *J. Chem. Soc., Chem. Commun.*, 1992, 210; C. Lopez, A. Caubet, S. Perez, X. Solans and M. Font-Bardia, *J. Organomet. Chem.*, 2003, **681**, 82; C. Lopez, S. Perez, X. Solans, M. Font-Bardia and T. Calvet, *New J. Chem.*, 2010, **34**, 676; A. K. Mahapatra, D. Bandyopadhyay, P. Bandyopadhyay and A. Chakravorty, *J. Chem. Soc., Chem. Commun.*, 1984, 999; D. N. Neogi, A. N. Biswas, P. Das, R. Bhawmick and P. Bandyopadhyay, *Inorg. Chim. Acta*, 2007, **360**, 2181; S. Perez, C. Lopez, A. Caubet, X. Solans, M. Font-Bardia, A. Roig and E. Molins, *Organometallics*, 2006, **25**, 596; A. R. B. Rao and S. Pal, *J. Organomet. Chem.*, 2011, **696**, 2660; J. M. Vila, T. Pereira, J. M. Ortigueira, M. L. Torres, A. Castineiras, D. Lata, J. J. Fernandez and A. Fernandez, *J. Organomet. Chem.*, 1998, **556**, 21.

26 J. Vicente, M. T. Chicote, S. Huertas, M. C. Ramírez de Arellano and P. G. Jones, *Eur. J. Inorg. Chem.*, 1998, 511.

27 J. Vicente, I. Saura-Llamas, M. G. Palin, P. G. Jones and M. C. Ramírez de Arellano, *Organometallics*, 1997, **16**, 826; A. D. Ryabov, *Chem. Rev.*, 1990, **90**, 403.

28 J. Vicente, I. Saura-Llamas, M. G. Palin and P. G. Jones, *J. Chem. Soc., Dalton Trans.*, 1995, 2535.

29 Anal Calcd for $C_{18}H_{14}N_2OPdS$: C, 52.38; H, 3.42; N, 6.79; S, 7.77. Found: C, 51.48; H, 3.35; N, 6.80; S, 7.33.

30 J. Vicente, J. A. Abad, A. D. Frankland and M. C. Ramírez de Arellano, *Chem. Commun.*, 1997, 959.

31 J. Vicente, A. Arcas, D. Bautista and P. G. Jones, *Organometallics*, 1997, **16**, 2127.

32 J. Vicente, A. Arcas, M. A. Blasco, J. Lozano and M. C. Ramírez de Arellano, *Organometallics*, 1998, **17**, 5374.

33 M. B. Smith and A. M. Z. Slawin, *Inorg. Chim. Acta*, 2000, **299**, 172; A. M. Z. Slawin, M. B. Smith and J. D. Woollins, *Polyhedron*, 1998, **17**, 4465.

34 D. Gibson, B. F. G. Johnson and J. Lewis., *J. Chem. Soc. A*, 1970, 367.

35 E. Pretsch, T. Clerc, J. Seibl and W. Simon, 'Tablas para la determinación estructural por métodos espectroscópicos', Springer-Verlag Ibérica, 1998.

36 K. Nakamoto. Infrarred and Raman Spectra of Inorganic and Coordination Compounds. Part B. Wiley and Sons, New Jersey, **2009**, 107

37 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.

38 J. Vicente, M. T. Chicote, P. González-Herrero and P. G. Jones, *Inorg. Chem.*, 1997, **36**, 5735.

39 Sheldrick, G. M. SHELX-97; University of Göttingen: Göttingen, Germany, 1997

40 SHELXTL Xlmp Crystal Structure Refinement - Multi-cpu Version Copyright(c) Bruker AXS Inc. 1993-2013, Version 2013/2