Synthesis and Chemistry of Dithiadiazole Free Radicals [4-(4′-C₅H₄N)CN₂S₂] and [4-(3′-C₅H₄N)CN₂S₂]; X-ray Crystal Structures of [Pd₃{μ-SNC(Ar′)NS–S,S′}₂(PPh₃)₄] (Ar′ = 4′-C₅H₄N, 4′-C₅H₄NBEt₃ and 3′-C₅H₄NBEt₃)

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Two new 1,2,3,5-dithiadiazoles, [4-(4′-C₅H₄N)CN₂S₂] (**L¹**) and [4-(3′-C₅H₄N)CN₂S₂] (**L²**), with different pyridyl groups at the 4-position were prepared. As Lewis bases, the dithiadiazoles reacted with Lewis acids via their pyridyl groups to form acid-base adducts with retention of the five-membered dithiadiazole ring. Ligands **L¹** and **L²** reacted with excess triethylborane to give **L¹**BEt₃ and **L²**BEt₃ (**1a** and **1b**) and with Mn(CO)₅Br to give the *fac*-Mn(CO)₃Br(L¹)₂ (**2a**) and *fac*-Mn(CO)₃Br(L²)₂ (**2b**) complexes. When reacted with Pd⁰ complexes, namely, Pd(PPh₃)₄ and a mixture of [Pd₂(dba)₃] and dppf, the dithiadiazoles underwent ring-opening reaction by reductive cleavage of the S–S bond of the dithiadiazole ring.

The resulting formation of Pd–S bonds gave the corresponding trinuclear complexes [Pd₃{μ-SNC(4′-C₅H₄N)NS-S,S′}₂(PPh₃)₄] (**3a**), [Pd₃{μ-SNC(3′-C₅H₄N)NS-S,S′}₂(PPh₃)₄] (**3b**), and [Pd₃{μ-SNC(4′-C₅H₄N)NS-S,S′}₂(dppf)₂] (**4**) [dba = dibenzylideneacetone, dppf = 1,1′-bis(diphenylphosphanyl)-ferrocene]. Complexes **3a** and **3b** reacted with excess triethylborane to give the corresponding acid-base adducts [Pd₃{μ-SNC(4′-C₅H₄NBEt₃)NS-S,S′}₂(PPh₃)₄] (**5a**) and [Pd₃{μ-SNC(3′-C₅H₄NBEt₃)NS-S,S′}₂(PPh₃)₄] (**5b**.) Complex **3a** reacted with Mn(CO)₅Br to give {[Pd₃{μ-SNC(4′-C₅H₄N)NS-S,S′}₂(PPh₃)₄][MnBr(CO)₃]}ₙ (**6**). The structures of **3a**, **5a**, and **5b** were established by X-ray crystallography.

Introduction

1,2,3,5-Dithiadiazoles belong to a remarkable and new class of stable free radicals which exist as a monomer–dimer equilibrium in the solid state and in solution.[1–10] These radicals have attracted special attention because they can act as molecular building blocks in the preparation of both conducting materials and "organic" magnets. Another interesting property is their ability to act as chelating or bridging ligands for transition metals. When reacted with low-valent transition metal complexes, the radical species underwent reductive cleavage of the S–S bond of the dithiadiazolyl ring with the formation of metal–sulfur bonds. However, so far only the reactivity of the phenyl derivative (PhCNSSN)₂ toward low-valent transition metal complexes has been studied.[11–15]

In this paper, we report the syntheses of two new 1,2,3,5-dithiadiazoles with different pyridyl groups at the 4-position and their reactivities toward low-valent transition metal complexes. These ligands have two different reactive sites, namely, the pyridyl group and the dithiadiazolyl ring. When reacted via the pyridyl group, these ligands simply act as Lewis bases with ring-retention. When reacted via the dithiadiazolyl group, these ligands undergo ring-opening reaction with the cleavage of the S–S bond and the formation of metal–sulfur bonds.

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Results and Discussion

Preparation of L¹ and L²

The compounds [4-(4′-NC₅H₄)CN₂S₂] (**L¹**) and [4-(3′-NC₅H₄)CN₂S₂] (**L²**) were prepared according to the synthetic routes shown in Scheme 1, in low to moderate yields (33% for **L¹**; 50% for **L²**) as black solids after sublimation. Both compounds are only slightly soluble in common organic solvents and are sensitive to air and moisture. The IR spectra (KBr) of ligands **L¹** and **L²** showed the characteristic absorption peaks for substituted dithiadiazole ring at 1140 (m), 810 (s), 656 (s), 510 (m), and 1146 (m), 809 (s), 667 (s), 511 (m) cm⁻¹, respectively.[1] The low-resolution mass spectra (LRMS) of **L¹** and **L²** operated in EI mode exhibited the highest mass peak at *m/z* 364 with the most abundant peak at *m/z* 182 corresponding to the dimer [(NC₅H₄)CN₂S₂]₂ and the monomer [(NC₅H₄)CN₂S₂], respectively. The solid-state EPR spectra of **L¹** and **L²** both displayed a broad peak compared with the diphenyl picrylhydrazyl (DPPH) standard. The *g*-value was determined to be 2.014 which is characteristic of a single unpaired electron. It is likely that dissociation of (RCN₂S₂)₂ (R = 4-pyridyl and 3-pyridyl) to the monomer, similar to that observed in (PhCN₂S₂)₂[16] and [S₆N₄]²⁺ salts,[17,18] takes place in the solid state.

Both **L¹** and **L²** exhibited concentration- and temperature-dependent solution EPR spectra. At their saturated concentration in toluene, the room temperature solution EPR spectra of both **L¹** and **L²** showed a broad peak at *g* = 2.014. However, when the solution was diluted ten-fold, the EPR spectra exhibited a simple 1:2:3:2:1 quintuplet pattern. These observations are indicative of the occurrence of
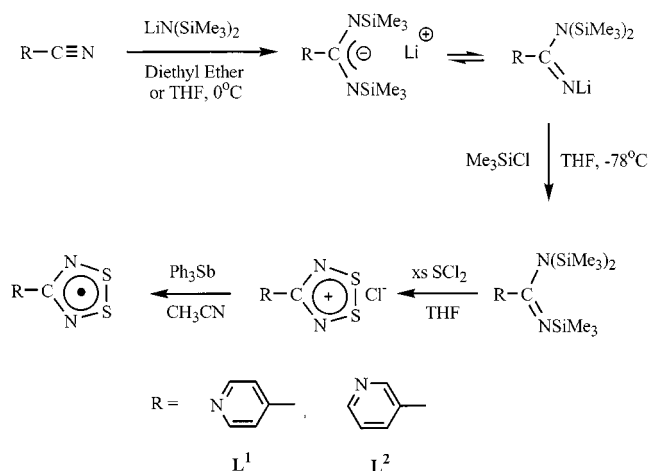
Scheme 1

an electron spin exchange process, commonly observed in free radical systems in solution, where two radicals collide and exchange electrons. At saturated concentration, the rate of this bi-molecular process is very high, resulting in a severe broadening of the EPR resonances. With a ten-fold dilution, the rate of this bi-molecular exchange became sufficiently slow that the intrinsic EPR resonances of the free radicals were not significantly affected and the hyperfine splitting pattern became observable. The 1:2:3:2:1 hyperfine splitting pattern of L^1 and L^2 suggested that the unpaired electron was delocalized over the five-membered ring and coupled to the two equivalent ^{14}N nuclei. The observation of a g-factor of 2.014 together with a hyperfine coupling constant A of ca. 0.50 mT indicates that the pyridyl group does not exert any significant effect on the single unpaired electron on the dithiadiazole ring. The solution became EPR-silent when cooled down to liquid-nitrogen temperature (i.e., –196°C), suggesting that L^1 and L^2 no longer exist as monomers at this temperature. Since an eclipsed dimeric structure has been found for the analogous 4-phenyl-1,2-dithia-3,5-diazole in its crystalline state,[19] the formation of such a dimeric structure for both L^1 and L^2 at –196°C, which will allow for an antiferromagnetic coupling between the two unpaired electrons on the two 5-membered rings, could well explain the quenching of the EPR signals observed at this temperature.

Reaction with Triethylborane

When a suspension of L^1 or L^2 was allowed to react with excess triethylborane in dichloromethane or toluene at ambient temperature, a dark-red clear solution was immediately obtained. The EPR behaviour of the resultant solution was very similar to that of L^1 or L^2. The EPR spectra exhibited a single peak at $g = 2.014$ and after dilution with a relevant solvent, a quintet signal with an intensity pattern of 1:2:3:2:1 and a g value of 2.014 ($A = 0.50$ mT). Attempts to isolate the products in pure crystalline form only led to the isolation of an air-sensitive dark-red viscous oil. The EPR data showed that the products retained the characteristics of the dithiadiazolyl ring. This suggested that the products were probably the acid-base adducts $L^1 \cdot BEt_3$ (**1a**) and $L^2 \cdot BEt_3$ (**1b**), which were formed by the interaction of the pyridyl group of L^1 and L^2 with triethylborane as shown in Scheme 2. However, this could not preclude the possibility that triethylborane also formed acid-base adducts with the dimers of L^1 and L^2.

Reaction with Mn(CO)$_5$Br

When ligand L^1 was allowed to react with an excess of Mn(CO)$_5$Br in tetrahydrofuran at 55 °C for 4 h, workup gave the stoichiometric product $C_{15}H_8BrMnN_6O_3S_4 \cdot 2.5 H_2O$ (**2a** · 2.5 H$_2$O), as reddish-brown tiny crystals, in moderate yield (56%). In the carbonyl region of its IR spectrum (KBr), **2a** exhibited three very strong absorptions at 2030, 1942, and 1909 cm^{-1}, characteristic of a fac-Mn(CO)$_3$ configuration. Complex **2a** exhibited a broad peak and a quintuplet with a relative intensity pattern of 1:2:3:2:1 in its solid state and tetrahydrofuran solution EPR spectra, respectively. The measured g value of 2.014 indicates the presence of a single electron and the five-line pattern ($A = 0.50$ mT) observed was due to the coupling of the single electron with two equivalent ^{14}N nuclei in the dithiadiazolyl ring. The EPR spectra of **2a** were similar to those of L^1, indicating retention of the dithiadiazolyl ring. LRMS (EI mode) of **2a** exhibited a peak at m/z 182 for L^1 while the parent peak of **2a** was not observed. Based on the above spectroscopic and analytical data, compound **2a** could be formulated as fac-Mn(CO)$_3$Br(L^1)$_2$.

Similarly, when L^2 was allowed to react with Mn(CO)$_5$Br, work up gave the reddish-brown stoichiometric solid $C_{15}H_8BrMnN_6O_3S_4 \cdot H_2O$ (**2b** · H$_2$O) in good yield (75%).
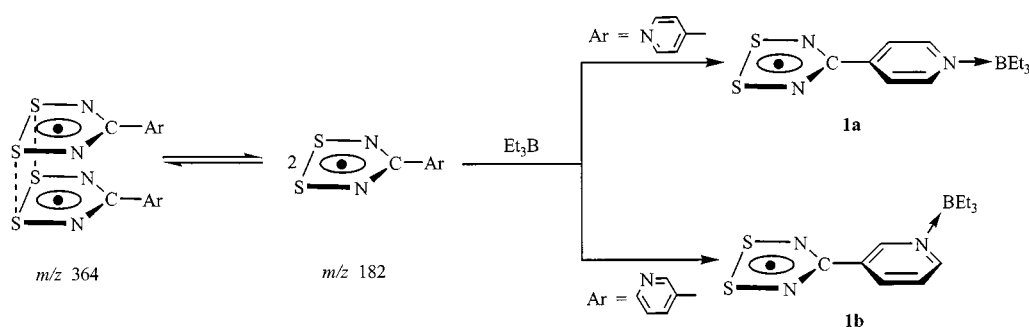
Scheme 2

The spectroscopic data of **2b** were very similar to those of **2a**. In the carbonyl region of its IR spectrum (KBr), **2b** showed three very strong absorptions at 2028, 1947, and 1912 cm^{-1}, characteristic of a *fac*-Mn(CO)$_3$ configuration. Compound **2b** also exhibited a broad peak and a quintet with an intensity pattern of 1:2:3:2:1 in its solid state and tetrahydrofuran solution EPR spectra, respectively. The measured *g*-value was 2.014 with the hyperfine coupling constant $A = 0.51$ mT. Compound **2b** was also formulated as *fac*-Mn(CO)$_3$Br(L^2)$_2$.
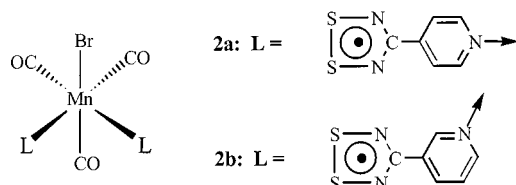

Preparation of [Pd$_3${μ-SNC(Ar′)NS–*S,S′*}$_2$(PPh$_3$)$_4$]

Ar′ = 4′-C$_5$H$_4$N

When **L^1** was allowed to react with 4 equivalents of Pd(PPh$_3$)$_4$ in toluene for 4 h at ambient temperature, workup gave red crystals of (Ph$_3$P)$_4$Pd$_3$-(C$_{12}$H$_8$N$_6$S$_4$) · 0.25 CH$_2$Cl$_2$, **3a** · 0.25 CH$_2$Cl$_2$, in good yield (70%) after recrystallization from a dichloromethane solution. In the IR spectrum of **3a**, absorption corresponding to L^1 (characterized by strong absorptions at 1140, 810, 656, and 510 cm^{-1}) were not observed. Instead three strong absorptions at 1434, 691, and 527 cm^{-1} were detected. This IR spectrum was indicative of a ring opening reaction between the two sulfur-sulfur atoms. In addition to the pyridyl and phenyl carbons, the ^{13}C-{^{1}H} NMR spectrum of **3a** gave a singlet at δ = 174.0 for the C=N carbon of the amidine group. The ^{1}H-NMR spectrum of **3a** showed resonances at δ = 8.52 (dd, 4 H, *J* = 4.6, 1.6 Hz) and 8.11 (dd, 4 H, *J* = 4.6, 1.6 Hz) for the pyridyl α- and β-protons, respectively, and at δ = 7.12 (t, 12 H, *J* = 7.3 Hz), 6.97 (t, 24 H, *J* = 7.3 Hz), and 6.83 (m, 24 H) for the phenyl protons. The ^{31}P-{^{1}H} NMR spectrum of **3a** in CDCl$_3$ exhibited only a singlet at δ = 27.5 for the PPh$_3$ groups, indicating that all the triphenylphosphane groups were equivalent. LRMS (positive FAB) of **3a** exhibited a parent peak at *m/z* 1731 [(M + 1) for ^{106}Pd]. Based on the above spectroscopic data, compound **3a** could be formulated as [Pd$_3${μ-SNC(4′-C$_5$H$_4$N)NS–*S,S′*}$_2$(PPh$_3$)$_4$] with a structure similar to that of [Pd$_3${μ-SNC(Ph)NS-*S,S′*}$_2$(PPh$_3$)$_4$] as shown below.[15] This was confirmed by an X-ray crystallographic study.

Crystals of **3a** · 2 (C$_2$H$_5$)$_2$O suitable for X-ray diffraction study were grown from a dichloromethane/diethyl ether mixture. A perspective drawing of **3a** is shown in Figure 1 and selected bond lengths and angles are given in Table 1. The solid state structure of **3a** is consistent with its spectroscopic data. The structure of **3a** is composed of a linear Pd$_3$ chain bridged by two SNC(4-C$_5$H$_4$N)NS ligands in which the terminal Pd atoms are related through a crystallographic inversion center at Pd(2). Both Pd(1) and Pd(2)

3a: Ar =

3b: Ar =

5a: Ar =

5b: Ar =
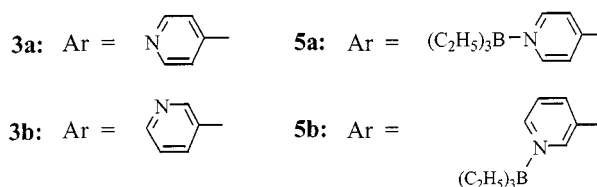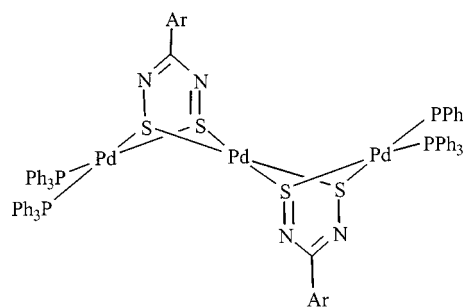
atoms possess a square planar geometry. The terminal Pd atoms have a PdP$_2$S$_2$ environment whereas the central Pd is bound only to the dithiadiazolyl S atoms, thus producing a PdS$_4$ coordination geometry. This structure is analogous to those of [Pt$_3${μ-SNC(Ph)NS-*S,S′*}$_2$(PPh$_3$)$_4$] and [Pd$_3${μ-SNC(Ph)NS-*S,S′*}$_2$(PPh$_3$)$_4$] reported previously.[15] In **3a**, the dithiadiazolyl ligands take up a bridging mode between Pd(1) and Pd(2) with a Pd···Pd distance of 2.852(1) Å. Such metal–metal distance is slightly longer than the sum of the metallic radii (2.76 Å for Pd), suggesting that no metal-metal bond exists.

As a bridging ligand, the S–S bond in the dithiadiazolyl ring has been broken. The S(1)–N(1) and S(2)–N(2) distances are 1.64(1) and 1.65(1) Å, respectively. The N(1)–C(1) and N(2)–C(1) distances of 1.34(1) and 1.331(1) Å, respectively, are also intermediate between those expected for carbon-nitrogen single (1.46 Å) and double (1.26 Å) bonds. All these indicate some degree of electron delocalization about the SNCNS framework. This delocalization is also reflected in the S(1)–N(1)–C(1) and S(2)–N(2)–C(1) bond angles of 125.6(9) and 124.2(9)°, respectively, which deviate significantly from that expected for a tetrahedral sp^3 nitrogen atom and are closer to a sp^2 nitrogen atom.

Ar′ = 3′-C$_5$H$_4$N

When two equivalents of **L^2** were allowed to react with 3 equivalents of Pd(PPh$_3$)$_4$ in toluene for 4 h at ambient temperature, workup gave a stoichiometric red solid, (Ph$_3$P)$_4$Pd$_3$(C$_{12}$H$_8$N$_6$S$_4$)1.7CH$_2$Cl$_2$ (**3b** · 1.7 CH$_2$Cl$_2$) in good yield (60%) after recrystallization from dichloromethane. The spectroscopic data of **3b** were very similar to those of **3a**. Compound **3b** exhibited a similar IR spectrum to that of **3a** with three strong absorptions at 1433, 692, and 526 cm^{-1}. In addition to the pyridyl and phenyl carbons, the ^{13}C-{^{1}H} NMR spectrum of **3a** exhibited a singlet at δ = 173.9 for the C=N carbon of the amidine group. The ^{31}P-{^{1}H} NMR spectrum of **3b** in CDCl$_3$ gave only a singlet at δ = 27.5 for the PPh$_3$ groups. The ^{1}H-NMR spectrum of **3b** exhibited resonances at δ = 9.46 (d, 2 H, *J* = 1.6 Hz), 8.50 (dd, 4 H, *J* = 4.6, 1.6 Hz), and 8.39 (dt, 2 H, *J* = 8.4, 1.6 Hz) for the pyridyl protons, and at δ = 7.25–6.82 (60
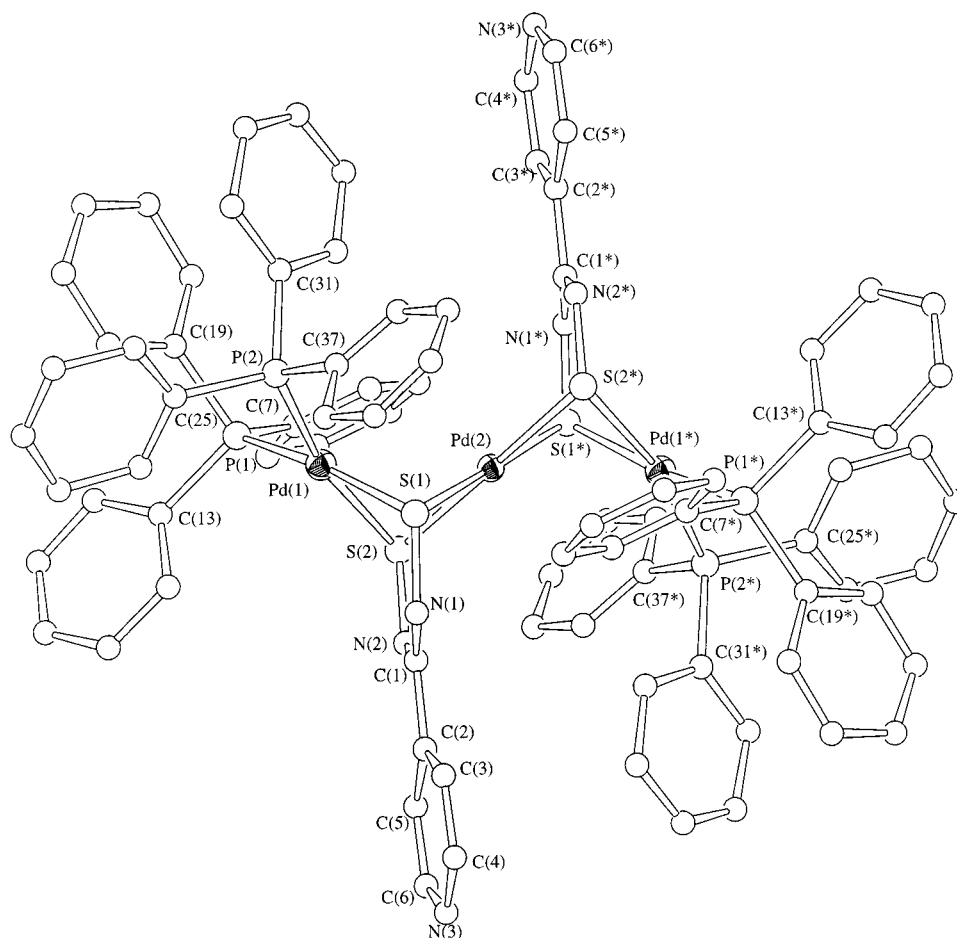
Figure 1. A perspective drawing of the molecular structure of **3a**

H, m) for the phenyl protons. LRMS (positive FAB) of **3b** exhibited a parent peak at *m/z* 1731 [(M + 1) for ^{106}Pd]. Based on the above spectroscopic and analytical data, a centrosymmetric trinuclear complex with a structure similar to that of **3a** was proposed for **3b**.

Preparation of [Pd$_3$$\{$μ-SNC(4′-NC$_5H_4$)NS–*S,S*′$\}_2$(dppf)$_2$] (4)

When one equivalent of **L^1** was allowed to react with a mixture of two equivalents of 1,1′-bis(diphenylphosphanyl)ferrocene (dppf) and one equivalent of tris(dibenzylideneacetone)dipalladium [Pd$_2$(dba)$_3$] in toluene for one day at room temperature, workup gave a stoichiometric red solid of (dppf)$_2$Pd$_3$(C$_{12}$H$_8$N$_6$S$_4$) · 0.5 CH$_2$Cl$_2$ (**4** · 0.25 CH$_2$Cl$_2$) in a moderate yield (50%). In addition to the pyridyl and phenyl carbon signals, the ^{13}C-$\{^1$H$\}$ NMR spectrum of **4** exhibited three broad singlets at δ = 73.3, 72.3, and 72.0 for the cyclopentadienyl carbon atoms. The ^{31}P-$\{^1$H$\}$ NMR spectrum of **4** in CDCl$_3$ exhibited only a singlet at δ = 25.5 for the phosphanyl groups. The ^{1}H-NMR spectrum of **4** exhibited two doublets at δ = 8.56 (d, 4 H, *J* = 6.2 Hz) and 8.22 (d, 4 H, *J* = 6.2 Hz) for the pyridyl protons, a complex multiplet at δ = 7.52–7.08 (m, 48 H) for the phenyl protons, and four singlets at δ = 3.92 (s, 4 H), 3.68 (s, 4 H), 3.65 (s, 4 H), and 3.61 (s, 4 H) for the cyclo-

pentadienyl protons. LRMS (positive FAB) of **4** exhibited a parent ion peak at *m/z* 1791 [(M + 1) for ^{106}Pd]. Based on the spectroscopic and analytical data, compound **4** could be formulated as [Pd$_3$$\{$μ-SNC(4′-NC$_5H_4$)NS-*S,S*′$\}_2$(dppf)$_2$] with the structure as shown below.

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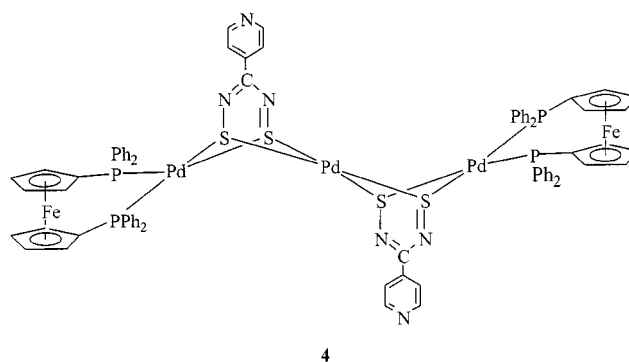
Reaction of Triethylborane with 3a and 3b

When an excess amount of triethylborane was allowed to react with **3a** and **3b** in CH$_2$Cl$_2$/hexane mixture for one day at ambient temperature, workup gave red crystals of **5a** and **5b** of the same stoichiometry (Ph$_3$P)$_4$Pd$_3$(C$_{12}$H$_8$N$_6$S$_4$)-(BEt$_3$)$_2$ in 74 and 71% yield, respectively. Compound **5a** exhibited a spectroscopic pattern similar to that of **3a**. In

Table 1. Selected bond lengths [Å] and angles [°] for compounds **3a**, **5a**, and **5b**

Compound **3a**					
Pd(1)···Pd(2)	2.852(1)	Pd(1)–P(1)	2.357(3)	S(1)–N(1)	1.64(1)
Pd(1)–S(1)	2.360(3)	Pd(1)–P(2)	2.341(4)	S(2)–N(2)	1.65(1)
Pd(1)–S(2)	2.388(3)	Pd(2)–S(1)	2.337(3)	N(1)–C(1)	1.34(1)
N(2)–C(1)	1.33(1)	Pd(2)–S(2)	2.357(3)		
Pd(1)–Pd(2)–Pd(1*)	180.0	S(1)–Pd(1)–P(2)	89.2(1)	S(1)–Pd(2)–S(2)	81.0(1)
S(1)–Pd(1)–P(1)	169.0(1)	S(2)–Pd(1)–P(2)	165.7(1)	Pd(1)–S(1)–Pd(2)	74.8(1)
S(2)–Pd(1)–P(1)	89.3(1)	S(1)–Pd(1)–S(2)	79.9(1)	Pd(1)–S(2)–Pd(2)	73.89(9)
S(1)–N(1)–C(1)	125.6(9)	N(1)–C(1)–N(2)	131(1)	Pd(2)–Pd(1)–S(2)	52.56(8)
S(2)–N(2)–C(1)	124.2(9)	Pd(2)–Pd(1)–S(1)	52.24(8)	P(1)–Pd(1)–P(2)	101.8(1)
Compound **5a**					
Pd(1)···Pd(2)	2.8638(5)	Pd(1)–P(1)	2.338(2)	S(1)–N(1)	1.641(5)
Pd(1)–S(1)	2.387(2)	Pd(1)–P(2)	2.338(2)	S(2)–N(2)	1.663(5)
Pd(1)–S(2)	2.368(2)	Pd(2)–S(1)	2.351(1)	N(1)–C(37)	1.333(8)
Pd(2)–S(2)	2.344(2)	N(2)–C(37)	1.326(7)	B(1)–N(3)	1.69(1)
Pd(1)–Pd(2)–Pd(1*)	180.0	P(1)–Pd(1)–P(2)	102.47(6)	S(1)–Pd(2)–S(2)	98.30(5)
S(1)–Pd(1)–P(1)	86.77(5)	S(2)–Pd(1)–P(2)	90.99(6)	Pd(1)–S(1)–Pd(2)	74.37(4)
S(2)–Pd(1)–P(1)	166.42(6)	S(1)–Pd(1)–S(2)	84.46(5)	Pd(1)–S(2)–Pd(2)	74.87(5)
S(1)–N(1)–C(37)	124.6(4)	N(1)–C(37)–N(2)	132.3(6)	Pd(2)–Pd(1)–S(2)	52.19(4)
S(2)–N(2)–C(37)	125.2(4)	Pd(2)–Pd(1)–S(1)	52.24(4)	C(40)–N(3)–B(1)	119.9(8)
Compound **5b**					
Pd(1)···Pd(2)	2.884(1)	Pd(2)–P(1)	2.348(2)	S(1)–N(1)	1.662(6)
Pd(1)–S(1)	2.342(2)	Pd(2)–P(2)	2.326(3)	S(2)–N(2)	1.663(6)
Pd(1)–S(2)	2.349(2)	Pd(2)–S(1)	2.378(3)	N(1)–C(1)	1.33(1)
N(2)–C(1)	1.33(1)	B(1)–N(3)	1.66(1)	Pd(2)–S(2)	2.371(2)
Pd(2)–Pd(1)–Pd(2*)	180.0	P(1)–Pd(2)–P(2)	101.06(7)	S(1)–Pd(2)–S(2)	80.04(7)
S(1)–Pd(2)–P(1)	88.95(7)	S(2)–Pd(2)–P(1)	167.11(8)	Pd(1)–S(1)–Pd(2)	75.31(7)
S(2)–Pd(2)–P(2)	90.90(7)	S(1)–Pd(1)–S(2)	81.26(7)	Pd(1)–S(2)–Pd(2)	75.32(7)
S(1)–N(1)–C(1)	123.7(5)	N(1)–C(1)–N(2)	132.7(7)	Pd(1)–Pd(2)–S(2)	51.98(5)
S(2)–N(2)–C(1)	125.0(5)	Pd(1)–Pd(2)–S(1)	51.77(5)	C(3)–N(3)–B(1)	120.1(8)

the IR spectrum (KBr), other than the three strong absorptions at 1435, 692, and 520 cm^{-1}, the observation of v(Py, CN) at 1619 cm^{-1}, a shift of ca. 34 cm^{-1} from that of **3a** (1585 cm^{-1}), indicated B–N bond formation. In addition to the ethyl resonance, the ^{1}H-NMR spectrum of **5a** also exhibited two resonances at δ = 8.47 (d, 4 H, J = 6.6 Hz) and 8.35 (d, 4 H, J = 6.6 Hz) for the α-H and β-H of the pyridyl group, respectively. The slight upfield shift of ca. 0.05 ppm for the α-H signal from that of **3a** (δ = 8.52) and downfield shift of ca. 0.24 ppm for the β-H signal from that of **3a** (δ = 8.11) were also characteristic of the formation of B–N dative bond. The ^{31}P-{^{1}H} NMR spectrum of **5a** in CDCl$_3$ exhibited a singlet at δ = 27.5 for the PPh$_3$ groups. LRMS (positive FAB) of **5a** exhibited an ion peak at m/z 1731 [(M – 2 BEt$_3$ + 1) for ^{106}Pd]. Based on the above spectroscopic data, compound **5a** could be envisaged as an acid-base adduct of the triethylborane and the pyridyl groups of **3a**, and formulated as [Pd$_3${μ-SNC(4′-C$_5$H$_4$NBEt$_3$)NS-S,S′}$_2$(PPh$_3$)$_4$].

Other than the phenyl protons, the ^{1}H-NMR spectrum of **5b** showed resonances of the triethylborane protons at δ = 0.60 (m, 18 H) and 0.51 (m, 12 H), and the pyridyl protons at δ = 9.47 (2 H, br s), 8.47 (m, 4 H), and 7.85 (s, 2 H). The ^{31}P-{^{1}H} NMR spectrum of **5b** in CDCl$_3$ exhibited only a singlet at δ = 26.9 for the PPh$_3$ groups. LRMS (positive FAB) of **5b** exhibited an ion peak at m/z 1731 [(M – 2 BEt$_3$ + 1) for ^{106}Pd]. Thus, compound **5b** could also be formulated as [Pd$_3${μ-SNC(3′-C$_5$H$_4$N · BEt$_3$)NS-S,S′}$_2$(PPh$_3$)$_4$]. The structures of both compounds **5a** and **5b** were ascertained by X-ray crystallography.
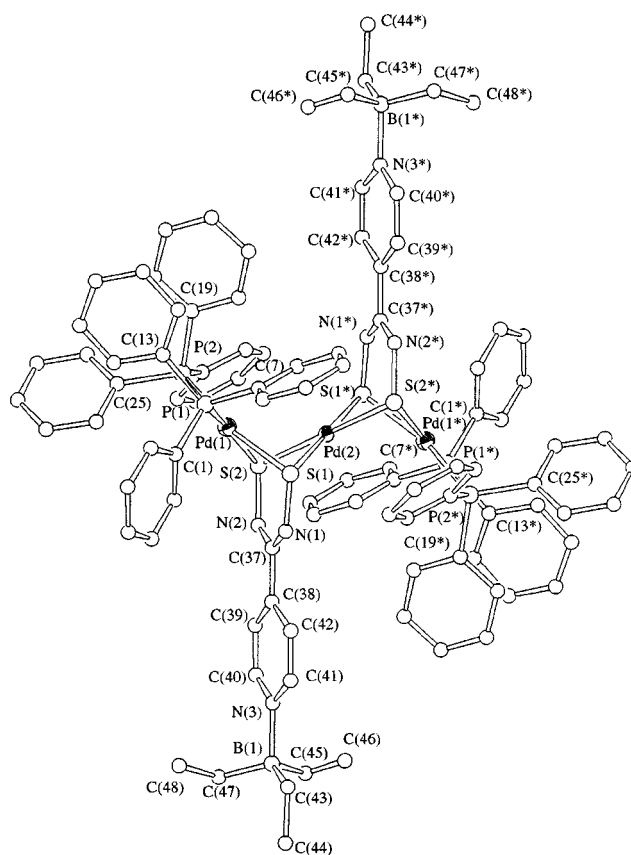
Figure 2. A perspective drawing of the molecular structure of **5a**

Crystals of **5a** · 4 CH$_2$Cl$_2$ and **5b** · 4 CH$_2$Cl$_2$ suitable for X-ray diffraction studies were grown from a solution of the respective compound in a dichloromethane/hexane mixture. Perspective drawings of the compounds are shown in Figure 2 and Figure 3, respectively. Selected bond lengths and angles are given in Table 1. The solid state structures of **5a** and **5b** are consistent with their spectroscopic data. Crystal structure analyses revealed that the triethylborane groups interact with the pyridyl groups of **3a** and **3b** forming acid-base adducts with a B–N distance of 1.69(1) and 1.66(1) Å, respectively. Other than the presence of triethylborane groups at the pyridyl groups, the structures of **5a** and **5b** are very similar to that of **3a** and **3b**.

Preparation of {[Pd$_3${μ-SNC(4′-C$_5$H$_4$N)NS–*S,S*′}$_2$-(PPh$_3$)$_4$][Mn(CO)$_3$Br]}$_n$ (6)

When **3a** was allowed to react with 2 equivalents of Mn(CO)$_5$Br in dichloromethane for one day at ambient tem-
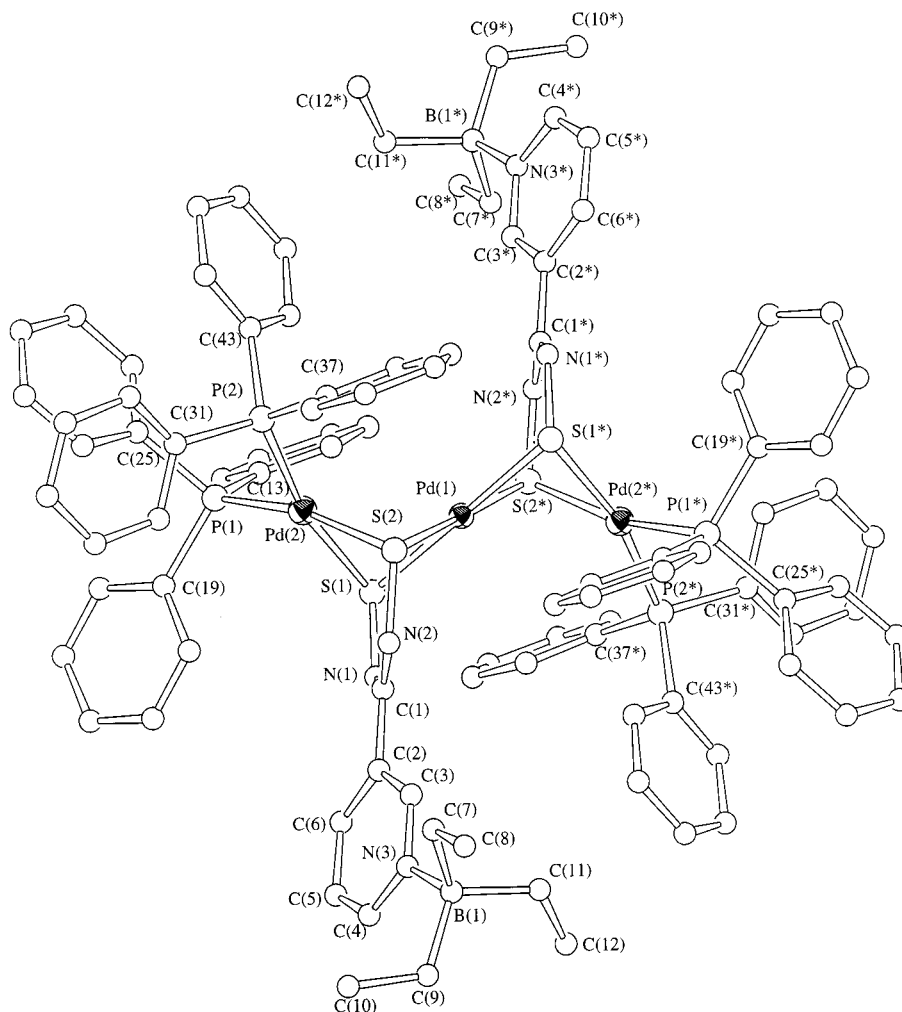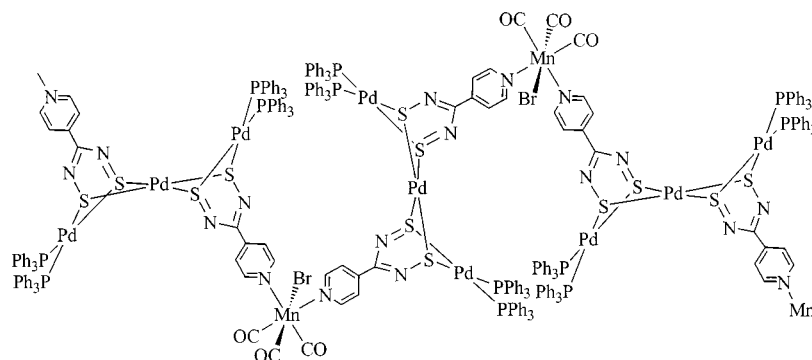

Figure 3. A perspective drawing of the molecular structure of **5b**

6

perature, workup gave a stoichiometric red solid of $(Ph_3P)_4Pd_3(C_{12}H_8N_6S_4)[Mn(CO)_3Br] \cdot 1.5 \; CH_2Cl_2$ (**6** · 1.5 CH_2Cl_2) in a moderate yield of 55%. In the IR spectrum (KBr), compound **6** exhibited three very strong absorptions in the terminal carbonyl region at 2024, 1935, and 1905 cm^{-1}, which were indicative of a *fac*-Mn(CO)$_3$ configuration; and *v*(Py, CN) at 1606 cm^{-1}, a shift of ca. 21 cm^{-1} from that of **3a** (1585 cm^{-1}), indicating the formation of Mn–N bonds. The Mn–N bond formation was also reflected in the chemical shifts of the pyridyl protons in the ^{1}H-NMR spectrum (CDCl$_3$), in which the α-H and β-H signals were shifted downfield from δ = 8.52 and 8.11 for **3a** to δ = 8.71 and 8.14 for **6**. The ^{1}H-NMR spectrum of **6** exhibited two resonances of relative intensity 4:30 for the pyridyl and phenyl protons, respectively. The ^{31}P-{^{1}H} NMR spectrum of **6** in CDCl$_3$ gave only a singlet at δ = 27.4 for the PPh$_3$ groups. LRMS (positive FAB) of **6** exhibited an ion peak at *m/z* 1730 {[M – MnBr(CO)$_3$] for ^{106}Pd}. Based on the spectroscopic and analytical data, compound **6** could be formulated as {[Pd$_3${μ-SNC(4′-C$_5$H$_4$N)NS-*S*,*S*′}$_2$(PPh$_3$)$_4$]-[Mn(CO)$_3$Br]}$_n$ with a possible structure shown below. In **6**, complex **3a** and Mn(CO)$_3$Br were linked alternately together in a linear manner, in which the central metal Mn possesses an octahedral geometry with the three carbonyl ligands in a *fac* configuration, while the two nitrogen atoms adopt a *cis* configuration. The two nitrogen atoms coordinated to the same metal Mn came from two different molecules of **3a**. Thus, **6** could also be described as two Mn(CO)$_3$Br and one bridging **3a** ligand alternately linking together in a linear geometry.

Experimental Section

General Procedures: Unless otherwise stated, manipulations were performed under oxygen-free nitrogen using standard techniques in a glovebox. Solvents were dried by standard procedures, distilled and de-aerated prior to use. All chemicals used were of reagent grade, obtained from the Aldrich Chemical Company and, where appropriate, degassed before use. The compounds Pd(PPh$_3$)$_4$,[20] dppf,[21] and Pd$_2$(dba)$_3$[22] were prepared according to literature methods. – Microanalyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, China. – The melting points were obtained in glass capillaries and were uncorrected. – Infrared spectra were recorded with a Nicolet Nagna-IR 550 spectrometer and NMR spectra with a JEOL EX270 spectrometer. Chemical shifts of ^{1}H and ^{13}C-{^{1}H} NMR spectra were referenced to internal deuterated solvents and then recalculated to SiMe$_4$ (δ = 0.00), those of ^{31}P-{^{1}H} NMR spectra were referenced to external 85% H$_3$PO$_4$ (δ = 0.00). The EPR spectra were obtained with an X-band JEOL JES TE-100 spectrometer at room temperature, low-resolution mass spectra with a Finnigan MAT SSQ-710 or MAT 95 spectrometer either in EI or FAB (positive ion) mode.

[4-(4′-NC$_5$H$_4$)CN$_2$S$_2$] L^1: A solution of Li[N(SiMe$_3$)$_2$], generated in situ by treating (Me$_3$Si)$_2$NH (32.94 g, 200 mmol) in diethyl ether (100 mL) with *n*BuLi (122 mL of 1.6 M, 200 mmol) in hexane, was slowly added to a solution of 4-cyanopyridine (20.8 g, 200 mmol) in tetrahydrofuran (70 mL) at 0 °C. The resulting dark-red solution was warmed to room temperature and allowed to react overnight.

The solvent was removed in vacuo to give a dark red residue that was then suspended in toluene (400 mL). A solution of Me$_3$SiCl (22.4 g, 200 mmol) in toluene (100 mL) was then slowly added to the suspension at room temperature. Upon complete addition, the solution mixture was stirred under reflux for 7 h, then at room temperature overnight. The resultant reaction mixture was then filtered to afford a red filtrate, which was pumped dry before acetonitrile (200 mL) was added. A solution of sulfur dichloride (42 g, 400 mmol) in acetonitrile (50 mL) was then slowly added. The mixture was stirred at room temperature for 24 h and then filtered to afford crude 4-(4′-pyridyl)dithiadiazolylium chloride as a yellow solid, which was washed once with a 1:1 mixture of acetonitrile/toluene (200 mL) and then suspended in acetonitrile (200 mL). A solution of triphenylantimony (72 g, 200 mmol) in acetonitrile (100 mL) was slowly added to the suspension at room temperature to give a dark purple precipitate. The reaction mixture was allowed to stir at room temperature for 2 h before the solvent was removed in vacuo to give a dark purple residue. Sublimation of the residual solid at 110°C/0.05 Torr afforded a dark red solid of [4-(4′-NC$_5$H$_4$)CN$_2$S$_2$]. Yield: 12.1 g, 33.3%; m. p. 252–254°C (dec.). – C$_6$H$_4$N$_3$S$_2$ · H$_2$O (200.25): calcd. C 36.0, H 3.0, N 21.0, S 32.0; found C 36.0, H 2.9, N 20.8, S 31.0. – IR (cm^{-1}, in KBr): ṽ = 3388 vs, 3332 s, 3266 s, 3120 m, 3028 m, 1945 w, 1693 m, 1649 m, 1599 s, 1560 w, 1417 vs, 1377 s, 1230 m, 1140 m, 1062 m, 1018 m, 1000 m, 913 w, 828 s, 810 s, 785 vs, 747 w, 736 w, 667 m, 656 vs, 618 w, 510 m, 464 w. – LRMS (EI mode); *m/z*: 364 [M$_2$ for ^{32}S] and 182 [M for ^{32}S]. – EPR (in toluene): *g* = 2.014, *A* = 0.52 mT (five lines with relative intensity 1:2:3:2:1).

[4-(3′-NC$_5$H$_4$)CN$_2$S$_2$] L^2: The compound was prepared as described for **L^1**. LiN(SiMe$_3$)$_2$ (2.7 g, 164 mmol), 3-cyanopyridine (17.4 g, 164 mmol), SiMe$_3$Cl (17.8 g, 164 mmol), sulfur dichloride (51.7 g, 492 mmol), and triphenylantimony (29.2 g, 82 mmol) were used. A dark red powder was obtained after sublimation (100°C/0.03 Torr). Yield: 14.9 g, 50%; m. p. 215–217°C (dec.). – C$_6$H$_4$N$_3$S$_2$ · 0.25 H$_2$O (186.74): calcd. C 38.6, H 2.4, N 22.5, S 34.3; found C 38.4, H 2.4, N 21.9, S 33.7. – IR (cm^{-1}, KBr): ṽ = 3608 w, 3423 m, 3067 m, 3038 m, 2964 w, 1686 m, 1589 m, 1480 w, 1429 m, 1375 vs, 1325 m, 1244 m, 1189 m, 1146 m, 1116 w, 1091 w, 1040 m, 1026 s, 905 w, 834 m, 809 vs, 782 vs, 698 vs, 667 s, 627 m, 511 m, 459 m. – LRMS (EI mode); *m/z*: 364 [M$_2$ for ^{32}S] and 182 [M for ^{32}S]. – EPR (in toluene): *g* = 2.013, *A* = 0.51 mT (five lines with relative intensity 1:2:3:2:1).

fac-MnBr(CO)$_3$(L^1)$_2$ (2a): Mn(CO)$_5$Br (0.58 g, 2.1 mmol) and **L^1** (0.19 g, 1.04 mmol) were stirred in tetrahydrofuran (20 mL) at 55°C for 4 h to yield a reddish-brown solution and a small amount of yellow precipitate. After cooling to room temperature, the solution was filtered. The red-brown filtrate was cooled to –5°C to give tiny reddish-brown needle crystals, which were filtered and dried in vacuo. Yield: 0.18 g, 56%; m. p. 167–169°C (dec.). – C$_{15}$H$_8$BrMnN$_6$O$_3$S$_4$ · 2.5 H$_2$O (628.37): calcd. C 28.7, H 2.1, N 13.4, S 20.4; found C 28.6, H 1.9, N 13.5, S 19.3. – IR (cm^{-1}, in KBr): ṽ = 3410 m, 3103 m, 2975 m, 2927 m, 2866 w, 2030 vs, 1942 vs, 1909 vs, 1686 m, 1612 m, 1421 m, 1375 m, 1222 m, 1098 m, 1059 m, 1019 m, 842 m, 778 m, 681 w, 648 w, 630 m, 517 m. – EPR (in THF): *g* = 2.014, *A* = 0.50 mT, quintuplet with relative intensity: 1:2:3:2:1. (in solid): *g* = 2.011.

fac-MnBr(CO)$_3$(L^2)$_2$ (2b): A solution of Mn(CO)$_5$Br (0.04 g, 0.15 mmol) and **L^2** (0.05 g, 0.27 mmol) in tetrahydrofuran (10 mL) was stirred under reflux for 4 h to yield a reddish-brown precipitate. The precipitate was filtered off, washed with tetrahydrofuran (3 × 4 mL) and dried in vacuo. Yield: 0.06 g, 74%; m. p. 155–157°C (dec.). – C$_{15}$H$_8$BrMnN$_6$O$_3$S$_4$ · H$_2$O (601.33): calcd. C 30.0, H 1.7,

N 14.0, S 21.3; found C 29.8, H 1.6, N 13.5, S 20.8. – IR (cm⁻¹, in KBr): ṽ = 3379 m, 3201 m, 3058 m, 2854 w, 2028 vs, 1947 vs, 1912 vs, 1610 m, 1573 w, 1463 m, 1435 s, 1415 m, 1331 w, 1258 w, 1193 w, 1102 m, 1027 w, 999 w, 830 w, 806 w, 744 m, 708 m, 694 s, 673 m, 635 m, 524 s, 492 w. – EPR (in THF): *g* = 2.014, *A* = 0.51 mT, quintuplet with relative intensity 1:2:3:2:1; (in solid): *g* = 2.014.

[Pd₃{μ-SNC(4′-NC₅H₄)NS-*S,S′*}₂(PPh₃)₄] (3a): Solid **L¹** (0.07 g, 0.38 mmol) was added to a stirred suspension of Pd(PPh₃)₄ (0.84 g, 0.73 mmol) in toluene (14 mL) at ambient temperature. The reaction mixture was then stirred for 4 h to give a red precipitate. The red precipitate was filtered off, washed with toluene (2 × 6 mL) and dried in vacuo. The red precipitate was then re-dissolved in hot dichloromethane (20 mL) to give a deep red solution, which was filtered and cooled to –30°C to give red block crystals. The crystals were filtered and dried in vacuo. Yield: 0.22 g, 66%; m. p. 250–252°C (dec.). – C₈₄H₆₈N₆P₄Pd₃S₄ · 0.25 CH₂Cl₂ (1753.97): calcd. C 57.7, H 3.9, N 4.8, S 7.3; found C 58.0, H 3.9, N 4.7, S 7.3. – IR (cm⁻¹, in KBr): ṽ = 3049 w, 2940 w, 2853 w, 1585 m, 1478 m, 1434 s, 1418 m, 1309 m, 1264 w, 1181 w, 1155 w, 1094 m, 1057 w, 1026 w, 998 w, 840 w, 821 w, 746 m, 737 m, 715 vs, 691 vs, 671 s, 618 w, 527 s, 519 vs, 506 s, 492 s, 459 w, 445 w, 424 w. – NMR (CDCl₃): ³¹P-{¹H}, PPh₃, δ = 27.5 (s); ¹³C-{¹H}, C=N carbon atom, 174.0 (br, s); pyridyl carbon atoms, 150.1, 149.4, and 121.7; phenyl carbon atoms, 133.9 (t, *J* = 6.1 Hz), 129.9, 128.2 (t, *J* = 4.9 Hz); ¹H, pyridyl protons, δ = 8.52 (dd, 4 H, *J* = 4.6, 1.6 Hz), 8.11 (dd, 4 H, *J* = 4.6, 1.6 Hz); phenyl protons, 7.12 (t, 12 H, *J* = 7.3 Hz), 6.97 (t, 24 H, *J* = 7.3 Hz), 6.83 (m, 24 H); dichloromethane protons, 5.23 (s). – LRMS (FAB: +ve mode) *m/z*: 1731 [(M + 1) for ¹⁰⁶Pd].

[Pd₃{μ-SNC(3′-NC₅H₄)NS-*S,S′*}₂(PPh₃)₄] (3b): The compound was prepared as described for **3a**. Pd(PPh₃)₄ (4.0 g, 3.46 mmol) and **L²** (0.42 g, 2.31 mmol) were used. Yield: 1.19 g, 55%; m. p. 254–256°C (dec.). – C₈₄H₆₈N₆P₄Pd₃S₄ · 1.7 CH₂Cl₂ (1877.11): calcd. C 54.8, H 3.8, N 4.5, S 6.8; found C 54.8, H 3.6, N 4.5, S 7.1. – IR (cm⁻¹, in KBr): ṽ = 3050 w, 2963 w, 1640 m (br), 1583 m, 1476 m, 1433 s, 1384 m, 1310 m, 1261 m, 1196 w, 1153 m, 1093 s, 1023 m,

997 m, 907 w, 801 s (br), 741 s (br), 719 m, 691 vs, 670 s, 618 w, 543 w, 526 s, 519 vs, 493 s, 431 w, 422 w, 406 w. – NMR (CDCl₃): ³¹P-{¹H}, PPh₃, δ = 27.5 (s); ¹³C-{¹H}, C=N carbon atom, 173.9 (s); pyridyl carbon atoms, 149.1, 148.7, 138.4 134.6 and 122.7; phenyl carbon atoms, 134.0 (t, *J* = 6.1 Hz), 131.0 (dd, *J* = 20.8, 19.5 Hz), 129.8, 128.2 (t, *J* = 4.9 Hz); ¹H, pyridyl protons: δ = 9.46 (d, 2 H, *J* = 1.6 Hz), 8.50 (dd, 4 H, *J* = 4.6, 1.6 Hz) and 8.39 (dt, 2 H, *J* = 8.4, 1.6 Hz); phenyl protons, 7.25–6.82 (m, 60 H); dichloromethane protons, 5.23 (s). – LRMS (FAB: +ve mode) *m/z*: 1731 [(M + 1) for ¹⁰⁶Pd].

[Pd₃{μ-SNC(4′-NC₅H₄)NS-*S,S′*}₂(dppf)₂] (4): Solid [4-(4′-NC₅H₄)-CN₂S₂]₂ (**L¹**) (0.20 g, 0.55 mmol) was added to a stirred solution of Pd₂(dba)₃ (0.50 g, 0.55 mmol) and dppf (0.61 g, 1.10 mmol) in toluene (18 mL) at ambient temperature. The reaction mixture was then stirred for one day to give a red precipitate, which was filtered, washed with toluene (6 mL), and dried in vacuo. Further washing the red precipitate with hot dichloromethane (20 mL) gave a red residue, which was dried in vacuo. The red residue was then recrystallized from hot chloroform to give tiny red crystals. Yield: 0.49 g, 49%; m. p. 256–258°C (dec.). – C₈₀H₆₄Fe₂N₆P₄Pd₃S₄ · 0.25 CHCl₃ (1822.62): calcd. C 52.9, H 3.5, N 4.6, S 7.0; found C 52.7, H 3.7, N 5.0, S 7.2. – IR (cm⁻¹, in KBr): ṽ = 3112 s, 2964 m, 2924 m, 2853 w, 1589 s, 1480 m, 1435 vs, 1420 s, 1402 m, 1310 s, 1261 w, 1164 m, 1098 m, 1027 m, 998 w, 524 m, 519 m, 487 vs, 464 m, 439 m. – NMR (CDCl₃): ³¹P-{¹H}, phosphanyl groups, δ = 25.5 (s); ¹³C-{¹H}, phenyl and pyridyl carbon atoms, 149.2, 135.6, 132.2, 131.1, 128.1, 125.1, 123.0 and 121.5; cyclopentadienyl carbon atoms, 73.3 (br, s), 72.3 (br, s) and 72.0 (br, s); ¹H, pyridyl protons, 8.56 (d, 4 H, *J* = 6.2 Hz), 8.22 (d, 4 H, *J* = 6.2 Hz); phenyl protons, 7.52–7.08 (m, 48 H); cyclopentadienyl protons, 3.92 (s, 4 H), 3.68 (s, 4 H), 3.65 (s, 4 H) and 3.61 (s, 4 H). – LRMS (FAB: +ve mode) *m/z*: 1791 [(M + 1) for ¹⁰⁶Pd].

[Pd₃{μ-SNC(4′-C₅H₄NBEt₃)NS-*S,S′*}₂(PPh₃)₄] (5a): A solution of triethylborane (0.2 mL of 1ᴍ, 0.2 mmol) in hexane was carefully layered over a solution of **3a** (0.17 g, 0.10 mmol) in dichloromethane (10 mL). The resultant solution was left undisturbed at ambi-

Table 2. Summary of crystal data for compounds **3a**, **5a**, and **5b**

	3a	5a	5b
Empirical formula	C₉₂H₈₈N₆O₂P₄Pd₃S₄	C₁₀₀H₁₀₆B₂Cl₈N₆P₄Pd₃S₄	C₁₀₀H₁₀₆B₂Cl₈N₆P₄Pd₃S₄
Molecular mass	1881.08	2268.56	2268.56
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	*P*–1 (no. 2)	*P*2₁/*n* (no. 14)	*P*1̄ (no. 2)
a [Å]	13.901(4)	15.671(1)	15.101(8)
b [Å]	13.925(2)	21.800(1)	15.91(1)
c [Å]	10.999(2)	17.187(1)	12.095(6)
α [°]	93.38(1)	90	101.41(5)
β [°]	98.69(2)	116.98(1)	104.28(5)
γ [°]	80.81(2)	90	107.59(5)
U [Å³]	2076.4(7)	5232.5(7)	2565(3)
Z	1	2	1
μ(Mo-*K*α) [cm⁻¹]	8.74	7.99	9.21
Temperature [K]	298	298	298
Reflections collected	5685	44557	6980
Independent reflections (*R*ᵢₙₜ)	5415 (0.030)	9555 (0.070)	6670 (0.033)
Observed reflections	3744 [*I* > 1.50σ(*I*)]	6347 [*I* > 1.50σ(*I*)]	4484 (*I* > 3.00σ(*I*)]
R	0.068	0.058	0.070
*R*ᵥᵥ [a]	0.084	0.054	0.082

[a] Weighting scheme $w = 4F_o^2/[\sigma^2(F_o^2) + pF_o^2]^2$.

ent temperature for 24 h to give red crystals, which were filtered and dried in vacuo. Yield: 0.16 g, 73%; m. p. 213–215°C (dec.). – $C_{96}H_{98}B_2N_6P_4Pd_3S_4 \cdot 3\ CH_2Cl_2$ (2183.50): calcd. C 54.5, H 4.8, N 3.9; found C 54.4, H 4.7, N 3.8. – IR (cm^{-1}, in KBr): $\tilde{\nu} = 3053$ m, 2900 m, 2859 s, 1619 s, 1587 m, 1480 m, 1435 vs, 1309 m, 1268 m, 1160 m, 1094 m, 1040 m, 998 m, 892 w, 852 m, 823 w, 798 m, 738 s, 723 vs, 692 vs, 662 s, 618 w, 527 s, 520 vs, 507 s, 492 m, 447 w, 430 w, 411 w. – NMR (CDCl$_3$): ^{31}P-{^{1}H}, PPh$_3$, $\delta = 27.5$ (s); ^{1}H, pyridyl protons, 8.47 (d, 4 H, $J = 6.6$ Hz), 8.35 (d, 4 H, $J = 6.6$, Hz); phenyl protons, 7.19 (t, 24 H, $J = 7.3$ Hz), 7.02 (t, 24 H, $J = 7.3$ Hz), 6.89 (m, 24 H); dichloromethane protons, 5.28 (s); ethyl protons, 0.66 (t, 18 H, $J = 7.6$ Hz) and 0.49 (q, 12 H, $J = 7.6$ Hz). – LRMS (FAB: +ve mode) m/z: 1731 [(M –2BEt$_3$ + 1) for ^{106}Pd].

[Pd$_3$\{μ-SNC(3′-NC$_5$H$_4$NBEt$_3$)NS-S,S'\}$_2$(PPh$_3$)$_4$] (5b): Compound **5b** was prepared as described for **5a**. Triethylborane (excess) and **3b** (0.14 g, 0.08 mmol) were used. Yield: 0.13 g, 71%; m. p. 208–210°C (dec.). – C$_{96}$H$_{98}$B$_2$N$_6$P$_4$Pd$_3$S$_4$ · 4 CH$_2$Cl$_2$ (2268.42): calcd. C 53.0, H 4.7, N 3.7; found C 53.2, H 4.7, N 3.8. – IR (cm^{-1}, in KBr): $\tilde{\nu} = 3054$ w, 2936 w, 2898 w, 2856 m, 2814 w, 1614 w, 1575 m, 1478 m, 1434 s, 1309 m, 1185 w, 1162 m, 1094 m, 1051 w, 1026 w, 996 w, 891 w, 874 w, 799 w, 742 s, 692 vs, 624 w, 521 s, 506 s, 436 m. – NMR (CDCl$_3$): ^{31}P-{^{1}H}, PPh$_3$, $\delta = 26.9$ (s); ^{1}H, pyridyl protons, 9.47 (br. s, 2 H), 8.47 (m, 4 H), 7.85 (s, 2 H); phenyl protons, 7.12 (t, 12 H, $J = 6.7$ Hz), 6.97 (t, 24 H, $J = 6.7$ Hz), 6.85 (m, 24 H); dichloromethane protons, 5.24 (s); ethyl protons, 0.60 (m, 18 H) and 0.51 (m, 12 H). – LRMS (FAB: +ve mode) m/z: 1731 [(M – 2 BEt$_3$ + 1) for ^{106}Pd].

\{[Pd$_3$\{μ-SNC(4′-NC$_5$H$_4$)NS-S,S'\}$_2$(PPh$_3$)$_4$][BrMn(CO)$_3$]\}$_n$ (6): A solution of Mn(CO)$_5$Br (0.045 g, 0.16 mmol) in dichloromethane (6 mL) was added to a solution of **3a** (0.14 g, 0.08 mmol) in dichloromethane (6 mL) at ambient temperature to give a deep-red solution. The resultant solution was stirred overnight at ambient temperature and then filtered. The solvent of the filtrate was removed in vacuo and the residue was washed with diethyl ether (3 × 5 mL) and dried in vacuo to afford a reddish-brown solid. Yield 0.09 g, 54%. m. p. 196–198°C (dec.). – C$_{87}$H$_{68}$BrMnN$_6$P$_4$Pd$_3$S$_4$O$_3$ · 1.5 CH$_2$Cl$_2$ (2079.00): calcd. C 51.1, H 3.4, Br 3.9, N 4.0, S 6.2; found C 51.0, H 3.4, Br 4.1, N 4.1, S 6.3. – IR (cm^{-1}, in KBr): $\tilde{\nu} = 3053$ m, 2024 vs, 1935 vs, 1905 vs, 1641 m, 1606 m, 1480 m, 1434 s, 1384 m, 1311 m, 1184 w, 1174 m, 1095 m, 1079 m, 1026 m, 998 m, 849 w, 494 m, 440 m (br). – NMR (CDCl$_3$): ^{31}P-{^{1}H}, PPh$_3$, $\delta = 27.4$ (s); ^{1}H, pyridyl protons, 8.71 (4 H$_\alpha$, br, s), 8.14 (4 H$_\beta$, br, s); phenyl protons, 7.15–6.84 (m). – LRMS (FAB: +ve mode) m/z 1730 \{[M – MnBr(CO)$_3$] for ^{106}Pd\}.

X-ray Crystallography: Suitable crystals of **3a**, **5a**, and **5b** were mounted and sealed in Lindemann capillaries. All pertinent crystallographic data and other experimental details are summarised in Table 2. Intensity data of **3a** and **5b** were collected with a Rigaku AFC7R diffractometer, and that for **5a** with an MAR research image plate scanner using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) at room temperature. All intensity data were corrected for Lorentz polarisation effects. Empirical absorption corrections based on the ψ-scan method were employed for **3a** and **5b**, whereas an approximation of absorption corrections by inter-image scaling was applied for **5a**. For **5a**, 60 3° frames with an exposure time of 5 min per frame were used. The structures were solved by a combination of direct methods (SIR 92) [23] and Fourier difference techniques, and refined by full-matrix least-squares analysis on F until convergence was reached. However, in compound **3a**, attempts to refine all non-hydrogen atoms anisotropically gave unreasonably high displacement parameters for the atoms. Therefore, only the heavy atoms (Pd, S, and P) were included in subsequent refinement

cycles. The atoms of the ether solvent molecule in **3a** were fixed throughout in the refinement processes. Hydrogen atoms on the organic moieties were generated at their ideal positions (C–H 0.95 Å) and allowed to ride on their respective parent carbon atoms. All calculations were performed with a Silicon-Graphics computer using the program package TEXSAN.[24] Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-135684 to -135686. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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