Pyrrole Thioaldehyde Complexes of Nickel, Palladium and Platinum

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Z. Naturforsch. **59b,** 1372 – 1378 (2004); received August 15, 2004

Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

The coordination chemistry of the unusual, pyrrole-stabilised thioaldehyde molecules, 3,5-dimethylpyrrole-2-carbothioaldehyde (HSPy^{MeHMe}) and 3,5-dimethyl-4-ethylpyrrole-2-carbothioaldehyde (HSPy^{MeEtMe}) has been investigated with nickel, palladium and platinum in the complexes [M(κ^2-SPy^{MeRMe})$_2$] (M = Ni, Pd, Pt; R = H, Et). The structure of the cyclometallated derivative [Pd(η^2-*C*,*N*-$C_6H_4CH_2NMe_2$)(κ^2-SPy^{MeEtMe})] was determined by X-ray diffraction.

Key words: Mixed-Donor Ligands, Thioaldehyde, Nickel, Palladium, Platinum

Introduction

Thioaldehydes [1] are usually considered to be unstable molecules with a tendency to form oligomers and polymers when not stabilised by heteroatoms or steric crowding [2]. The instability of this type of thiocarbonyl compounds stems from the reluctance of sulfur to participate in multiple bond formation. This is due to the unfavourable orbital overlap between the carbon *2p* and sulfur *3p* orbitals in the π-bonding component. Introducing a heteroatom attached directly to the CS carbon atom, or in conjugation with it, allow the C=S bond to be polarised to the more stable C^+-S^- form and leads to delocalisation of the resultant positive charge. This is demonstrated by the two examples in Fig. 1.

Since the first report of a coordinated thioformaldehyde ligand by Roper [3], many thioaldehyde complexes have been prepared [4]. These consist of complexes such as that reported by Roper, in which the thioaldehyde moeity is coordinated through both carbon and sulfur in an η^2 fashion [4 – 7], and examples where the thioaldehyde is bonded solely through the sulfur lone pair [4, 8 – 11]. A number of routes to this latter type of complex have been discovered. These include reaction of an anionic complex containing an -SH ligand with (usually aromatic) aldehydes [8] or aldimines [10] and treatment of Fischer carbene complexes with elemental sulfur. The selenium and tellurium analogues are also accessible by the second route [9].

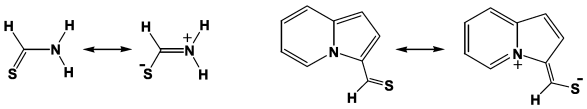

Fig. 1. Polarization of C=S bond and delocalisation of charge through heteroatom interaction.

We have recently started work on the preparation of a series of thioaldehyde molecules stabilised through coordination to a pyrrole ring [12]. These molecules are capable of acting as bidentate donors through both nitrogen and sulfur atoms and thus can be considered mixed-donor ligands. Our current research programme centres on the investigation of these chelates with particular emphasis on hemilabile behaviour and its utility in catalytic processes. We report here the synthesis of a new type of pyrrole carbothialdehyde ligand and its coordination chemistry with the group 10 metals.

Synthesis and Characterisation of Complexes

Various methods have been explored for the preparation of carbothialdehydes, such as the thionation of aldehydes by P_4S_{10} [13]. However, the most convenient and efficient method has proved to be the use of Vilsmaier salts [13 – 16]. A variation on this method using sodium hydrogen sulfide was used to prepare the carbothioaldehyde species reported here. A solu-

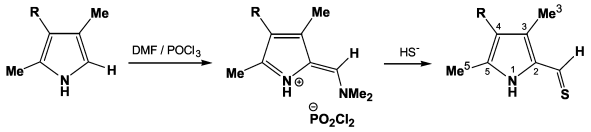

Fig. 2. Route to 3,5-dimethylpyrrole-2-carbothioaldehyde ($HSPy^{MeHMe}$) *via* the Vilsmaier salt showing numbering scheme for $HSPy^{MeHMe}$ (R = H) and $HSPy^{MeEtMe}$ (R = Et) ligands.

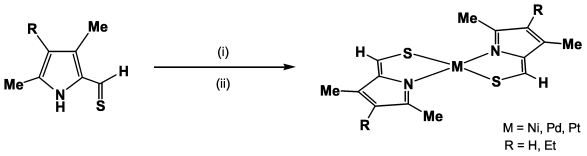

Fig. 3. Preparation of complexes **1**–**6**. (i) $NiCl_2 6H_2O$ or $Ni(OAc)_2$, $PdCl_2(NCMe)_2$, $PtCl_2(pyridine)_2$; (ii) NaOMe.

tion of 2,4-dimethylpyrrole in dimethylformamide was added to a solution of phosphorus oxychloride in the same solvent to give the corresponding Vilsmaier salt (Fig. 2).

In situ solvolysis of these salts with aqueous sodium hydrogen sulfide yielded 3,5-dimethylpyrrole-2-carbothioaldehyde ($HSPy^{MeHMe}$) as an orange microcrystalline product in good yield after column chromatography and crystallisation. The pyrrole ring substituents were observed in the ^{1}H NMR spectrum at 2.24, 2.26 (Me^3 and Me^5, respectively) and 5.99 (H^4) ppm. The assignment of the methyl resonances follows from two-dimensional NMR experiments on the related 3,5-dimethyl-4-ethylpyrrole-2-carbothioaldehyde ($HSPy^{MeEtMe}$) [12]. Two low field singlets were also observed at 8.30 and 10.34 ppm. The former was assigned to the pyrrole proton and its broadened shape was taken to indicate a degree of intermolecular hydrogen bonding (between C=S and NH groups) in solution. The sharper resonance at 10.34 ppm was attributed to the CSH proton. The other spectroscopic (^{13}C NMR, IR), mass spectral and microanalytical data were in agreement with the proposed formulation.

Reaction of 2.2 equivalents of the $HSPy^{MeHMe}$ ligand with one equivalent of either $Ni(OAc)_2$ or $NiCl_2 \cdot 6H_2O$ in the presence of sodium methoxide in methanol led to the isolation of a dark brown product. The ^{1}H NMR spectrum of this material consisted of two methyl peaks at 2.15 and 2.46 ppm and two singlet resonances at 5.90 and 7.65 ppm. The singlet at 5.90 ppm was assigned to the H^4 proton on the pyrrole ring and the lower field resonance attributed to the thioaldehyde proton. The upfield shift of 2.7 ppm for this resonance compared to the corresponding feature at 10.34 ppm in the spectrum of the free ligand indicates a considerable de-shielding effect resulting from coordination to the metal. The solid state infrared spectrum (Nujol) showed a number of bands attributable to the thioaldehyde ligand, in particular strong absorptions at 1574, 1252, 904 and 857 cm^{-1}. No N-H band was observed in the IR spectrum and no N-H resonance was seen in the ^{1}H NMR spectrum of any of the metal complexes. This suggested that the ligands were coordinated in the deprotonated (bidentate) form in all cases. The overall formulation of the complex [Ni(κ^2-Spy^{MeHMe})$_2$] (**1**) was confirmed by a molecular ion at $m/z = 336$ and elemental analysis. The complex [Ni(κ^2-SPy^{MeEtMe})$_2$] (**2**) was prepared in a similar manner using the $HSPy^{MeEtMe}$ ligand with the presence of the ethyl subsitituent being confirmed by resonances at 0.93 (t, $J_{HH} = 7.90$ Hz) and 2.18 (q, J_{HH} = 7.90 Hz) ppm in the ^{1}H NMR spectrum. The general reaction scheme for the complexation reactions is depicted in Fig. 3.

Both *cis* and *trans* geometries are possible for the homoleptic products and, due to the equivalence of the environments of the nuclei, NMR spectroscopy cannot be used satisfactorily to distinguish them. However, on steric grounds it is likely that the *trans* configuration shown in Fig. 3 is favoured, allowing the Me^5 methyl substituents to be accommodated on opposite sides of the metal centre.

The remaining homoleptic palladium and platinum complexes (**3**–**6**) were prepared in a completely analogous fashion and exhibited similar spectroscopic data to complexes **1** and **2**. The greater solubility of [Pd(κ^2-SPy^{MeEtMe})$_2$] (**4**) in chlorinated solvents allowed a two-dimensional NMR study to be performed. A Heteronuclear Multiple Bond Correlation (HMBC) experiment was carried out on complex **4** which permitted complete assignment of the protons and carbon nuclei. Four high field resonances were observed for the substituents of the pyrrole ring at 10.9 (Me^3), 14.3 (CH_2CH_3), 17.5 (Me^5) and 18.2 (CH_2CH_3) ppm. The pyrrole ring carbons gave rise to four resonances at 134.2, 134.8, 156.2 and 168.7 ppm corresponding to the C^4, C^3, C^2 and C^5 carbons. An interesting feature in the ^{13}C NMR spectrum of complex **4** is the resonance due to the CSH carbon at 157.1 ppm which displays a dramatic upfield shift of 33.5 ppm from the corresponding value for $HSPy^{MeEtMe}$ (190.6 ppm) [12]. The C^2 and C^5 resonances are also shifted relative to the free ligand, but to low field. The C^2 resonance is

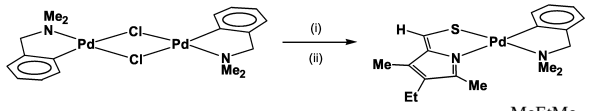

Fig. 4. Preparation of complex **7**. (i) $HSPy^{MeEtMe}$; (ii) NaOMe.

displaced by 15 ppm from 141.2 ppm (free ligand) to 156.2 ppm (in **4**) and the C^5 resonance shifts by 26.5 ppm from 142.2 ppm (free ligand) to 168.7 ppm (in **4**). Comparing the ^{1}H NMR spectra of $HSPy^{MeEtMe}$ and complex **4**, the greatest change of chemical shift is observed in the CSH resonance, which moves from 10.23 ppm in the free ligand to the higher field value of 7.67 ppm when coordinated to palladium. These spectroscopic observations indicate a substantial change in electron density distribution in the ligand on coordination to the metal. From the shielding and de-shielding effects discussed above, it appears that electron density is removed from the nitrogen donor and displaced towards the sulfur atom. This is reflected in the structural analysis discussed below for complex [Pd(η^2-*C,N*-$C_6H_4CH_2NMe_2$)(κ^2-SPy^{MeEtMe})] (**7**). Complex 7 was prepared by the reaction of the chloro-bridged dimer [Pd(η^2-*C,N*-$C_6H_4CH_2NMe_2$)Cl]$_2$ [21] with 2.2 equivalents of $HSPy^{MeEtMe}$ in the presence of sodium methoxide as shown in Fig. 4.

In addition to the features corresponding to the thioaldehyde ligand, the ^{1}H NMR spectrum of the resulting bright orange microcrystalline product displayed resonances due to the cyclometallated ligand at 2.93 (NMe_2), 3.97 (CH_2N), 6.98 (CH) and 7.37 (CH). The overall formulation was confirmed by the presence of a molecular ion in the Fast Atom Bombardment (FAB) mass spectrum at $m/z = 406$. Single crystals suitable for X-ray diffraction were obtained to allow a structural study to be performed.

Structural Discussion

The geometry of the complex is essentially square planar with no palladium-bonded atom deviating from the mean plane by more than 0.1 Å. However, the five-membered ring of the cyclometallated ligand displays a torsion angle of 27.80° for the atoms N2-C12-C13-C14. Comparison with the same chelate in other structurally characterised complexes where a sulfur donor is bonded *trans* to nitrogen reveals that this is a characteristic of this particular chelate. In the bridging thiatriazole thiolate complex [Pd(κ^2-*C,N*-$C_6H_4CH_2NMe_2$)(κ^2-*N,S*-CN_3S_2)]$_2$ [17], the corresponding torsion angle for the *N,S*-chelates (which are crystallographically equivalent) is 27° and in the bridging quinoline thiolate compound [Pd(κ^2-*C,N*-$C_6H_4CH_2NMe_2$)(κ^2-*N,S*-C_9H_6NS)]$_2$ [18], this value is 29°/31° (in this complex the chelates are crystallographically distinct). The Pd-N distances for the cyclometallated ligand in the two literature compounds are 2.115 Å and 2.139 Å / 2.145 Å, respectively. These bond lengths compare well to the Pd-N distance of 2.1443(16) Å for the cyclometallated ligand in complex **7**. There is no clear precedent for the bidentate thioaldehyde ligand in the literature. This structural study reveals that the bond lengths of the atoms in the pyrrole ring are actually consistent with the thiolate form in which the C1-C2, C3-C4 and C5-N1 bond lengths are significantly shorter than the C2-C3, C4-C5 and N1-C2 lengths. The C1-S1 distance is 1.700 Å which is halfway between the standard values for C-S single and double bonds and considerably longer than the C-S distance of 1.615(9) Å in the thioaldehyde complex [Ru(η^5-C_5H_5){S=CH(C_6H_4Cl-4)}(dppm)]PF_6 [11].

Unfortunately, it was not possible to obtain single crystals of $HSPy^{MeHMe}$ or $HSPy^{MeEtMe}$ to permit a comparison of bonding in the free ligand with that in the coordinated form.

Table 1. Selected bond lengths (Å) and angles (°) for **7**.

Pd(1)-N(2)	2.1443(16)	C(14)-Pd(1)-N(2)	81.04(7)
Pd(1)-C(14)	1.991(2)	C(14)-Pd(1)-S(1)	89.13(6)
Pd(1)-S(1)	2.2816(5)	N(2)-Pd(1)-N(1)	105.14(6)
Pd(1)-N(1)	2.1722(17)	N(1)-Pd(1)-S(1)	84.39(5)
S(1)-C(1)	1.700(2)	C(1)-S(1)-Pd(1)	98.38(7)
C(1)-C(2)	1.359(3)	C(2)-N(1)-Pd(1)	111.54(13)
C(2)-C(3)	1.444(3)	C(1)-C(2)-N(1)	120.25(18)
C(3)-C(4)	1.364(3)	C(5)-N(1)-C(2)	105.68(16)
C(4)-C(5)	1.448(3)		
N(1)-C(5)	1.327(3)		

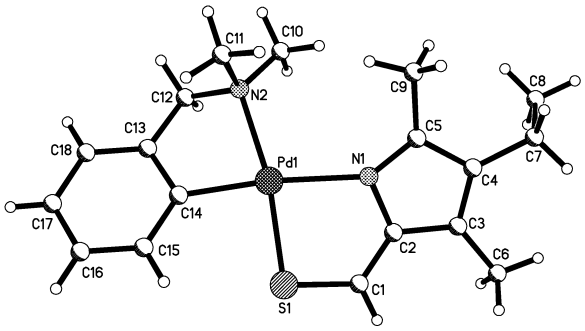

Fig. 5. Molecular structure of complex **7**.

Conclusion

A new thioaldehyde ligand has been prepared and a systematic investigation of its coordination chemistry undertaken to yield homoleptic examples of all three elements of Group 10. One- and two-dimensional NMR experiments reveal that the spectroscopic features associated with the ligand change substantially on coordination. These observations have been augmented by a structural study which reveals that the thiolate bonding mode predominates over coordination as a conventional thioaldehyde ligand. Studies on ruthenium and osmium complexes of this ligand type are currently taking place to further examine the properties (*e.g.*, hemilabile behaviour) of this unusual ligand.

Experimental Section

Apart from where stated, all manipulations were carried out under aerobic conditions using commercially available (undried) solvents and reagents as received. Infrared and NMR spectroscopy was performed using Shimadzu FTIR 8700 and Bruker AMX-300 spectrometers, respectively. Spectra were measured at 25 °C. FAB-MS spectra (nitrobenzyl alcohol matrices) were recorded using a VG 70-SB magnetic sector mass spectrometer. All solid state infrared samples were measured with KBr plates unless stated otherwise. Elemental microanalyses were performed in the Department of Chemistry, University College London. The complexes *cis*-$[PdCl_2(NCMe)_2]$ [19], *cis*-$[PtCl_2(py)_2]$ [20], $[Pd(\eta^2\text{-}C,N\text{-}C_6H_4CH_2NMe_2)Cl]_2$ [21], 2,4-dimethylpyrrole [22] and 3,5-dimethyl-4-ethylpyrrole-2-carbothioaldehyde [12] were prepared according to published procedures. All other materials (including Ni, Pd and Pt salts) were purchased and used as received.

Preparation of 3,5-dimethylpyrrole-2-carbothioaldehyde ($HSPy^{MeHMe}$)

A solution of 2,4-dimethylpyrrole (0.95 g, 9.99 mmol) in dimethylformamide (10 ml) was added dropwise over a period of 10 mins to a stirred solution of phosphorus oxychloride (1 ml, 1.65 g, 10.76 mmol) in dimethylformamide (10 ml). The resulting solution was stirred at room temperature for 30 min and then poured into aqueous (2M) sodium hydrogen sulfide (50 ml). The mixture was diluted with water (200 ml) before being extracted with diethyl ether (3×100 ml). The extracts were washed with water (6×100 ml), dried and evaporated to dryness. The residue was dissolved in a minimum volume of benzene and chromatographed on alumina with benzene as eluant. The eluates of the single band obtained were collected and all solvent removed. The residue was dissolved in the minimum volume of methanol and the solvent volume slowly reduced until precipitation of the orange product was complete. Yield: 0.97 g, (70%). The product was stored at 4 °C in the dark. IR (nujol): 3220, 1556, 1308, 1242, 1155, 1119, 1005, 951, 889, 799, 723, 623 cm^{-1}. – ^1H NMR (299.87 MHz, $CDCl_3$): δ 2.24 (s, Me^3, 3H), 2.26 (s, Me^5, 3H), 5.99 (s, H^4, 1H), 9.43 (s(br), NH, 1H), 10.34 (s, CSH, 1H) ppm. – ^{13}C NMR (75.41 MHz, $CDCl_3$): δ 11.2 (q, Me^3, $J_{CH} = 127.3$ Hz), 13.8 (q, Me^5, $J_{CH} = 128.8$ Hz), 114.4 (d, C^4, $J_{CH} = 172.8$ Hz), 133.5 (s, C^3), 142.0 (s, C^2), 143.9 (s, C^5), 192.8 (d, CSH, $J_{CH} = 165.2$ Hz) ppm. – MS (FAB) *m/z* (%): 140 (100) $[M]^+$. – C_7H_9NS (139.22): calcd. C 60.4, H 6.5, N 10.1; found C 60.3, H 6.7, N 10.0.

*Preparation of $[Ni(\kappa^2\text{-}SPy^{MeHMe})_2]$ (**1**)*

a) $[Ni(OAc)_2]$ (200 mg, 1.131 mmol) was dissolved in methanol (10 ml) and added to a solution of $HSPy^{MeHMe}$ (346 mg, 2.485 mmol) in methanol (10 ml). The mixture was stirred for 1 h and the precipitate filtered. This was washed with methanol (10 ml), hexane (10 ml) and dried. Yield: 223 mg (59%). **b)** $[NiCl_2] \cdot 6\,H_2O$ (40 mg, 0.160 mmol) was suspended in methanol (20 ml) and treated with $HSPy^{MeHMe}$ (49 mg, 0.352 mmol) as a solid. A colour change from pale green to orange occurred. Sodium methoxide (20 mg, 0.370 mmol) in methanol (10 ml) was added prompting a dark red colouration. The mixture was stirred for 1 h and the solvent volume reduced until precipitation of the product was complete. This was washed with water (5 ml), ethanol (10 ml) and hexane (5 ml). The dark brown product can be recrystallised from dichloromethane and ethanol. Yield: 41 mg (76%). IR (nujol): 1575, 1544, 1366, 1252, 1145, 1036, 971, 904, 892, 857, 782 cm^{-1}. – ^1H NMR (299.87 MHz $CDCl_3$): δ 2.15 (s, Me^3, 3H), 2.46 (s, Me^5, 3H), 5.90 (s, H^4, 1H), 7.65 (s, CHS, 1H) ppm. – MS (FAB) *m/z* (%): 352 (28) $[M+H_2O]^+$, 336 (23) $[M]^+$. – $C_{14}H_{16}N_2NiS_2$ (335.12): calcd. C 50.2, H 4.8, N 8.4; found C 49.9, H 5.0, N 8.2.

*Preparation of $[Ni(\kappa^2\text{-}SPy^{MeEtMe})_2]$ (**2**)*

a) $[Ni(OAc)_2]$ (200 mg, 1.131 mmol) was dissolved in methanol (10 ml) and added to a solution of $HSPy^{MeEtMe}$ (416 mg, 2.487 mmol) in methanol (10 ml). The mixture was stirred for 1 h and the precipitate filtered. This was washed with methanol (10 ml) and dried. Yield: 283 mg (64%). **b)** $[NiCl_2] \cdot 6\,H_2O$ (20 mg, 0.080 mmol) was suspended in methanol (20 ml) and treated with $HSPy^{MeEtMe}$ (30 mg, 0.180 mmol) as a solid. A colour change from pale green to orange occurred. Sodium methoxide (10 mg, 0.185 mmol) in methanol (10 ml) was added prompting a dark red colouration. The mixture was stirred for 1 h and the solvent volume reduced until precipitation of the product was complete. This was washed with water (5 ml), ethanol (10 ml) and hexane (5 ml). Yield: 27 mg (86%). The dark brown product

can be recrystallised from dichloromethane and ethanol. IR (nujol): 1575, 1245, 1119, 1062, 984, 963, 898, 856, 786, 728 cm^{-1}. – ^1H NMR (299.87 MHz, $CDCl_3$): δ 0.93 (t, CH_2CH_3, 3H, $J_{HH} = 7.90$ Hz), 2.06 (s, Me^3, 3H), 2.18 (q, CH_2CH_3, 2H, $J_{HH} = 7.90$ Hz), 2,46 (s, Me^5, 3H), 7.52 (s, CHS, 1H) ppm. – MS (FAB) *m/z* (%): 390 (58) $[M]^+$. – $C_{18}H_{24}N_2NiS_2$ (391.22): calcd. C 55.3, H 6.2, N 7.2; found C 55.4, H 6.3, N 7.2.

*Preparation of [Pd(κ²-SPy^{MeHMe})$_2$] (**3**)*

Cis-[$PdCl_2(NCMe)_2$] (50 mg, 0.193 mmol) and $HSPy^{MeHMe}$ (59 mg, 0.424 mmol) were partially dissolved in methanol (20 ml) to give an orange solution. An immediate precipitation occurred on treatment with sodium methoxide (23 mg, 0.426 mmol) in methanol (10 ml). The mixture was stirred for 30 min and ethanol added. The solvent volume was reduced until precipitation of a brick red product was complete. This was washed with water (5 ml), methanol (10 ml) and hexane (10 ml). The product can be recrystallised from dichloromethane and ethanol. Yield: 53 mg (72%). IR (NaCl/nujol): 1617, 1578, 1529, 1364, 1322, 1257, 1012, 984, 931, 859, 818, 747, 701 cm^{-1}. – ^1H NMR (299.87 MHz, $CDCl_3$): δ 2.19 (s, Me^3, 3H), 2.49 (s, Me^5, 3H), 5.91 (s, H^4, 1H), 7.84 (s, CHS, 1H) ppm. – MS (FAB) *m/z* (%): 383 (3) $[M]^+$, 202 (40) $[M\text{-}SPy]^+$. – $C_{14}H_{16}N_2PdS_2$ (382.85): calcd. C 43.9, H 4.2, N 7.3; found C 43.8, H 4.3, N 7.3.

*Preparation of [Pd(κ²-SPy^{MeEtMe})$_2$] (**4**)*

cis-[$PdCl_2(NCMe)_2$] (49 mg, 0.189 mmol) and $HSPy^{MeEtMe}$ (70 mg, 0.419 mmol) were partially dissolved in methanol (20 ml) to give an orange solution. An immediate precipitation occurred on treatment with sodium methoxide (25 mg, 0.463 mmol) in methanol (10 ml). The mixture was stirred for 30 min and ethanol added. The solvent volume was reduced until precipitation of a red-orange product was complete. This was washed with water (5 ml), methanol (10 ml) and hexane (10 ml). The product can be recrystallised from dichloromethane and ethanol. Yield: 59 mg (71%). IR (nujol): 1585, 1366, 1251, 1119, 984, 958, 902, 862, 780, 723 cm^{-1}. – ^1H NMR (299.87 MHz, $CDCl_3$): δ 0.99 (t, CH_2CH_3, 3H, $J_{HH} = 7.80$ Hz), 2.11 (s, Me^3, 3H), 2.28 (q, CH_2CH_3, 2H, $J_{HH} = 7.80$ Hz), 2.47 (s, Me^5, 3H), 7.67 (s, CHS, 1H) ppm. – $^{13}C\{^1H\}$ NMR (75.41 MHz, $CDCl_3$): δ 10.9 (Me^3), 14.3 (CH_2CH_3), 17.5 (Me^5), 18.2 (CH_2CH_3), 134.2 (C^4), 134.8 (C^3), 156.2 (C^2), 157.1 (CSH), 168.7 (s, C^5) ppm. – MS (FAB) *m/z* (%): 438 (33) $[M]^+$. – $C_{18}H_{24}N_2PdS_2$ (438.95): calcd. C 49.3, H 5.5, N 6.4; found C 49.3, H 5.3, N 6.1.

*Preparation of [Pt(κ²-SPy^{MeHMe})$_2$] (**5**)*

cis-[$PtCl_2(py)_2$] (50 mg, 0.118 mmol) was dissolved in dichloromethane (10 ml) and methanol (20 ml) added. This solution was treated with $HSPy^{MeEtMe}$ (18 mg, 0.129 mmol) and sodium methoxide (7 mg, 0.130 mmol) in methanol (10 ml). The mixture was stirred for 5 h and all solvent removed. The crude product was dissolved in the minimum volume of dichloromethane and filtered through diatomaceous earth (celite) to remove NaCl. All solvent was again removed and diethyl ether (10 ml) added and the product triturated to provide a red-brown product. This was washed with diethyl ether (5 ml) and dried. The product can be recrystallised from dichloromethane and diethyl ether. Yield: 38 mg (68%). IR (nujol): 1562, 1242, 1093, 1072, 1038, 984, 931, 889, 858, 806 cm^{-1}. – ^1H NMR (299.87 MHz, $CDCl_3$): δ 2.17 (s, Me^3, 3H), 2.44 (s, Me^5, 3H), 6.12 (s, H^4, 1H), 7.86 (s, CHS, 1H) ppm. – MS (FAB) *m/z* (%): 471 (100) $[M]^+$. – $C_{14}H_{16}N_2PtS_2^{\cdot}2(CH_2Cl_2)$ (641.38): calcd. C 30.0, H 3.1, N 4.4; found C 29.8, H 2.9, N 4.1. Analysed product was determined to be a bis(dichloromethane) solvate by integration of ^1H NMR spectrum.

*Preparation of [Pt(κ²-SPy^{MeEtMe})$_2$] (**6**)*

cis-[$PtCl_2(py)_2$] (50 mg, 0.118 mmol) was suspended in methanol (20 ml) and treated with $HSPy^{MeEtMe}$ (44 mg, 0.263 mmol) and sodium methoxide (15 mg, 0.278 mmol, excess) in methanol (10 ml). The mixture was stirred for 2 h and the precipitate filtered. This was washed with water (5 ml), methanol (10 ml) and hexane (5 ml). The red-brown product can be recrystallised from dichloromethane and ethanol. Yield: 38 mg (61%). IR (nujol): 1585, 1251, 1206, 1116, 903, 870, 772, 722 cm^{-1}. – ^1H NMR (299.87 MHz, $CDCl_3$): δ 1.02 (t, CH_2CH_3, 3H, $J_{HH} = 7.58$ Hz), 2.21 (s, Me^3, 3H), 2.29 (q, CH_2CH_3, 2H, $J_{HH} = 7.62$ Hz), 2.62 (s, Me^5, 3H), 7.84 (s, CHS, 1H) ppm. – MS (FAB) *m/z* (%): 527 (80) $[M]^+$. – $C_{18}H_{24}N_2PtS_2$ (527.62): calcd. C 41.0, H 4.6, N 5.3; found C 41.3, H 4.4, N 5.2.

*Preparation of [Pd(η²-C,N-$C_6H_4CH_2NMe_2$)-(κ²-SPy^{MeEtMe})] (**7**)*

[Pd(η²-*C,N*-$C_6H_4CH_2NMe_2$)Cl]$_2$ (95 mg, 0.172 mmol) was suspended in methanol (20 ml) and treated with $HSPy^{MeEtMe}$ (64 mg, 0.383 mmol) and sodium methoxide (21 mg, 0.389 mmol) in methanol (10 ml). The mixture was stirred for 30 min and the precipitate filtered. This was washed with water (5 ml), ethanol (10 ml) and hexane (10 ml). The bright orange product can be recrystallised from dichloromethane and ethanol. Yield: 52 mg (74%). IR (nujol): 1568, 1332, 1244, 1119, 1046, 1025, 984, 973, 896, 847, 775, 745 cm^{-1}. – ^1H NMR (299.87 MHz, $CDCl_3$): δ 1.03 (t, CH_2CH_3, 3H, $J_{HH} = 7.48$ Hz), 2.11 (s, Me^3, 3H), 2.30 (q, CH_2CH_3, 2H, $J_{HH} = 7.48$ Hz), 2.37 (s, Me^5, 3H), 2.93 (s, NMe_2, 6H), 3.97 (s, CH_2N, 2H), 6.98 (m, C_6H_4, 3H), 7.37 (d, C_6H_4, 1H, $J_{HH} = 6.72$ Hz), 7.84 (s, CHS, 1H) ppm. – MS

(FAB) *m/z* (%): 406 (10) $[M]^+$. – $C_{18}H_{24}N_2PdS$ (406.89): calcd. C 53.1, H 6.0, N 6.9; found C 53.0, H 6.0, N 6.8.

X-Ray Crystallography

Orange blocks of [Pd(κ^2-*C,N*-$C_6H_4CH_2NMe_2$)(κ^2-SPy^{MeEtMe})] (**7**) were grown by slow diffusion of a dichloromethane solution of the complex into methanol. A single crystal of compound **7** was mounted on a glass fibre and all geometric and intensity data were taken from this sample on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) at 150 ± 2 K. Data reduction and integration was carried out with SAINT+ and absorption corrections applied using the programme SADABS. The structure were solved by direct methods and developed using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and their displacement parameters linked to those of the atoms to which they were attached (riding model). Structure solution and refinement used the SHELXTL PLUS V6.10 program package [23].

Crystal data for compound $C_{18}H_{24}N_3PdS$: $M = 406.85$, monoclinic, orange, $0.32 \times 0.28 \times 0.18$ mm, $a = 13.2302(9)$, $b = 16.7511(11)$, $c = 15.9926(10)$ Å, $\beta = 102.6560(10)$, $V = 3458.2(4)$ Å^3, space group $C2/c$, $Z = 8$, μ (Mo-K_α) 11.92 cm^{-1}, calcd. density = 1.563 g/cm^3, 15062 measured and 4116 unique relections ($R_{\rm int} = 0.0212$), wR_2' (all data)= 0.0632, $R_1 = 0.0354$ for 4116 reflections ($I > 2\sigma(I)$) and 199 parameters, residual eÅ$^{-3} = 0.993$ (max) and -0.508 (min).

Crystallographic data for the structure of complex **7** have been deposited with the Cambridge Crystallographic Data Centre, CCDC 246387. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code +44 (1223) 336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

Acknowledgements

J. D. E. T. W.-E. gratefully acknowledges the Ramsay Memorial Trust for provision of a Fellowship. We thank the Department of Chemistry, University College London and the University of London Central Research Fund for provision of equipment and funds.

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