A Comparative Study of Cyclometallated Palladium(II) Compounds with Terdentate [C,N,S] Pincer Ligands − Crystal and Molecular Structure of [Pd{4-$MeC_6H_3C(Me)$=NNC(=S)NHMe}(PPh_3)] and [Pd{4-$MeOC_6H_3C(H)$=N[2-$(SMe)C_6H_4$]}(Cl)]

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Treatment of the thiosemicarbazone ligands 4-$MeC_6H_4C(Me)$=NN(H)C(=S)NHMe (**a**), 4-$MeC_6H_4C(Me)$=NN(H)C(=S)NHEt (**b**), and 4-$MeC_6H_4C(Me)$=NN(H)C(=S)NHPh (**c**) with $K_2[PdCl_4]$ produced the tetranuclear palladium(II) compounds [Pd{4-$MeC_6H_3C(Me)$=NNC(=S)-NHMe}]$_4$ (**1a**), [Pd{4-$MeC_6H_3C(Me)$=NNC(=S)NHEt}]$_4$ (**1b**), and [Pd{4-$MeC_6H_3C(Me)$=NNC(=S)NHPh}]$_4$ (**1c**) with deprotonation of the NH group. Treatment of thiosemicarbazones 4-$MeOC_6H_4C(H)$=NN(Me)C(=S)NH_2 (**d**) and 3-$MeOC_6H_4C(H)$=NN(Me)C(=S)NH_2 (**e**) with $K_2[PdCl_4]$ gave the mononuclear palladium(II) compounds [Pd{4-$MeOC_6H_3$-C(H)=NN(Me)C(=S)NH_2}(Cl)] (**1d**) and [Pd{3-$MeOC_6H_3$-C(H)=NN(Me)C(=S)NH_2}(Cl)] (**1e**). Treatment of the Schiff base 4-$MeOC_6H_4C(H)$=N[2-$(SMe)C_6H_4$] (**f**) with $Li_2[PdCl_4]$ afforded [Pd{4-$MeOC_6H_3C(H)$=N[2-$(SMe)C_6H_4$]}(Cl)] (**1f**). All the ligands are terdentate through the [C,N,S] atoms and the Pd–S bond formed is sufficiently strong to tolerate treatment with nucleophiles without bond cleavage. Treatment of **1a**, **1b**, and **1c** with triphenylphosphane gave the mononuclear species **2a**, **2b**, and **2c**, which upon treatment with hydrochloric acid resulted in the 1:1 electrolytes **3a**, **3b**, and **3c**, with NH and C=S groups. Coordination of PPh_3 to Pd in **1f** was achieved by treatment of the compound with sodium perchlorate, followed by the nucleophile in a 1:1 molar ratio, to yield **2f**. The crystal structures of compounds **2a** and **1f** are described.

Introduction

Cyclometallated compounds, as a class within the organometallic family, are quite numerous and they have been intensively studied.[1−7] This is due especially to the wide variety of organic ligands bearing an appropriate donor atom that may sustain metallation with formation of the stable five-membered ring. When the ligand to be metallated has more than one donor atom, a second ring, bonded to the metal ion through the corresponding non-carbon donor atoms, may be created, thus giving compounds with two fused rings at the metal center. We have previously met with this situation with terdentate [C,N,N] Schiff bases,[8−10] terdentate [C,N,O] semicarbazones,[11] and terdentate [C,N,S] thiosemicarbazones.[12] The last case is clearly distinct from the former two, in that the sulfur atom strongly binds to the metal ion, palladium(II) and platinum(II) in our case, thus making the ligands excellent pincer species that powerfully secure three of the four coordination positions of the metal ion, allowing only the fourth coordination site to undergo further reaction with nucleophiles such as tertiary phosphanes. Even with the use of strongly chelating diphosphanes, the palladium− or platinum−sulfur bond remains uncleaved, in contrast to the breakage of the oxygen− or nitrogen−metal bonds of the chelate ring found in the cases of semicarbazone or Schiff base ligands, respectively. Another interesting issue relating to these ligands is the tetrameric nature of the compounds obtained upon treatment of the ligand with the corresponding metal salt; these are cyclometallated thiosemicarbazone Pd_4 or Pt_4 clusters, which also form polymers through hydrogen bonds.[12] The outstanding question still to be answered is whether these findings are dependent on the structure of the −C(R)=N−X(R′)−C(S)−NH(R′′) chain (X = C, N; R, R′, R′′ = H, alkyl, aryl) that supports the rings at the metal atom and how modification of this chain may alter the nature of the resulting products and their properties. That is the purpose of this paper, and here we report results concerning ligands with three different chain se-

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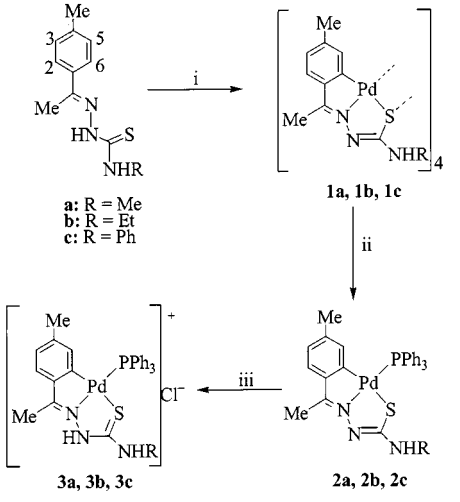
quences, −C(Me)=N−N(H)−C(NHR)−S (R = Me, Et, Ph), −C(H)=N−N(Me)−C(NH_2)−S, and −C(H)=N−C−C−SMe, in order to undertake a comparative study of the complexes.

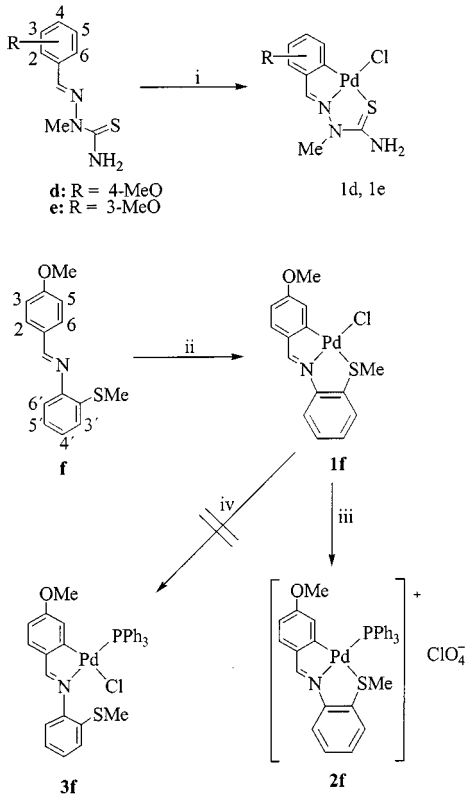
Results and Discussion

The thiosemicarbazones **a**, **b**, **c**, **d**, and **e** were prepared by treatment of 4-methylthiosemicarbazide, 4-ethylthiosemicarbazide, 4-phenylthiosemicarbazide, or 2-methylthiosemicarbazide with 4-methylacetophenone, 4-methoxybenzaldehyde, or 3-methoxybenzaldehyde as appropriate, whilst ligand **f** was prepared by treatment of 4-methoxybenzaldehyde with 2-(methylthio)aniline (see Exp. Sect.). All the ligands showed the characteristic ν(C=N) stretch in their IR spectra, and ligands **a**−**e** also showed the ν(C=S) band (Exp. Sect.); although bands involving the C=S group are often difficult to assign, we have located the ν(C=S) mode in the free ligands in the 850−820 cm^{-1} range [for a more detailed study concerning the ν(C=S) mode, see ref.[12]]. The NH protons in **a**, **b**, and **c** showed signals at δ ≈ 8−9.5. From these ligands, new cyclometallated compounds were obtained, and these are shown in Schemes 1 and 2. In a typical experiment, a suspension of potassium tetrachloropalladate in ethanol/water was treated with the corresponding thiosemicarbazone ligand to give complexes [Pd{4-$MeC_6H_3C(Me)$=NNC(=S)NHMe}]$_4$ (**1a**), [Pd{4-$MeC_6H_3C(Me)$=NNC(=S)NHEt}]$_4$ (**1b**), and [Pd{4-$MeC_6H_3C(Me)$=NNC(=S)NHPh}]$_4$ (**1c**) as yellow, air-stable solids, with the ligand in the (*E*,*Z*) configuration.



Scheme 1. (i) $K_2[PdCl_4]$/EtOH or $Pd(AcO)_2$/glacial acetic acid; (ii) PPh_3/Me_2CO (1:4); (iii) HCl(aq)

The products were characterized by elemental analysis (C, H, N) and IR and ^1H and ^{13}C {^1H} NMR spectroscopy. For complexes **1a**, **1b**, and **1c**, the mass spectra (FAB) showed peaks at *m*/*z* = 1302.9, 1359.0, and 1551.2, respectively, suggesting tetranuclear complexes similar to others obtained by us[12] and by others.[13−15] In addition, the absence of signals for the NH groups in the ^1H NMR spectra attested to deprotonation, as observed previously.[13,14,16,17]



Scheme 2. (i) $K_2[PdCl_4]$/EtOH; (ii) $Li_2[PdCl_4]$/NaAcO/MeOH; (iii) $AgClO_4/PPh_3/Me_2CO$; (iv) PPh_3/Me_2CO

The metallation of the ligand was clear, from the absence of the AA′XX′ systems of the *para*-substituted phenyl rings, and the three remaining proton resonances were unequivocally assigned (see Exp. Sect.). The ^{13}C-{^1H} data confirmed metallation of the phenyl ring:[18] the C=N, C(1), and C(6) resonances were shifted to low field relative to those of the free ligands, whilst the N*C*S resonance was shifted upfield. The ν(C=N) band shifted to lower wavenumbers on complex formation,[19] contrary to the trend observed for other thiosemicarbazone complexes, which show a shift to higher wavenumbers.[20] The ν(C=S) band disappeared, in agreement with loss of the double bond character upon deprotonation of the NH group, which is necessary in order to preserve the electroneutrality of the tetranuclear complexes. In view of these results, we reasoned that, if deprotonation of the NH group could be hindered, then the N(H)−C=S moiety would not be able to adopt the N···C···S character needed for the tetrameric species. In order to achieve this, we synthesized ligands **d** and **e**, in which the chain sequence on the metallated aromatic ring was −C(H)=N−N(Me)−C(NH_2)−S. The stronger N−Me bond, in place of the N−H bond, should keep the −N(Me)−C=S moiety unaltered, providing a mononuclear compound. Thus, treatment of ligands **d** or **e** with potassium tetrachloropalladate in ethanol/water gave the complexes [Pd{4-$MeOC_6H_3C(H)$=NN(Me)C(=S)NH_2}(Cl)] (**1d**) and [Pd{3-$MeOC_6H_3C(H)$=NN(Me)C(=S)NH_2}(Cl)] (**1e**), as yellow, air-stable solids, which were fully characterized (see Exp. Sect.).

The ^{1}H and ^{13}C-{^{1}H} data showed metallation of the aromatic ring (vide supra). The mass spectra (FAB) in each case showed a peak at *m*/*z* = 364.2. The IR spectra showed ν(C=S) bands (absent in **1a**, **1b**, and **1c**) at 831 and 837 cm^{-1} for **1d** and **1e**, respectively, and ν(Pd−Cl) bands (also absent in **1a**, **1b**, and **1c**, in accordance with the absence of the chloride ligand in the palladium coordination environment) at 310 and 306 cm^{-1} for **1d** and **1e**, respectively. These findings are in good agreement with mononuclear species and establish that the −N(Me)−C=S group remains unchanged, confirming our initial assumption. Having established how modification of the chain alters the nature of the compounds synthesized, another issue to be considered was the reactivity of the complexes; that is, whether similar variations would influence the excellent pincer properties of the terdentate [C,N,S] ligands so far studied by us, the thiosemicarbazones, which strongly retain three metal coordination positions. For this purpose we included the sequence −C(H)=N−C=C−SMe (ligand **f**, in which the −C−C− group is part of an aryl ring) and synthesized compound **1f** for more detailed comparative study. Thus, treatment of 4-MeOC$_6$H$_4$C(H)=N[2-(SMe)C$_6$H$_4$] with lithium tetrachloropalladate in methanol gave compound [Pd{4-MeOC$_6$H$_3$C(H)=N[2-(SMe)C$_6$H$_4$]}(Cl)] as an air-stable, fully characterized solid (see Exp. Sect.). The shift of the ν(C=N) stretch towards lower wavenumbers[21] and the upfield shift of the HC=N resonance in the ^{1}H NMR spectrum supported nitrogen coordination to the metal center.[22] The metallated ligand showed the absence of the AA′XX′ system of the *para*-substituted phenyl ring (vide supra). The C=N, C(1), and C(6) resonances in the ^{13}C-{^{1}H} NMR spectrum were shifted downfield from those of the free ligand, in accordance with metallation and Pd−N coordination.[18] The S*Me* resonance was shifted downfield in both the ^{1}H and the ^{13}C-{^{1}H} NMR spectra, in agreement with Pd−S coordination. The crystal and the molecular structure of **1f** are described below.

Reactivity of the Complexes

For **1a**, **1b**, and **1c**, a reactivity pattern similar to that observed by us earlier[12] was found. Thus, treatment of **1a**, **1b**, and **1c** with triphenylphosphane in a 1:4 molar ratio gave compounds [Pd{4-MeC$_6$H$_3$C(Me)=NNC(=S)NHMe}(PPh$_3$)] (**2a**), [Pd{4-MeC$_6$H$_3$C(Me)=NNC(=S)NHEt}(PPh$_3$)] (**2b**), and [Pd{4-MeC$_6$H$_3$C(Me)=NNC(=S)NHPh}(PPh$_3$)] (**2c**), which were fully characterized (see Exp. Sect.). The ^{1}H NMR spectra showed the H(5) resonance shifted upfield and coupled to the phosphorus nucleus. The C=S, C=N, C(1), and C(6) signals in the ^{13}C-{^{1}H} spectra appeared shifted as shown above. The ^{31}P resonance was a singlet and the chemical shift values were consistent with a geometry with the phosphorus atom *trans* to the nitrogen atom.[23−26] Treatment of complexes **1a**, **1b**, and **1c** with hydrochloric acid gave compounds [Pd{4-MeC$_6$H$_3$C(Me)=NNC(=S)NHMe}(PPh$_3$)]$^+$Cl$^-$ (**3a**), [Pd{4-MeC$_6$H$_3$C(Me)=NNC(=S)NHEt}(PPh$_3$)]$^+$Cl$^-$ (**3b**), and [Pd{4-MeC$_6$H$_3$C(Me)=NNC(=S)NHPh}(PPh$_3$)]$^+$Cl$^-$ (**3c**) as fully characterized 1:1 electrolytes, as shown by electric conductivity measurements[27] (see Exp. Sect.). The most noticeable feature of these compounds is the protonation of their NC(=S) nitrogen atoms, as shown by the resonances at δ ≈ 9.0 in their ^{1}H NMR spectra, and bands attributable to ν(C=S) in the 840−820 cm^{-1} range. We then treated complex **1f** with triphenylphosphane to compare its behavior with that of the thiosemicarbazone complexes **1a**−**1c**, which did not show cleavage of the Pd−S bond even with a large excess of the triphenylphosphane ligand and use of prolonged reaction times (compounds **1d** and **1e** displayed similar behavior, and neither the Pd−S bond nor the Pd−Cl bond were cleaved). Under similar reaction conditions, the Pd−S bond in **1f** remained uncleaved and compound **3f** was not formed (Scheme 2). Triphenylphosphane could be coordinated to the metal atom only after abstraction of the chlorine ligand; this was achieved by treatment of compound **1f** with silver perchlorate, followed by addition of the phosphane ligand to give compound [Pd{4-MeOC$_6$H$_3$C(H)=N[2-(SMe)C$_6$H$_4$]}(PPh$_3$)](ClO$_4$) (**2f**) as a fully characterized (see Exp. Sect. and Scheme 2) 1:1 electrolyte. The removal of the chlorine ligand was confirmed by the absence of the ν(Pd−Cl) band. The H(5) resonance in the ^{1}H NMR spectrum showed an upfield shift and appeared as a multiplet, due to coupling to the ^{31}P nucleus, whilst the MeO resonance was shifted to lower frequency by 0.20 ppm, due to shielding by the phosphane phenyl ring.

Crystal and Molecular Structures of 2a and 1f

Suitable crystals were grown by slow concentration of chloroform solutions of complexes **2a** and **1f**. The labelling schemes for the complexes are shown in Figures 1 and 2, respectively. Both crystals consist of discrete molecules separated by normal van der Waals distances. Crystallographic data and selected interatomic distances and angles are listed in Tables 1 and 2.

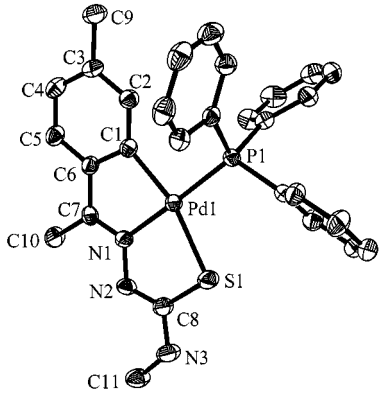


Figure 1. Molecular structure of complex [Pd{4-MeC$_6$H$_3$C(Me)=NNC(=S)NHMe}(PPh$_3$)] (**2a**), with labelling scheme; hydrogen atoms have been omitted for clarity

In compound **2a**, the structure comprises a molecule with the palladium(II) atom bonded in a slightly distorted square-planar environment to four different donor atoms, a terdentate thiosemicarbazone through the aryl C(1) carbon, the imine N(1) nitrogen, the thioamide S(1) sulfur atom,

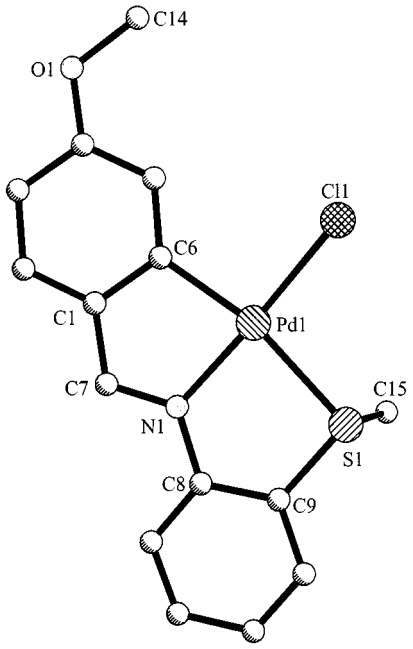


Figure 2. Molecular structure of complex [Pd{4-MeOC$_6$H$_3$C(H)=N[2-(SMe)C$_6$H$_4$]}(Cl)] (**1f**), with labelling scheme; hydrogen atoms have been omitted for clarity

Table 2. Selected bond lengths [Å] and angles [°] for complexes **2a** and **1f**

2a		**1f**	
Pd(1)−C(1)	2.044(4)	Pd(1)−C(6)	2.004(5)
Pd(1)−N(1)	2.024(3)	Pd(1)−N(1)	2.013(4)
Pd(1)−P(1)	2.2519(9)	Pd(1)−Cl(1)	2.303(4)
Pd(1)−S(1)	2.3419(11)	Pd(1)−S(1)	2.387(3)
S(1)−C(8)	1.757(4)	S(1)−C(9)	1.791(5)
N(1)−C(7)	1.290(4)	N(1)−C(7)	1.314(5)
N(1)−Pd(1)−C(1)	81.03(13)	N(1)−Pd(1)−C(6)	81.7(2)
N(1)−Pd(1)−P(1)	176.93(9)	N(1)−Pd(1)−S(1)	85.6(2)
C(1)−Pd(1)−P(1)	97.05(10)	C(6)−Pd(1)−Cl(1)	95.6(2)
N(1)−Pd(1)−S(1)	82.77(9)	S(1)−Pd(1)−Cl(1)	97.13(12)
C(1)−Pd(1)−S(1)	163.74(10)	C(6)−Pd(1)−S(1)	167.30(12)
P(1)−Pd(1)−S(1)	99.19(4)	N(1)−Pd(1)−Cl(1)	176.91(10)
C(7)−N(1)−Pd(1)	117.6(2)	C(1)−C(6)−Pd(1)	111.2(3)
C(6)−C(1)−Pd(1)	110.4(2)	C(6)−C(1)−C(7)	116.1(4)
C(1)−C(6)−C(7)	116.8(3)	C(1)−C(7)−N(1)	115.7(4)
N(1)−C(7)−C(6)	114.2(3)	C(7)−N(1)−Pd(1)	115.0(3)

Table 1. Crystal data for compounds **2a** and **1f**

	2a	**1f**
Empirical formula	$C_{29}H_{28}N_3PPdS$	$C_{15}H_{14}ClNOPdS$
Formula mass	587.97	398.18
T [K]	293(2)	150(2)
λ [Å]	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions		
a [Å]	9.977(1)	8.117(10)
b [Å]	11.536(1)	11.814(13)
c [Å]	12.680(1)	15.69(2)
α [°]	93.214(1)	90
β [°]	108.285(1)	98.05(15)
γ [°]	108.000(1)	90
V [Å^3]	1298.8(1)	1490(3)
Z	2	4
Density (calcd.) [Mg/m^3]	1.503	1.775
μ [mm^{-1}]	0.880	1.558
Crystal size [mm]	0.20 × 0.10 × 0.05	0.34 × 0.21 × 0.21
θ range for data collection [°]	1.72 to 28.26	2.17 to 27.89
Reflections collected	8873	4021
Independent reflections	6173 (R_{int} = 0.0243)	2755 (R_{int} = 0.0209)
Final *R* indices [$I > 2.0\sigma(I)$]	R_1 = 0.0447, wR_2 = 0.0923	R_1 = 0.0350, wR_2 = 0.0747
R indices (all data)	R_1 = 0.0659, wR_2 = 0.1038	R_1 = 0.0527, wR_2 = 0.0810
Largest diff. peak and hole [eÅ^{-3}]	0.542 and −0.475	0.725 and −0.846

zone ligand. The angles N(1)−Pd(1)−C(1), at 81.03(3)°, and N(1)−Pd(1)−S(1), at 82.77(9)°, are less than 90°, whilst C(1)−Pd(1)−P(1), at 97.05(10)°, and S(1)−Pd(1)−C(1), at 99.19(4)°, are thus greater than 90°; the sum of angles at the palladium center in the equatorial plane is 360.04°. All and the phosphorus atom P(1) of the triphenylphosphane ligand.

The deviations from the mean plane are as follows: Pd −0.0096, C(1) −0.0320, N(1) 0.0403, P(1) 0.0282, S(1) −0.0269 Å. The angles between adjacent atoms in the coordination geometry of the metal atom are close to the expected value of 90°, in the 99.19(4) to 81.03(13)° range, with the most noticeable distortions being in the thiosemicarba-bond lengths are within the expected range, with allowance for the strong *trans* influence of the phosphorus donor ligand,[28] which is reflected in the Pd(1)−N(1) distance of 2.024(3) Å [a value larger than the sum of the covalent radii for Pd and N: 2.01 Å]. The Pd(1)−C(1) length, at 2.044(4) Å, and the Pd(1)−P(1) length, at 2.2519(9) Å, are shorter than the expected values of 2.081 Å and 2.41 Å,[29] respectively; this suggests some degree of multiple bond character

in the Pd−C(aryl)[30−32] and Pd−P linkages.[33] The S(1)−C(8) bond length, at 1.757(4) Å, and the N(2)−C(8) length, at 1.306(5) Å, are consistent with increased single- and double-bond character, respectively; the former is similar to that found for the Pd−S single bond in compound **1f** (vide infra). The metallacycle Pd, C(1), C(6) C(7), N(1) is planar, with mean deviations from the plane in the ±0.0113 Å range.

The crystal structure of **1f** consists of molecules with the palladium(II) atom bonded to a terdentate Schiff base system through the aryl C(6) carbon, the imine N(1) nitrogen, and the S(1) sulfur atoms, and also to the chlorine Cl(1) atom, thus yielding the palladium ion bonded to four different atoms.

The deviations from the mean plane are as follows: Pd −0.0088, C(6) −0.0162, N(1) 0.0218, S(1) −0.0127, and Cl(1) 0.0160 Å. The angles between adjacent atoms in the palladium coordination sphere show deviations from the ideal 90° similar to those described above for compound **2a**, with the most noticeable distortion in the N(1)−Pd(1)−C(6) angle of 81.7(2)°, a consequence of chelation; the sum of angles around the palladium atom is 360.03°. All bond lengths are within the expected ranges, with a shorter Pd(1)−C(aryl) linkage than in compound **2a** (vide supra). The Pd(1)−N(1) distance is also shorter in **1f** than in **2a**, reflecting the smaller *trans* influence of the chlorine atom in comparison with that of the phosphorus atom of the phosphane ligand. The metallacycle Pd, C(1), C(6), C(7), N(1) and the coordination ring Pd(1), N(1), C(8), C(9), S(1) are planar, with mean deviations from the plane in the ±0.0236 Å and ±0.0097 Å ranges, respectively, and they form angles with the Pd(1), C(6), N(1), S(1), Cl(1) palladium coordination plane of 2.63 and 0.72°, respectively.

Conclusion

We have shown that cyclometallation of organic ligands may be controlled, to provide different species through the introduction of appropriate changes in the chain bonded to the metallated aryl ring, and which contains the donor atoms that afford the metallated and coordination rings at the metal center. Thus, polynuclear metal compounds or mononuclear complexes may be synthesized by impeding cleavage of the N−H linkage on the hydrazine nitrogen atom. Furthermore, we have also demonstrated that the ligands discussed in this paper are good terdentate [C,N,S] pincer species that firmly sustain three metal coordination sites, allowing only one remaining position to undergo further reactions with nucleophiles, and they are therefore most suitable for providing a means to protect the metal ion against undesirable side reactions. Our goal now is to extend these findings to related ligands and also to examine their behavior in six-coordinate metals.

Experimental Section

General Remarks: Solvents were purified by standard methods.[34] Chemicals were reagent grade. Lithium tetrachloropalladate was prepared in situ by treatment of palladium(II) chloride with lithium chloride in methanol or ethanol. Palladium(II) acetate, potassium tetrachloropalladate, and palladium(II) chloride were purchased from Alfa Products, triphenylphosphane from Aldrich-Chemie. Microanalyses were carried out at the Servicio de Análisis Elemental at the University of Santiago, with a Carlo Erba Elemental Analyzer Model 1108. IR spectra were recorded as Nujol mulls or KBr discs with a Perkin−Elmer 1330 and with a Mattson spectrophotometer. NMR spectra were obtained as $CDCl_3$ solutions and referenced to $SiMe_4$ (^1H, ^{13}C) or 85% H_3PO_4 (^{31}P-{^1H}) and were recorded with Bruker WM250 and AMX 300 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.

CAUTION: Perchlorate salts of metal complexes are potentially explosive. Extreme caution should be exercised when handling these materials.

Synthesis of 4-$MeC_6H_4C(Me)$=NN(H)C(=S)NHMe (a): 4′-Methylacetophenone (650 mg, 4.84 mmol) and hydrochloric acid (35%, 0.65 mL) were added to a suspension of 4-methyl-3-thiosemicarbazide (510 mg, 4.84 mmol) in water (25 mL) to give a clear solution, which was stirred at room temperature for 4 h. The white solid that precipitated was filtered off, washed with cold water, and dried in air. Yield: 858 mg, 80%. $C_{11}H_{15}N_3S$ (221.3): calcd. C 59.7, H 6.8, N 19.0, S 14.5; found C 59.5, H 6.6, N 18.6, S 13.9. IR: $\tilde{\nu}$ = 1620 [s, ν(C=N)], 849 [m, ν(C=S)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.61 (s, 1 H, NH), 7.63 (br, 1 H, N*H*Me), 7.59 (d, 2 H, H2, H6, *N* = 8.3 Hz), 7.21 (d, 2 H, H3, H5, *N* = 8.3 Hz), 3.27 (d, 3 H, NMe, $^3J_{HH}$ = 4.9 Hz), 2.38 (s, 3 H, C4−Me), 2.25 (s, 3 H, =C−Me). ^{13}C-{^1H} NMR (62.46 MHz, $CDCl_3$): δ = 179.3 (C=S), 147.3 (C=N), 140.3 (C1), 135.0 (C4), 129.7 (C2, C6), 126.6 (C3, C5), 31.7 (NHMe), 21.7 (C4−Me), 13.9 (*Me*C=N).

Thiosemicarbazones b−e: These were prepared by similar procedures.

4-$MeC_6H_4C(Me)$=NN(H)C(=S)NHEt (b): Yield: 992 mg, 87%. $C_{12}H_{17}N_3S$ (235.4): calcd. C 61.2, H 7.3, N 17.9, S 13.6; found C 61.0, H 7.2, N 17.8, S 13.2. IR: $\tilde{\nu}$ = 1617 [m, ν(C=N)], 835 [m, ν(C=S)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.56 (s, 1 H, NH), 7.57 (d, 2 H, H2, H6, *N* = 8.5 Hz), 7.50 (br, N*H*Et), 7.21 (d, 2 H, H3, H5, *N* = 8.5 Hz), 3.77 (m, 2 H, N*CH*$_2$CH$_3$), 2.37 (s, 3 H, C4−Me), 2.24 (s, 3 H, =C−Me), 1.30 (t, 3 H, NCH$_2$*CH*$_3$, $^3J_{HH}$ = 7.1 Hz). ^{13}C {^1H} NMR (62.46 MHz, $CDCl_3$): δ = 178.1 (C=S), 147.3 (C=N), 140.3 (C1), 135.1 (C4), 129.7 (C2, C6), 126.6 (C3, C5), 39.8 (N*CH*$_2$CH$_3$), 21.7 (C4−Me), 14.9 (NCH$_2$*CH*$_3$), 14.0 (*Me*C=N).

4-$MeC_6H_4C(Me)$=NN(H)C(=S)NHPh (c): Yield: 1263 mg, 92%. $C_{16}H_{17}N_3S$ (283.4): calcd. C 67.8, H 6.0, N 14.8, S 11.3; found C 68.0, H 6.2, N 14.8, S 11.0. IR: $\tilde{\nu}$ = 1611 [s, ν(C=N)], 828 [m, ν(C=S)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 9.41 (s, 1 H, NH), 8.77 (br, N*H*Me), 7.63 (d, 2 H, H2, H6, *N* = 8.2 Hz), 7.23 (d, 2 H, H3, H5, *N* = 8.2 Hz), 2.39 (s, 3 H, C4−Me), 2.32 (s, 3 H, =C−Me).^{13}C-{^1H} NMR (62.46 MHz, $CDCl_3$): δ = 176.6 (C=S), 147.9 (C=N), 140.7 (C1), 138.4 (C4), 129.2 (C2, C6), 124.6 (C3, C5), 21.8 (C4−Me), 14.2 (*Me*C=N).

4-$MeOC_6H_4C(H)$=NN(Me)C(=S)NH_2 (d): Yield: 906 mg, 85%. $C_{10}H_{13}N_3OS$ (223.3): calcd. C 53.8, H 5.9, N 18.8, S 14.4; found C 53.4, H 6.0, N 18.5, S 15.3. IR: $\tilde{\nu}$ = 1619 [m, ν(C=N)], 836 [m, ν(C=S)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.27(s, 1 H, NH_2), 8.22 (s, 1 H, NH_2), 7.84 (s, 1 H, HC=N), 7.86 (d, 2 H, H2, H6, *N* = 8.6 Hz), 6.96 (d, 2 H, H3, H5, *N* = 8.6 Hz), 3.78 (s, 3 H, MeO),

3.74 (s, 1 H, NMe). ^{13}C {^1H} NMR (62.46 MHz, $CDCl_3$): δ = 180.5 (C=S), 161.0 (C4), 141.4 (C=N), 129.8 (C2, C6), 127.4 (C1), 114.4 (C3, C5), 55.6 (MeO), 33.1 (NMe).

3-MeOC$_6$H$_4$C(H)=NN(Me)C(=S)NH$_2$ (e): Yield: 906 mg, 85%. $C_{10}H_{13}N_3OS$ (223.3): calcd. C 53.8, H 5.9, N 18.8, S 14.4; found C 53.6, H 6.0, N 18.6, S 15.0. IR: $\tilde{\nu}$ = 1615 [m, ν(C=N)], 840 [m, ν(C=S)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.38 (s, 1 H, NH_2), 8.31 (s, 1 H, NH_2), 7.85 (s, 1 H, HC=N), 7.50 (s, 1 H, H2), 7.45 [d, 1 H, H6, ^3J(H5H6) = 7.5 Hz], 7.32 (t, 1 H, H5, $^3J_{H4H5}$ = 7.5 Hz), 6.96 (d, 1 H, H4), 3.79 (s, 3 H, MeO), 3.76 (s, 3 H, NMe). ^{13}C {^1H} NMR (62.46 MHz, $CDCl_3$): δ = 180.9 (C=S), 159.9 (C3), 141.5 (C=N), 136.2 (C1), 130.0, 121.2, 116.3, 112.4 (C2, C4, C5, C6), 55.6 (MeO), 33.2 (NMe).

Preparation of 4-MeOC$_6$H$_4$C(H)=N[2-(SMe)C$_6$H$_4$] (f): 4-Methoxybenzaldehyde (500 mg, 3.67 mmol) and 2-methylthioaniline (518 mg, 3.72 mmol) were heated together under reflux in a Dean−Stark apparatus. After the mixture had cooled to room temperature, the solvent was evaporated to dryness, and the residue was dried under vacuum to give an oily yellow product from which the desired ligand was obtained as a yellow solid. Yield: 785 mg, 83%. $C_{15}H_{15}NOS$ (257.4): calcd. C 70.0, H 5.9, N 5.4, S 12.5; found C 70.1, H 6.0, N 5.7, S 12.3. IR: $\tilde{\nu}$ = 1626 [s, ν(C=N)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.44 (s, 1 H, HC=N), 7.88 (d, 2 H, H2, H6, *N* = 8.0 Hz), 7.2 (m, 4 H), 7.07 (d, 2 H, H3, H5, *N* = 8.0 Hz), 3.82 (s, 3 H, MeO), 2.37 (s, 3 H, SMe). ^{13}C {^1H} NMR (62.46 MHz, $CDCl_3$): δ = 165.1 (C−SMe), 162.4 (C=N), 151.5 (C4), 137.0 (C−N), 133.6 (C2, C6), 132.0 (C1), 129.2, 128.0, 127.0, 120.4 (N-ring C atoms), 117.4 (C3, C5), 58.5 (MeO), 16.7 (SMe).

Preparation of [Pd{4-MeC$_6$H$_3$C(Me)=NNC(=S)NHMe}]$_4$ (1a). − Method 1: Ethanol (40 mL) was added to a stirred solution of potassium tetrachloropalladate (200 mg, 0.61 mmol) in water (6 mL). The obtained fine, yellow suspension of potassium tetrachloropalladate was treated with 4-MeOC$_6$H$_4$C(Me)=N(H)C(=S)NHMe (**a**) (148 mg, 0.67 mmol). The mixture was stirred for 48 h at room temperature. The yellow precipitate was filtered off, washed with ethanol, and dried. Yield: 178 mg, 89%. $C_{44}H_{52}N_{12}Pd_4S_4$ (1302.9): calcd. C 40.6, H 4.0, N 12.9, S 9.8; found C 40.1, H 3.8, N 12.3, S 9.5. IR: $\tilde{\nu}$ = 1590 [m, ν(C=N)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.27 (d, 1 H, H5, $^4J_{H3H5}$ = 1.3 Hz), 6.71 (dd, 1 H, H3, $^3J_{H2H3}$ = 7.8 Hz), 6.65 (d, 1 H, H2), 5.03 (q, 1 H, N*H*Me, $^3J_{HH}$ = 5.0 Hz), 2.98 (d, 3 H, NH*Me*), 2.30 (s, 3 H, C4−Me), 1.65 (s, 3 H, =C−Me). ^{13}C {^1H} NMR (62.46 MHz, $CDCl_3$): δ = 169.6 (C=S), 165.9 (C=N), 165.1 (C1), 147.2 (C6), 138.0 (C4), 134.2 (C2), 125.8, 125.0 (C3, C5), 33.1 (NHMe), 22.3 (C4−Me), 13.0 (*Me*C=N). − **Method 2:** Ligand **a** (201 mg, 0.91 mmol) and palladium(II) acetate (204 mg, 0.91 mmol) were added to glacial acetic acid (45 mL) to give a clear solution, which was heated to 60° C for 8 h. After this had cooled to room temperature, the yellow precipitate was filtered off, washed with ethanol, and dried. Yield: 169 mg, 57%.

[Pd{4-MeC$_6$H$_3$C(Me)=NNC(=S)NHEt}]$_4$ (1b). − Method 1: Analogous to **1a**. Yield: 181 mg, 87%. $C_{48}H_{60}N_{12}Pd_4S_4$ (1359.0): calcd. C 42.4, H 4.5, N 12.4, S 9.4; found C 41.9, H 3.6, N 11.8, S 8.7. IR: $\tilde{\nu}$ = 1586 [m, ν(C=N)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.30 (s, 1 H, H5), 6.71 (d, 1 H, H3, $^3J_{H2H3}$ = 7.4 Hz), 6.64 (d, 1 H, H2), 5.03 (m, 1 H, N*H*Et), 3.44 (m, 2 H, N*CH$_2$*CH$_3$), 2.29 (s, 3 H, C4−Me), 1.65 (s, 3 H, =C−Me), 1.26 (t, 3 H, NCH$_2$*CH$_3$*, $^3J_{HH}$ = 7.1 Hz). ^{13}C {^1H} NMR (62.46 MHz, $CDCl_3$): δ = 169.1 (C=S), 165.8 (C=N), 165.0 (C1), 147.5 (C6), 137.5 (C4), 134.3 (C2), 125.8, 125.0 (C3, C5), 41.4 (N*CH$_2$*CH$_3$), 22.2 (C4−Me), 15.0 (NCH$_2$*CH$_3$*), 13.0 (*Me*C=N). − **Method 2:** Ligand **b** (186 mg, 0.79 mmol) and palladium(II) acetate (177 mg, 0.79 mmol) were added to glacial acetic acid (40 mL) to give a clear solution, which was heated to 60° C for 8 h. After this had cooled to room temperature, the acetic acid was removed under vacuum. The residue was diluted with water and extracted with dichloromethane. The combined extracts were dried with anhydrous sodium sulfate, filtered, and concentrated in vacuo to give a yellow solid. This was chromatographed on a column packed with silica gel. Elution with dichloromethane/ethanol (1%) afforded product **1b** as a yellow solid after concentration. Yield: 169 mg, 63%.

[Pd{4-MeC$_6$H$_3$C(Me)=NNC(=S)NHPh}]$_4$ (1c): Compound **1c** was obtained through a similar procedure to that used for **1a** (method 1). Yield: 226 mg, 95%. $C_{64}H_{60}N_{12}Pd_4S_4$ (1551.2): calcd. C 49.6, H 3.9, N 10.8, S 8.3; found C 49.9, H 3.6, N 10.2, S 7.9. IR: $\tilde{\nu}$ = 1574 [m, ν(C=N)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.24 (br, 1 H, H5), 6.94 (s, 1 H, NHPh), 6.78 (br, 2 H, H2, H3), 2.16 (s, 3 H, C4−Me), 1.74 (s, 3 H, =C−Me).^{13}C {^1H} NMR (62.46 MHz, $CDCl_3$): δ = 172.1 (C=S), 166.5 (C=N), 161.0 (C1), 147.0 (C6), 139.4 (C4), 134.5 (C2), 126.5, 125.4 (C3, C5), 22.1 (C4−Me), 13.7 (*Me*C=N).

[Pd{4-MeC$_6$H$_3$C(Me)=NNC(=S)NHMe}(PPh$_3$)] (2a): Triphenylphosphane (40 mg, 0.152 mmol) was added to a suspension of complex **1a** (50 mg, 0.038 mmol) in acetone (15 mL). The mixture was stirred for 3 h and the resulting yellow solid was filtered off and dried. Yield: 55 mg, 61%. $C_{29}H_{28}N_3PPdS$ (588.0): calcd. C 59.2, H 4.8, N 7.1, S 5.5; found C 59.1, H 4.7, N 7.0, S 5.4. IR: $\tilde{\nu}$ = 1588 [m, ν(C=N)] cm^{-1}. ^{31}P {^1H} NMR ($CDCl_3$): δ = 36.7 (s). ^1H NMR ($CDCl_3$): δ = 6.95 (d, 1 H, H2, $^3J_{H2H3}$ = 7.7 Hz), 6.64 (d, 1 H, H3), 6.05 (d, 1 H, H5, $^4J_{PH5}$ = 4.3 Hz), 4.63 (m, 1 H, N*H*Me), 2.90 (d, 3 H, NH*Me*, $^3J_{HH}$ = 4.5 Hz), 2.35 (s, 3 H, C4−Me), 1.73 (s, 3 H, =C−Me).

Compounds 2b and 2c: These were synthesized by a similar procedure.

[Pd{4-MeC$_6$H$_3$C(Me)=NNC(=S)NHEt}(PPh$_3$)] (2b): Yield: 47 mg, 53%. $C_{30}H_{30}N_3PPdS$ (602.1): calcd. C 59.9, H 5.0, N 7.0, S 5.3; found C 59.8, H 4.9, N 6.9, S 5.1. IR: $\tilde{\nu}$ = 1588 [m, ν(C=N)] cm^{-1}. ^{31}P {^1H} NMR ($CDCl_3$): δ = 36.8 (s). ^1H NMR ($CDCl_3$): δ = 6.96 (d, 1 H, H2, $^3J_{H2H3}$ = 7.5 Hz), 6.65 (dd, 1 H, H3, $^4J_{H3H5}$ = 1.1 Hz), 6.07 (dd, 1 H, H5, $^4J_{PH5}$ = 3.5 Hz), 4.63 (m, 1 H, N*H*Et), 3.35 (m, 2 H, N*CH$_2$*CH$_3$), 2.35 (s, 3 H, C4−Me), 1.71 (s, 3 H, =C−Me), 1.12 (t, 3 H, NCH$_2$*CH$_3$*, $^3J_{HH}$ = 7.2 Hz).

[Pd{4-MeC$_6$H$_3$C(Me)=NNC(=S)NHPh}(PPh$_3$)] (2c): Yield: 48 mg, 57%. $C_{34}H_{30}N_3PPdS$ (650.1): calcd. C, 62.8, H 4.7, N 6.5, S 4.9; found C 62.5, H 4.6, N 6.3, S 4.7. IR: ν(C=N) 1577m, cm^{-1}. ^{31}P {^1H} NMR ($CDCl_3$): δ = 36.7 (s). ^1H NMR ($CDCl_3$): δ = 7.02 (d, 1 H, H2, $^3J_{H2H3}$ = 7.2 Hz), 6.68 (d, 1 H, H3), 6.63 (s, 1 H, NHPh), 6.10 (d, 1 H, H5, $^4J_{PH5}$ = 3.1 Hz), 2.46 (s, 3 H, C4−Me), 1.73 (s, 3 H, =C−Me).

[Pd{4-MeC$_6$H$_3$C(Me)=NNC(=S)NHMe}(PPh$_3$)]$^+$Cl$^-$ (3a): A suspension of complex **2a** (50 mg, 0.085 mmol) in ethanol (15 mL) was treated with three drops of concentrated hydrochloric acid (35%). The resulting mixture was stirred for 3 h and the yellow solid formed was filtered off and dried. Yield: 49 mg, 92%. $C_{29}H_{29}ClN_3PPdS$ (624.5): calcd. C 55.8, H 4.7, N 6.7, S 5.1; found C 55.6, H 4.6, N 6.7, S 4.9. IR: $\tilde{\nu}$ = 1574 [m, ν(C=N)], 840 [m, ν(C=S)] cm^{-1}. Λ_M (acetonitrile, 3×10^{-3} mol L^{-1}) = 97 Ω^{-1} cm^2 mol^{-1}. ^{31}P {^1H} NMR ($CDCl_3$): δ = 38.4 (s). ^1H NMR ($CDCl_3$): δ = 9.05 (s, 1 H, NH), 7.05 (d, 1 H, H2, $^3J_{H2H3}$ = 7.6 Hz), 6.68 (d, 1 H, H3), 6.09 (d, 1 H, H5, $^4J_{PH5}$ = 4.5 Hz), 5.9 (m, 1 H, N*H*Me), 3.05 (d, 3 H, NH*Me*, $^3J_{HH}$ = 4.0 Hz), 2.33 (s, 3 H, C4−Me), 1.93 (s, 3 H, =C−Me).

Compounds 3b and 3c: These were synthesized by a similar procedure.

[Pd{4-MeC$_6$H$_3$C(Me)=NNC(=S)NHEt}(PPh$_3$)]$^+$Cl$^-$ (3b): Yield: 49 mg, 93%. $C_{30}H_{31}ClN_3PPdS$ (638.5): calcd. C 56.4, H 4.9, N 6.6, S 5.0; found C 56.2, H 4.7, N 6.5, S 4.9. IR: $\tilde{\nu}$ = 1576 [m, ν(C=N)], 832 [m, ν(C=S)] cm^{-1}. Λ_M (acetonitrile, 3×10^{-3} mol L^{-1}) = 92 Ω^{-1} cm^2 mol^{-1}. ^{31}P {^{1}H} NMR ($CDCl_3$): δ = 38.5 (s). ^{1}H NMR ($CDCl_3$): δ = 9.07 (s, 1 H, NH), 7.03 (d, 1 H, H2, $^3J_{H2H3}$ = 7.1 Hz), 6.80 (dd, 1 H, H3, $^4J_{H3H5}$ = 7.0 Hz), 6.10 (dd, 1 H, H5, $^4J_{PH5}$ = 3.6 Hz), 6.12 (m, 1 H, N*H*Et), 3.45 (m, 2 H, N*CH$_2$*CH$_3$), 2.36 (s, 3 H, C4−Me), 1.91 (s, 3 H, =C−Me), 1.29 (t, 3 H, NCH$_2$*CH$_3$*, $^3J_{HH}$ = 7.0 Hz).

[Pd{4-MeC$_6$H$_3$C(Me)=NNC(=S)NHPh}(PPh$_3$)]$^+$Cl$^-$ (3c): Yield: 48 mg, 91%. $C_{34}H_{31}ClN_3PPdS$ (686.6): calcd. C, 59.5, H 4.6, N 6.1, S 4.7; found C 59.2, H 4.5, N 6.0, S 4.4. IR: $\tilde{\nu}$ = 1570 [m, ν(C=N)], 825 [m, ν(C=S)] cm^{-1}. Λ_M (acetonitrile, 3×10^{-3} mol L^{-1}) = 95 Ω^{-1} cm^2 mol^{-1}. ^{31}P {^{1}H} NMR ($CDCl_3$): δ = 38.6 (s). ^{1}H NMR ($CDCl_3$): δ = 9.04 (s, 1 H, NH), 7.6 (s, 1 H, NHPh), 7.18 (d, 1 H, H2, $^3J_{H2H3}$ = 7.0 Hz), 7.02 (d, 1 H, H3), 6.17 (d, 1 H, H5, $^4J_{PH5}$ = 3.4 Hz), 2.53 (s, 3 H, C4−Me), 1.92 (s, 3 H, =C−Me).

Compounds 1d and 1e: These were prepared in a similar fashion to **1a** (Method 1).

[Pd{4-MeOC$_6$H$_3$C(H)=NN(Me)C(=S)NH$_2$}(Cl)] (1d): Yield: 185 mg, 83%. $C_{10}H_{12}ClN_3OPdS$ (364.2): calcd. C 33.0, H 3.3, N 11.5, S 8.8; found C 31.9, H 3.3, N 11.1, S 9.2. IR: $\tilde{\nu}$ = 1589 [m, ν(C=N)], 309 [m, ν(Pd−Cl)], 834 [m, ν(C=S)] cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 8.14 (s, 1 H, HC=N), 7.24 (d, 1 H, H2, $^3J_{H2H3}$ = 8.4 Hz), 6.93 (d, 1 H, H5, $^4J_{H3H5}$ = 2.2 Hz), 6.53 (dd, 1 H, H3), 3.72 (s, 3 H, MeO), 3.46 (s, 3 H, NMe). ^{13}C {^{1}H} NMR (62.46 MHz, $CDCl_3$): δ = 189.1 (C=S), 163.5 (C4), 160.1 (C6), 157.6 (C=N), 139.6 (C1), 130.1 (C2), 118.6 (C3), 109.7 (C5), 55.4 (MeO), 35.4 (NMe).

[Pd{3-MeOC$_6$H$_3$C(H)=NN(Me)C(=S)NH$_2$}(Cl)] (1e): Yield: 185 mg, 83%. $C_{10}H_{12}ClN_3OPdS$ (364.2): calcd. C 33.0, H 3.3, N 11.5, S 8.8; found C 32.9, H 3.2, N 11.3, S 9.1. IR: $\tilde{\nu}$ = 1591 [m, ν(C=N)], 315 [m, ν(Pd-Cl)], 842 [m, ν(C=S)] cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 9.47 (s, 1 H, NH$_2$), 8.74 (s, 1 H, NH$_2$), 8.18 (s, 1 H, HC=N), 7.23 (d, 1 H, H5, $^3J_{H4H5}$ = 8.4 Hz), 6.94 (d, 1 H, H2, $^4J_{H2H4}$ = 2.7 Hz), 6.67 (dd, 1 H, H4), 3.68 (s, 3 H, MeO), 3.47 (s, 3 H, NMe). ^{13}C {^{1}H} NMR (62.46 MHz, $CDCl_3$): δ = 174.6 (C=S), 160.1 (C6), 157.8 (C=N), 157.1 (C3), 146.7 (C1), 133.2 (C2), 114.1 (C5), 113.4 (C4), 55.4 (MeO), 35.5 (NMe).

[Pd{4-MeOC$_6$H$_3$C(H)=N[2-(SMe)C$_6$H$_4$]}(Cl)] (1f): 4-MeOC$_6$H$_4$C(H)=N[2-(SMe)C$_6$H$_4$] (**f**) (217 mg, 0.84 mmol) and sodium acetate (500 mg, 6.1 mmol) were added to a stirred solution of palladium(II) chloride (135 mg, 0.76 mmol) and lithium chloride (65 mg, 1.53 mmol) in methanol (40 mL). The mixture was stirred for 48 h at room temperature under nitrogen. The yellow precipitate was filtered off, washed with ethanol, and dried. Yield: 252 mg, 83%. $C_{15}H_{14}ClNOPdS$ (398.18): calcd. C 45.2, H 3.5, N 3.5, S 8.1; found C 45.0, H 3.4, N 3.4, S 8.0. IR: $\tilde{\nu}$ = 1603 [m, ν(C=N)], 310 [m, ν(Pd−Cl)] cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 9.12 (s, 1 H, HC=N), 7.98 (d, 1 H, H6′, $^3J_{H5'H6'}$ = 8.4 Hz), 7.83 (d, 1 H, H3′, $^3J_{H3'H4'}$ = 7.9 Hz), 7.55 (t, 1 H, H4′, $^3J_{H4'H5'}$ = 8.0 Hz), 7.53 (d, 1 H, H2, $^3J_{H2H3}$ = 8.8 Hz), 7.44 (t, 1 H, H5′), 7.11 (d, 1 H, H5, $^4J_{H3H5}$ = 2.7 Hz), 6.71 (dd, 1 H, H3), 3.80 (s, 3 H, MeO), 2.75 (s, 3 H, SMe). ^{13}C {^{1}H} NMR (62.46 MHz, $CDCl_3$): δ = 169.7 (C=N), 168.0 (C−S), 167.1 (C4), 147.5 (C−N), 143.1 (C6), 133.2 (C1), 133.0 (C2), 135.3, 131.6, 129.9, 119.5 (N-ring C atoms), 118.3, 111.4 (C3, C5), 55.8 (MeO), 24.8 (SMe).

Synthesis of [Pd{4-MeOC$_6$H$_3$C(H)=N[2-(SMe)C$_6$H$_4$]}(PPh$_3$)](ClO$_4$) (2f): $AgClO_4$ (29 mg, 0.14 mmol) was added to compound **1f** (56 mg, 0.14 mmol) in acetone (15 mL). The resulting suspension was stirred for 3 h and filtered through Celite to remove the silver chloride precipitate. PPh_3 (37 mg, 0.14 mmol) was added to the filtrate and the solution was stirred for 3 h. The solvent was removed and the product was recrystallized from dichloromethane/hexane as a yellow solid. Yield: 84 mg, 83%. $C_{33}H_{29}ClNO_5PPdS$ (724.5): calcd. C 54.7, H 4.0, N 1.9, S 4.4; found C 54.2, H 3.9, N 1.8, S 4.7. IR: $\tilde{\nu}$ = 1607 [m, ν(C=N)] cm^{-1}. Λ_M (acetonitrile, 3×10^{-3} mol L^{-1}) = 91 Ω^{-1} cm^2 mol^{-1}.^{1}H NMR ($CDCl_3$): δ = 9.18 (d, 1 H, HC=N, $^4J_{PH}$ = 8.4 Hz), 8.06 (d, 1 H, H6′, $^3J_{H5'H6'}$ = 8.0 Hz), 7.86 [d, 1 H, H3′, $^3J_{H3'H4'}$ = 8.4 Hz), H4′, H2, H5′ (signals hidden by the phosphane resonances)], 6.57 (d, 1 H, H3, $^4J_{H3H5}$ = 2.7 Hz), 6.71 (dd, 1 H, H5, $^4J_{PH}$ = 5.5 Hz), 3.60 (s, 3 H, MeO), 2.75 (s, 3 H, SMe).

X-ray Crystallographic Study:[35] Crystals of complexes **2a** and **1f** were mounted on a glass fiber and transferred to the diffractometer. Three-dimensional, room-temperature X-ray data were collected with Siemens (**2a**) and Bruker (**1f**) SMART CCD diffractometers by the ω-scan method, using graphite-monochromated Mo-K_α radiation. All the measured reflections were corrected for Lorentz and polarization effects and for absorption by semiempirical methods based on symmetry-equivalent and repeated reflections [T_{max}/T_{min} = 0.9573/0.8437 (**2a**) and 0.7356/0.6194 (**1f**)]. The structure was solved by direct methods and refined by full-matrix, least squares on F^2. Hydrogen atoms were included in calculated positions (except H3 in **2a**, which was located from a Fourier-difference map) and refined in the riding mode. Refinement converged at a final R = 0.0447 (**2a**) and 0.0349 (**1f**) (observed data, F) and wR_2 = 0.1038 (**2a**) and 0.0811 (**1f**) (all unique data, F^2), with allowance for thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron densities: −0.475 and 0.542 e Å^{-3} (**2a**), 0.726 and −0.839 e Å^{-3} (**1f**). The structure solutions and refinements were carried out with the SHELX-97 program package.[36]

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[35] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-167981 (**2a**) and -167980 (**1f**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].
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