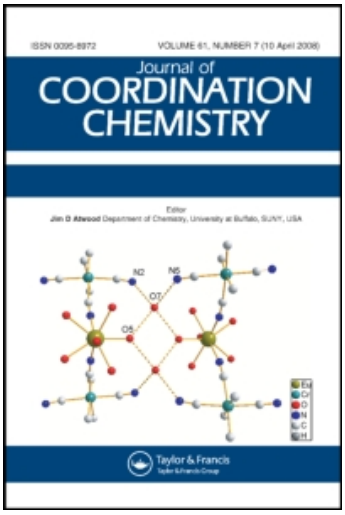

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Platinum(II), palladium(II), nickel(II), and gold(I) complexes of the "electrospray-friendly" thiolate ligands 4-$SC_5H_4N^-$ and 4-$SC_6H_4OMe^-$

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The series of platinum(II), palladium(II), and nickel(II) complexes [ML_2(dppe)] [M = Ni, Pd, Pt; L = 4–SC_5H_4N or 4–SC_6H_4OMe; dppe = $Ph_2PCH_2CH_2PPh_2$] containing pyridine-4-thiolate or 4-methoxybenzenethiolate ligands, together with the corresponding gold(I) complexes [AuL(PPh_3)], were prepared and their electrospray ionization mass spectrometric behavior compared with that of the thiophenolate complexes [M($SPh)_2$(dppe)] (M = Ni, Pd, Pt) and [Au(SPh)(PPh_3)]. While the pyridine-4-thiolate complexes yielded protonated ions of the type $[M + H]^+$ and $[M + 2H]^{2+}$ ions in the Ni, Pd, and Pt complexes, an $[M + H]^+$ ion was only observed for the platinum derivative of 4-methoxybenzenethiolate. Other ions, which dominated the spectra of the thiophenolate complexes, were formed by thiolate loss and aggregate formation. The X-ray crystal structure of [Pt(SC_6H_4OMe–4)$_2$(dppe)] is also reported.

Keywords: Thiolate ligands; Electrospray ionization mass spectrometry; Platinum complexes; Palladium complexes; Nickel complexes; Gold complexes

1. Introduction

Electrospray ionization mass spectrometry (ESI MS) is now a well-established technique for the characterization of metal complexes [1]. Nonetheless, the successful application of this technique is dependent on the ability of the analyte in question to form ions. Charged complexes typically give excellent spectra [2], provided the charge density of the ion is not too high. For neutral complexes, ionization may occur by one or more processes, including association with a proton (from a protic solvent used such as methanol or water), an ammonium, alkali metal or other cation [1], or loss of an anionic ligand such as a halide [3]. There remain, however, many compounds that ionize poorly and remain relatively inaccessible to analysis by ESI MS. This problem can be addressed by the use of appropriate ligands which contain an ionization-promoting functionality; the ligands should ideally be chemically similar to the "parent" ligand, such that the overall chemistry of the system is not perturbed by the ligand

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modification. One means of achieving this is by *para*-substitution of an aromatic ring. We previously described such ligands as having an "electrospray-friendly" nature, and a series of *para*-substituted triphenyl-phosphine, -arsine, and -stibine ligands were prepared containing protonatable methoxy (–OMe) or dimethylamino ($-NMe_2$) groups, which permitted the ESI MS observation of a range of neutral metal-carbonyl derivatives, where the parent (e.g., PPh_3) derivatives were invisible to ESI MS analysis [4].

A wide range of other electrospray-friendly ligands have been reported in the literature and applications of these ligands are being exploited, particularly in the study of catalytic processes [5, 6]. Examples include phosphines containing highly basic proton sponge {1,8-bis(dimethylamino)naphthalene} groups [7], cationic monoalkylated bisphosphines [8], neutral bisphosphine monoxides [9], cobalt carbonyl clusters containing organosilicon ligands [10], organostannoxanes [11], and organomercury compounds [12]. There have been various studies on the ESI MS behavior of metal-thiolate complexes, such as organo-mercury derivatives of cysteine and cysteinyl-peptides [13, 14], the anti-arthritic gold(I) thiolate drug Auranofin [15], and thiolate complexes of Zn and Cd [16, 17]. To date, however, we are unaware of any thiolate ligands that have been reported specifically as being "electrospray-friendly". The thiolate sulfur is a soft ligand with a poor proton affinity when coordinated to soft (late transition) metals, so that neutral metal thiolate complexes might be expected to ionize poorly in the absence of suitable charging sites.

In this article we report the synthesis and ESI MS behavior of a series of platinum(II), palladium(II), nickel(II), and gold(I) complexes of thiolate ligands derived from 4-methoxybenzenethiol (4-HSC_6H_4OMe, HS*) and 4-mercaptopyridine (4-HSC_5H_4N, $HS^{\bullet}$) containing protonatable methoxy and pyridine functionalities, respectively. These thiols are commercially available analogues of thiophenol (PhSH). HS* has been commonly employed when a variety of *para*-substituted thiophenolate complexes were investigated, for example, for their structural [18–20], kinetic [21], or photophysical [22] properties, or simply when substituent effects on classical physical properties were the primary concern [23, 24]. $S^{\bullet-}$ can potentially act as a pyridine as well as thiolate ligand. However, while there are many examples of coordination through the S atom [25, 26], N coordination is rather rare and involves $S^{\bullet-}$ in the form of a poorly coordinating disulfide or other derivative [27, 28].

2. Experimental

2.1. *Materials and instrumentation*

Thiophenol (Riedel-de Haën), 4-methoxybenzenethiol (Aldrich), 4-mercaptopyridine (Aldrich), and triethylamine (BDH) were used as supplied. The compounds [$NiCl_2$(dppe)] [29] and [AuCl(PPh_3)] [30] were prepared by literature procedures; dppe was prepared from PPh_3, Li metal, and $ClCH_2CH_2Cl$ by modification of the literature procedure for $Ph_2PCH_2PPh_2$ [31]. The complexes [MCl_2(dppe)] were prepared by ligand displacement from the cyclo-octa-1,5-diene complexes [MCl_2(cod)] (M = Pd [32] and M = Pt [33]) by reaction with 1 mol equivalent of dppe in CH_2Cl_2 solution, followed by precipitation of the product with petroleum spirits (b.p. 60–80°C).

ESI MS were recorded in positive-ion mode on a VG Platform II instrument. Samples were prepared by dissolving the complexes in a few drops of CH_2Cl_2 before adding approximately 1 mL of the mobile phase (methanol, unless otherwise stated). Spectra were acquired using a cone voltage of 20 V, unless otherwise stated. Assignment of ions was aided by use of the ISOTOPE simulation program [34]. NMR spectra were recorded on a Bruker AC300P spectrometer at 300.13 (^{1}H) or 121.51 MHz (^{31}P) in $CDCl_3$ solution and were referenced relative to residual $CHCl_3$ (^{1}H) or external 85% H_3PO_4 (^{31}P). Elemental microanalytical measurements were from the Campbell Microanalytical Laboratory, University of Otago, Dunedin, NZ.

Reactions were carried out in LR grade methanol. Products were recrystallized from dichloromethane and diethyl ether that were dried and distilled (from CaH_2 and sodium-benzophenone ketyl, respectively) under a nitrogen atmosphere prior to use.

2.2. *General method for the synthesis of thiolate complexes*

All complexes were prepared by the following method, without regard for the exclusion of air or moisture: Et_3N and the thiol were added to a suspension of the metal halide in methanol. After refluxing for 30 min, the solution was cooled to room temperature. If necessary, water was added to induce precipitation. After cooling to −20°C overnight, the product was collected by filtration, washed with a small amount of cold methanol, and dried under vacuum.

2.2.1. [Ni(SC$_5$H$_4$N)$_2$], [NiS$^{\bullet}_2$(dppe)]. [$NiCl_2$(dppe)] (0.050 g, 0.086 mmol), Et_3N (0.01 mL, 0.17 mmol), and HS$^{\bullet}$ (0.019 g, 0.17 mmol) in MeOH (10 mL) gave [NiS$^{\bullet}_2$(dppe)] as dark red crystals. Yield: 0.018 g (31%); m.p. 174–176°C. Found (%): C, 63.32; H, 4.71; N, 4.30. $C_{36}H_{32}N_2P_2NiS_2$ requires (%): C, 63.81; H, 4.73; N, 4.14. ^{31}P{^{1}H} NMR: δ 57.4 (s). ^{1}H NMR: δ 7.83–7.47 (24H, m, Ph of dppe and H2′ of S$^{\bullet}$), 7.05 (4H, m, H3′ of S$^{\bullet}$), 2.27 (4H, m, $C_2\underline{H}_4$ of dppe). ^{13}C{^{1}H} NMR: δ 156.8 (s), 146.6 (m), 133.5 (m), 131.7 (s), 129.0 (m), 128.5 (m), 128.1 (m), 27.5 (m, $\underline{C}_2H_4$ of dppe). ESI MS, cone voltage 20 V: $[M+2H]^{2+}$ m/z 340 (100%), $[M-S^{\bullet}]^+$ m/z 566 (32%), $[M+H]^+$ m/z 677 (65%). Cone voltage 40 V: $[M-S^{\bullet}]^+$ m/z 566 (100%). Cone voltage 60 V: $[M-S^{\bullet}]^+$ m/z 566 (100%).

2.2.2. [Pd(SC$_6$H$_4$OCH$_3$)$_2$(dppe)], [PdS$^*_2$(dppe)]. [$PdCl_2$(dppe)] (0.250 g, 0.43 mmol), Et_3N (0.072 mL, 1 mmol), and HS* (0.15 mL, 1 mmol) in MeOH (20 mL) gave [PdS$^*_2$(dppe)] as red crystals. Yield: 0.18 g (54%); m.p. 156–159°C. Found (%): C, 61.09; H, 4.81. $C_{40}H_{38}O_2P_2PdS_2$ requires (%): C, 61.35; H, 4.86. ^{31}P{^{1}H} NMR: δ 54.9 (s). ^{1}H NMR: δ 7.73–7.37 (20H, m, Ph of dppe), 7.05 (4H, d, $^3J_{H3',H2'} = 8.5$ Hz, H2′ of S*), 6.25 (4H, d, $^3J_{H2',H3'} = 9.0$ Hz, H3′ of S*), 3.65 (6H, s, OC$\underline{H}_3$), 2.21 (4H, m, $C_2\underline{H}_4$ of dppe). ^{13}C{^{1}H} NMR: δ 156.2 (s, C4′), 135.5 (m), 133.6 (m), 131.2 (s), 128.8 (m), 112.8 (m), 54.8 (s, O$\underline{C}H_3$), 29.4 (m, $\underline{C}_2H_4$). ESI MS: $[Pd_2(\mu\text{-}S^*)_2(dppe)_2]^{2+}$ m/z 643 (100%), $[Pd_2(\mu\text{-}S^*)_2(dppe)_2 + PdS^*_2(dppe)]^{2+}$ m/z 1035 (8%), unassigned m/z 1332 (1 + ion, 4%), $[PdS^*(dppe) + PdS^*_2(dppe)]^+$ m/z 1428 (12%).

2.2.3. [Pd(SC$_5$H$_4$N)$_2$(dppe)], [PdS$^{\bullet}_2$(dppe)]. [$PdCl_2$(dppe)] (0.165 g, 0.29 mmol), Et_3N (0.043 mL, 0.6 mmol), and HS$^{\bullet}$ (0.065 g, 0.59 mmol) in MeOH (20 mL) gave

[PdS$_2^{\bullet}$(dppe)] as orange crystals. Yield: 0.13 g (63%). M.p. 192–194°C. Found (%): C, 59.64; H, 4.54; N, 4.04%. $C_{36}H_{32}N_2P_2PtS_2$ requires (%): C, 59.64; H, 4.42; N, 3.87. $^{31}P\{^1H\}$ NMR: δ 57.2 (s). ^1H NMR: δ 7.79–7.43 (24H, m, Ph of dppe and H2′ of S$^{\bullet}$), 7.03 (4H, d, $^3J_{H2',H3'} = 5.2$ Hz, H3′ of S$^{\bullet}$), 2.43 (4H, m, $C_2\underline{H}_4$ of dppe). $^{13}C\{^1H\}$ NMR: δ 156.8 (s), 147.0 (s), 133.4 (m), 133.0 (m), 132.0 (s), 129.2 (m), 128.6 (m), 128.0 (m), 29.8 (m, $\underline{C}_2H_4$ of dppe). ESI MS cone voltage 20 V: $[M+2H]^{2+}$ m/z 364 (34%), $[M-S^{\bullet}]^+$ m/z 614 (8%), $[M+H]^+$ m/z 724 (100%), $[2M-S^{\bullet}]^+$ m/z 1341 (5%), $[2M+H]^+$ m/z 1452 (10%). Cone voltage 40 V: $[M-S^{\bullet}]^+$ m/z 613 (100%), $[M+H]^+$ m/z 724 (22%), $[2M-S^{\bullet}]^+$ m/z 1341 (10%). Cone voltage 60 V: $[M-S^{\bullet}]^+$ m/z 613 (100%), $[M+H]^+$ m/z 724 (5%), $[2M-S^{\bullet}]^+$ m/z 1340 (8%).

2.2.4. [Pt(SC$_6$H$_4$OCH$_3$)$_2$(dppe)], [PtS$_2^*$(dppe)]. [$PtCl_2$(dppe)] (0.153 g, 0.23 mmol), Et_3N (0.46 mmol, 0.06 mL) and HS* (0.033 mL, 0.46 mmol) in MeOH (20 mL) gave [PtS$_2^*$(dppe)] as yellow crystals. Yield: 0.195 g (98%); m.p. 196–197°C. Found (%): C, 54.96; H, 4.54. $C_{40}H_{38}O_2P_2PtS_2$ requires (%): C, 55.11; H, 4.36. $^{31}P\{^1H\}$ NMR: δ 46.5 (s, $^1J_{Pt,\ P} = 2892$ Hz). ^1H NMR: δ 7.77–7.39 (20H, m, Ph of dppe), 6.99 (4H, d, $^3J_{H3',H2'} = 8.3$ Hz, H2′ of S*), 6.25 (4H, d, $^3J_{H2',H3'} = 8.1$ Hz, H3′ of S*), 3.64 (6H, s, OC$\underline{H}_3$), 2.18 (4H, m, $C_2\underline{H}_4$ of dppe). $^{13}C\{^1H\}$ NMR: δ 156.3 (s, C4′), 135.2 (s, C2′), 133.5 (m, C2), 131.2 (s, C4), 128.6 (m, C3), 112.5 (s, C3′), 55.2 (s, O$\underline{C}H_3$), 23.4 (m, $\underline{C}_2H_4$). ESI MS (MeCN/H_2O): $[Pt_2(\mu\text{-}S^*)_2(dppe)_2]^{2+}$ m/z 732 (100%), $[M+H]^+$ m/z 873 (10%), $[Pt_2(\mu\text{-}S^*)_2(dppe)_2 + PtS_2^*(dppe)]^{2+}$ m/z 1168 (15%), unassigned m/z 1411 (2 + ion, 5%), unassigned m/z 1500 (1 + ion, 5%), $[Pt_2(\mu\text{-}S^*)_2(dppe)_2 + 2\,PtS_2^*(dppe)]^{2+}$ m/z 1603 (3%), unassigned m/z 1848 (2 + ion, 5%).

2.2.5. [Pt(SC$_5$H$_4$N)$_2$(dppe)], [PtS$_2^{\bullet}$(dppe)]. [$PtCl_2$(dppe)] (0.240 g, 0.361 mmol), Et_3N (0.3 mL, 2.3 mmol), and HS$^{\bullet}$ (0.080 g, 0.721 mmol) in MeOH (30 mL) gave [PtS$_2^{\bullet}$(dppe)] as yellow crystals. Yield: 0.263 g (89%); m.p. 218–220°C. Found (%): C, 52.3; H, 3.76; N, 3.36. $C_{36}H_{32}N_2P_2PtS_2$ requires (%): C, 53.1; H, 3.94; N, 3.44. $^{31}P\{^1H\}$ NMR: δ 46.8 (s, $^1J_{Pt,P} = 2890$ Hz). ^1H NMR: δ 7.83–7.23 (24H, m, Ph of dppe and H2′ of S$^{\bullet}$), 7.05 (4H, m, H3′ of S$^{\bullet}$), 2.19 (4H, m, $C_2\underline{H}_4$ of dppe). $^{13}C\{^1H\}$ NMR: δ 146.6 (s), 133.5 (m), 132.0 (s), 129.0 (m), 128.1 (m), 126.8 (m), 29.1 (m, $\underline{C}_2H_4$ of dppe). ESI MS: $[M+2H]^{2+}$ m/z 408 (50%), $[M-S^{\bullet}]^+$ m/z 704 (4%), $[2M-S^{\bullet}]^{2+}$ m/z 759 (8%), $[M+H]^+$ m/z 814 (100%), $[2M-S^{\bullet}]^+$ m/z 1517 (15%), $[2M+H]^+$ m/z 1627 (5%).

2.2.6. [Au(SC$_6$H$_4$OCH$_3$)(PPh$_3$)], [AuS*(PPh$_3$)]. [AuCl(PPh_3)] (0.200 g, 0.4 mmol), Et_3N (0.05 mL, 0.4 mmol), and HS* (0.03 mL, 0.4 mmol) in MeOH (20 mL) gave [AuS*(PPh_3)] as yellow crystals. Yield: 0.240 g (99%); m.p. 62–64°C. Found (%): C, 50.33; H, 3.70. $C_{40}H_{38}O_2P_2PtS_2$ requires (%): C, 50.17; H, 3.68. $^{31}P\{^1H\}$ NMR: δ 39.2. ^1H NMR: δ 7.59–7.28 (17H, m, Ph of PPh_3 and H2′ of S*), 6.71 (2H, d, $^3J_{H2',H3'} = 8.59$ Hz, H3′ of S*), 3.76 (3H, s, OC$\underline{H}_3$). $^{13}C\{^1H\}$ NMR: δ 156.9 (s, C4′), 134.5 (d, $^2J_{C2,P} = 10.4$ Hz, C2), 134.0 (s, C2′), 132.0 (d, $^4J_{C4,P} = 1.5$ Hz, C4), 131.5 (s, C1′), 129.9 (d, $^1J_{C1,P} = 42.3$ Hz, C1), 129.5 (d, $^3J_{C3,P} = 8.6$ Hz C3), 55.72 (s, O$\underline{C}H_3$). ESI MS: $[Au(PPh_3)_2]^+$ m/z 721 (42%), $[(Ph_3P)_2Au_2S^*]^+$ m/z 1057 (100%), $[(Ph_3P)_3Au_2S^*]^+$ m/z 1319 (43%), $[(Ph_3P)_3Au_3S^*_2]^+$ m/z 1655 (40%).

The following known complexes were also prepared by the general method described above, and their purity confirmed by elemental analysis and/or NMR spectroscopy:

2.2.7. [Ni(SPh)$_2$(dppe)] [35]. [NiCl$_2$(dppe)] (0.05 g), Et$_3$N (0.014 mL), and HSPh (0.02 mL) gave [Ni(SPh)$_2$(dppe)] as a red powder in 79% yield; m.p. 250–254°C [lit. 250–260°C]. ^{31}P{^{1}H} NMR: δ 55.9 (s). ^{1}H NMR: δ 7.84–6.64 (30H, m, Ph of dppe and SPh), 2.12 (4H, m, C$_2$H$_4$ of dppe). ESI MS: [Ni$_2$(μ-SPh)$_2$(dppe)$_2$]$^{2+}$ m/z 565 (100%), unassigned m/z 902 (1+ion, 22%), unassigned m/z 1176 (1+ion, 15%), [Ni$_2$(μ-SPh)$_2$(dppe)$_2$ + 2 Ni(SPh)$_2$(dppe)]$^{2+}$ and [Ni(SPh)(dppe) + Ni(SPh)$_2$(dppe)]$^+$ m/z 1239 (8%).

2.2.8. [Ni(SC$_6$H$_4$OCH$_3$)$_2$(dppe)], [NiS$_2^*$(dppe)]. This complex has been previously prepared from [NiCl$_2$(dppe)] and NaS* [36]. [NiCl$_2$(dppe)] (0.060 g), Et$_3$N (0.017 mL), and HS* (0.03 mL) gave [NiS$_2^*$(dppe)] as a brown powder in 77% yield; m.p. 166–168°C. Found (%): C, 64.66; H, 5.11. C$_{40}$H$_{38}$O$_2$P$_2$NiS$_2$ requires (%): C, 65.26; H, 5.17. ^{31}P{^{1}H} NMR: δ 56.06 (s) [lit. 55.7]. ^{1}H NMR: δ 7.86–7.38 (20H, m, Ph of dppe), 7.01 (4H, d, $^3J_{H3',H2'}$ = 8.60 Hz, H2′ of S*), 6.25 (4H, d, $^3J_{H2',H3'}$ = 8.59 Hz, H3′ of S*), 3.65 (6H, s, OCH$_3$), 2.06 (4H, m, C$_2$H$_4$ of dppe). ^{13}C{^{1}H} NMR: δ 157.9 (s, C4′), 135.4 (m), 133.7 (m), 130.9 (m), 128.9 (m), 114.4 (m), 54.8 (s, OCH$_3$), 21.8 (m, C$_2$H$_4$). ESI MS: [Ni$_2$(μ-S*)$_2$(dppe)$_2$]$^{2+}$ m/z 595 (100%), unassigned m/z 764 (2+ion, 5%), unassigned m/z 932 (2+ion, 15%), unassigned m/z 1236 (1+ion, 7%).

2.2.9. [Pd(SPh)$_2$(dppe)] [37]. [PdCl$_2$(dppe)] (0.25 g), Et$_3$N (0.072 mL), and HSPh (0.1 mL) gave [Pd(SPh)$_2$(dppe)] as orange crystals in 75% yield; m.p. 208–212°C [lit. 210–215°C]. ^{31}P{^{1}H} NMR: δ 55.3 (s). ^{1}H NMR: δ 7.74–6.67 (30H, m, Ph of dppe and SPh), 2.28 (4H, m, C$_2$H$_4$ of dppe). ESI MS: [Pd$_2$(μ-SPh)$_2$(dppe)$_2$]$^{2+}$ m/z 613 (100%), [Pd$_2$(μ-SPh)$_2$(dppe)$_2$ + Pd(SPh)$_2$(dppe)]$^{2+}$ m/z 975 (10%), [Pd$_2$(μ-SPh)$_2$(dppe)$_2$ + 2 Pd(SPh)$_2$(dppe)]$^{2+}$ m/z 1273 (3%), unassigned m/z 1336 (1+ion, 8%).

2.2.10. [Pt(SPh)$_2$(dppe)] [38]. [PtCl$_2$(dppe)] (0.330 g), Et$_3$N (0.1 mL), and HSPh (0.1 mL) gave [Pt(SPh)$_2$(dppe)] as yellow microcrystals in 85% yield; m.p. 228–229°C [lit. 225–226°C]. ^{31}P{^{1}H} NMR: δ 46.4 (s, $^1J_{Pt,P}$ = 2884 Hz) [lit. δ 45.6 (s, $^1J_{Pt,P}$ = 2885 Hz)]. ^{1}H NMR: δ 7.79–6.68 (30H, m, Ph of dppe and SPh), 2.19 (4H, m, C$_2$H$_4$ of dppe). ESI MS: [Pt$_2$(μ-SPh)$_2$(dppe)$_2$]$^{2+}$ m/z 701 (100%), [Pt$_2$(μ-SPh)$_2$(dppe)$_2$ + Pt(SPh)$_2$(dppe)]$^{2+}$ m/z 1106 (50%), [Pt$_2$(μ-SPh)$_2$(dppe)$_2$ + 2 Pt(SPh)$_2$(dppe)]$^{2+}$ m/z 1513 (8%), unassigned m/z 1732 (2+ion, 50%), [Pt$_2$(μ-SPh)$_2$(dppe)$_2$ + 3 Pt(SPh)$_2$(dppe)]$^{2+}$ m/z 1920 (5%).

2.2.11. [Au(SPh)(PPh$_3$)] [39, 40]. [AuCl(PPh$_3$)] (0.248 g), Et$_3$N (0.035 mL), and HSPh (0.055 mL) gave [Au(SPh)(PPh$_3$)] as a grey powder in 76% yield; m.p. 155–160°C. Found (%): C, 50.50; H, 3.52. C$_{24}$H$_{20}$AuPS requires (%): C, 50.70; H, 3.52. ^{31}P{^{1}H} NMR: δ 39.5 (s) [lit. 38.6]. ^{1}H NMR: δ 7.58–6.97 (24H, m, Ph of PPh$_3$ and SPh). ESI MS: [Au(PPh$_3$)$_2$]$^+$ m/z 721 (29%), [(Ph$_3$P)$_2$Au$_2$(SPh)]$^+$ m/z 1027 (100%), [(Ph$_3$P)$_3$Au$_2$(SPh)]$^+$ m/z 1289 (30%), [(Ph$_3$P)$_3$Au$_3$(SPh)$_2$]$^+$ m/z 1595 (50%).

2.2.12. [Au(SC$_5$H$_4$N)(PPh$_3$)], [AuS$^{\cdot}$(PPh$_3$)] [41]. [AuCl(PPh$_3$)] (0.495 g), Et$_3$N (0.08 mL) and HS$^{\cdot}$ (0.11 g) gave [AuS$^{\cdot}$(PPh$_3$)] as yellow crystals in 62% yield; m.p. 174–176°C. Found (%): C, 48.59; H, 3.67; N, 2.16. $C_{23}H_{19}AuNPS$ requires (%): C, 48.51; H, 3.34; N, 2.46. $^{31}P\{^1H\}$ NMR: δ 39.6 (s); [lit. 39.76]. ^1H NMR: δ 8.18 (2H, m, $^3J_{H2',\,H3'} = 3.26$ Hz, H3′ of S$^{\cdot}$), 7.60–7.42 (7H, m, aromatic H of PPh$_3$ and H2′ of S$^{\cdot}$). ESI MS: $[M+H]^+$ m/z 570 (55%), $[Au(PPh_3)_2]^+$ m/z 721 (100%).

2.3. *X-ray structure determination on* [PtS$_2^*$(dppe)]

X-ray data were collected on a Bruker Apex II CCD diffractometer and corrected for absorption by a multi-scan method (SADABS) [42]. The structure was solved and refined (on F_o^2) using the SHELX-97 programs [43]. The thiolate rings were partially disordered, tilted by 26.4° about the C(32)–C(33) edge but this was readily modeled. The molecule lies on a two-fold axis in *C2/c*. Attempts to refine an ordered molecule in Cc gave severe correlation and suggestions of ''racemic twinning'' so the disordered model in the higher symmetry space group was preferred. The lattice also contained two disordered water molecules. The final difference map showed a residual peak of 4 e Å^{-3}, too close to Pt to be anything other than an artifact.

2.3.1. Crystal and refinement data. $C_{40}H_{38}O_2P_2S_2Pt.2H_2O$, M_r 907.88, monoclinic, space group *C2/c*, $a = 11.644(1)$, $b = 24.084(1)$, $c = 14.569(1)$ Å, $\beta = 111.381(2)°$, $V = 3804.7(3)$ Å^3, $D_{Calcd} = 1.578$ g cm^{-3}, $Z = 4$, μ(Mo-Kα) = 3.9 mm^{-1}, size 0.27 × 0.10 × 0.10 mm^3, $F(000) = 1800$, $T = 93(2)$ K. Total data 21799, unique data 4550 (R_{int} 0.040), $2° < \theta < 28°$, $T_{max,min}$ 0.695, 0.417, $R_1 = 0.0359$, [$I > 2\sigma(I)$ data], wR_2 (all data) 0.1027, GOF 1.152.

3. Results and discussion

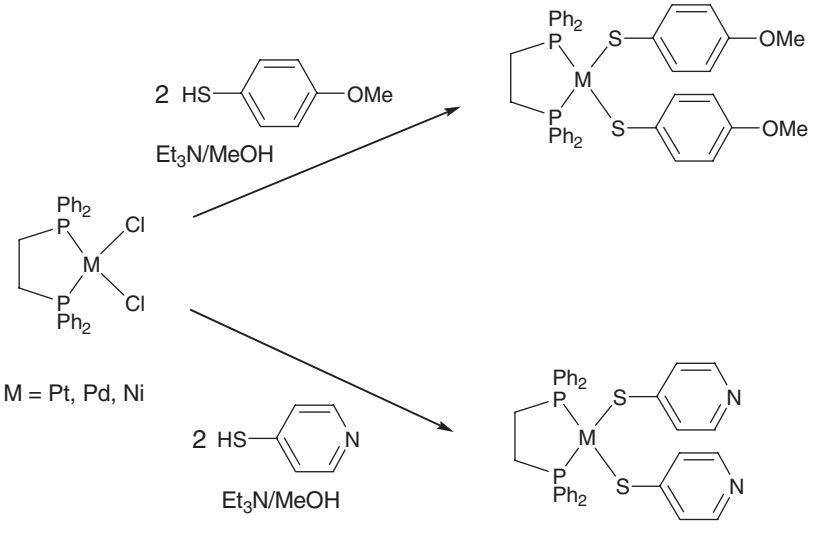
For the choice of electrospray-friendly thiolate ligands, the same concepts apply as for previously described electrospray-friendly phosphine ligands [4]; incorporation of a basic group in a *para* position of an aromatic ring should promote formation of $[M+H]^+$ ions in ESI MS.

The series of known complexes containing the unsubstituted thiophenolate (SPh$^-$) ligand [M(SPh)$_2$(dppe)] (M = Ni, Pd, Pt; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) were initially prepared by reaction of the halide complexes [MCl$_2$(dppe)] with PhSH and triethylamine in methanol. The chelating dppe ligand was chosen to maintain a *cis* configuration of all complexes. The known gold(I) complex [Au(SPh)(PPh$_3$)] was also prepared by the same method starting from [AuCl(PPh$_3$)]. The purity of the complexes was ascertained by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and in some cases by microelemental analysis.

As expected, none of the thiophenolate complexes gave $[M+H]^+$ ions in ESI MS analysis, due to the absence of protonatable sites in the complexes. However, a number of ions were observed for the complexes [M(SPh)$_2$(dppe)]; at a cone voltage of 20 V, the most intense ions were from the dimeric $[M_2(\mu\text{-SPh})_2(dppe)_2]^{2+}$. Other ions were associated with coordination of various combinations of $[M_2(\mu\text{-SPh})_2(dppe)_2]^{2+}$ with

$[M(SPh)_2(dppe)]$ and are listed in the "Experimental" section. These ions could be trace impurities in the products, which, being cationic, would have a very large ionization efficiency compared to neutral $[M(SPh)_2(dppe)]$ and would be expected to dominate the MS. This phenomenon has been observed previously [1]. Alternatively, a solution-based exchange process of the type $2[M(SPh)_2(dppe)] = [(dppe)M(SPh)_2M(dppe)]^{2+} + 2SPh^-$ cannot be ruled out as a source of traces of ionic species. Similarly, the only observed ions for the gold complex $[Au(SPh)(PPh_3)]$ originated from $[(Ph_3P)_2Au_2(SPh)]^+$, $[(Ph_3P)_3Au_2(SPh)]^+$, and $[(Ph_3P)_3Au_3(SPh)_2]^+$, together with $[Au(PPh_3)_2]^+$, which is ubiquitous in ESI MS analysis of PPh_3-Au complexes. Such ligand scrambling in gold-phosphine complexes has been observed previously [44], including ESI MS studies [45–47] and the structures of such thiophenolate-bridged polygold species have been determined or proposed [48–51].

A series of nickel(II), palladium(II), and platinum(II) complexes of S^{*-} and $S^{\cdot-}$ were prepared by the reaction of $[MCl_2(dppe)]$ with the thiol in the presence of Et_3N, as shown in scheme 1. The gold(I) phosphine complexes $[AuS^*(PPh_3)]$ and $[AuS^{\cdot}(PPh_3)]$ were also prepared under the same conditions from $[AuCl(PPh_3)]$. $[AuS^{\cdot}(PPh_3)]$ [41] and $[NiS_2^*(dppe)]$ [36] have been reported previously, including applications of the former as a metallo-ligand (coordinating to other metal centers through the pyridine nitrogen) [52, 53] and in the formation of a pyridinethiolate-functionalized Au_{11} cluster [54]. However, the other S* and S$^{\cdot}$ complexes are new. The complexes were characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy where all showed the expected and largely unextraordinary features. However, the literature data [36] for $[NiS_2^*(dppe)]$ reports the ^1H NMR chemical shift of the OMe protons as δ 5.7, whereas we find it to occur at δ 3.65, similar to the other S* complexes described herein. The purity of the complexes was supported by satisfactory elemental microanalytical data. ^{31}P NMR data indicate that the thiolate ligands have similar electronic properties, with little variation in the $^1J_{Pt,P}$ coupling constants in the series $[Pt(SR)_2(dppe)]$ [R = Ph 2884 Hz; R = C_6H_4OMe, 2892 Hz; R = SC_5H_4N, 2890 Hz].



Scheme 1. Synthesis of the functional thiolate complexes $[M(SC_6H_4OMe)_2(dppe)]$ and $[M(SC_5H_4N)_2(dppe)]$.

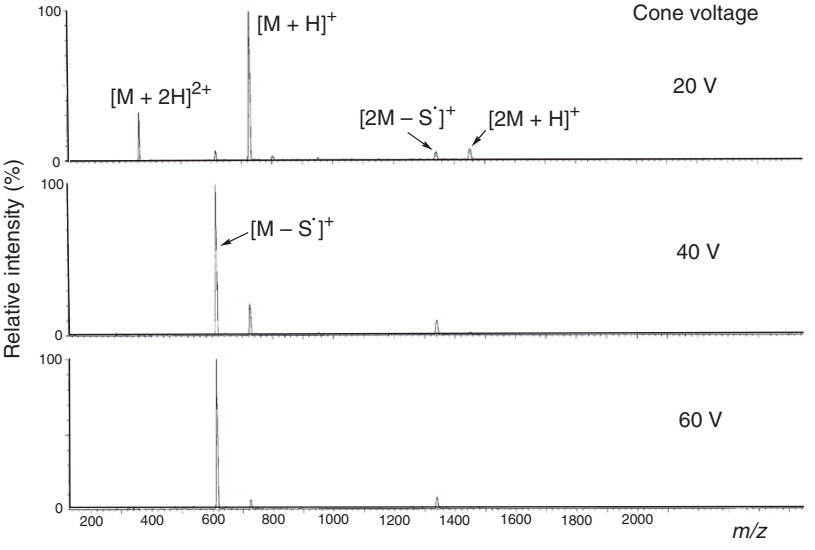


Figure 1. Positive-ion ESI MS of the complex $[Pd(SC_5H_4N)_2(dppe)]$, $[PdS^{\bullet}_2(dppe)]$ in methanol, at cone voltages of 20, 40, and 60 V.

Surprisingly, none of the S* complexes, although having a basic site for protonation, gave an $[M+H]^+$ ion in their ESI MS, but instead all behaved very much like non-electrospray-friendly thiophenolate complexes. The only exception was $[PtS^*_2(dppe)]$, for which an $[M+H]^+$ ion was detected. However, the intensity of this signal was relatively weak with a low signal to noise ratio, suggesting low efficiency ionization. Other ions were from ionic species similar to those observed for the parent thiophenolate complexes. This phenomenon was reproducible on numerous occasions, and the Pt complex was the only example where the desired monomeric species was observed as its $[M+H]^+$ ion. The formation of dimers and oligomers of Ni, Pd, and Pt thiolate complexes has been studied [55], and it was found that within the triad, platinum was the metal most likely to form monomers, while nickel and palladium appeared to have a stronger tendency to form dimers, oligomers, and eventually insoluble polymers through thiolate bridges. This is directly related to the lower lability of platinum(II) complexes compared to the corresponding palladium(II) or nickel(II) ones.

In contrast, all $S^{\bullet}$ complexes ionized by protonation. Based on the higher basicity of pyridine (0.661) compared to anisole (0.247) on the Kamlet-Taft β scale [56], the pyridine-derived thiolate ligand $S^{\bullet}$ would be expected to be the most basic when coordinated, and most efficient in promoting ionization in ESI MS analysis. For the Ni, Pd, and Pt complexes with two thiolate ligands, one or both nitrogens were protonated, yielding $[M+H]^+$ as well as $[M+2H]^{2+}$ ions. Additionally, these complexes ionized by losing a thiolate ligand, forming the $[M-S^{\bullet}]^+$ ion, with the nickel complex showing the greatest propensity to do so, because of the weakest metal-sulfide bond. This is the ionization pathway commonly observed for metal halide complexes [3]. To some extent, the reactivity and electronic structure of thiolates are comparable to those of halide ligands (e.g., terminal RS^- ligands can replace halide ligands and *vice versa* [57]).

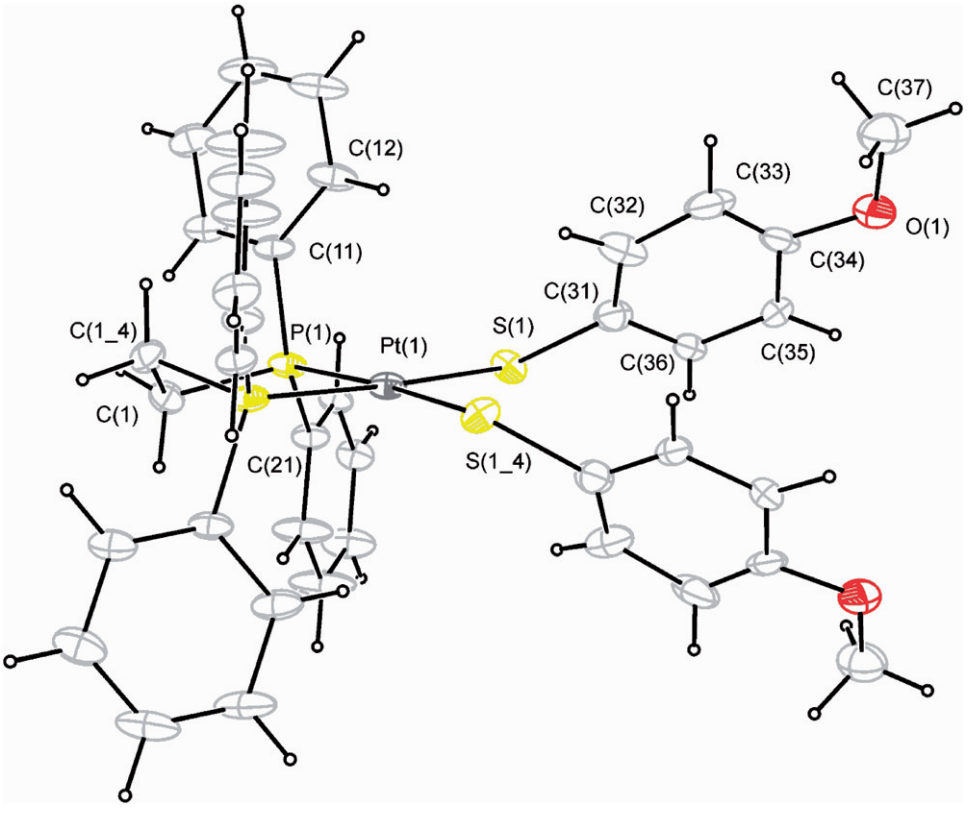


Figure 2. The molecular structure of $[PtS^*_2(dppe)]$. Only one orientation of the disordered $MeOC_6H_4S$ rings is shown, and lattice water molecules are omitted. Bond lengths (Å) include: Pt(1)–P(1) 2.2521(14); Pt(1)–S(1) 2.3558(15); S(1)–C(31) 1.751(7). Bond angles (°): P(1)–Pt(1)–P(1)′ 86.19(8); S(1)–Pt(1)–S(1)′ 101.13(8); P(1)–Pt(1)–S(1) 86.35(5); Pt(1)–S(1)–C(31) 112.8(2).

The observed ions depended very much on the cone voltages used; figure 1 illustrates for the complex $[PdS^*_2(dppe)]$ how protonation dominates at low cone voltages, while signals associated with thiolate loss are more intense at higher cone voltages. For the gold complex $[AuS^*(PPh_3)]$ an $[M+H]^+$ ion was observed, but the base peak was again the gold(I) phosphine ion $[Au(PPh_3)_2]^+$.

The X-ray crystal structure of $[PtS^*_2(dppe)]$ was determined on crystals grown by vapor diffusion from dichloromethane-diethyl ether. The structure is shown in figure 2 and shows the expected square-planar geometry around Pt (to ± 0.03 Å). The S–Pt–S angle is 101.13(8)°, wider than expected for square-planar coordination but similar to the equivalent angle in other $[Pt(SR)_2(dppe)]$ examples (R = Ph (KIXGUT), Ph^F (YILMAI), $C_6H_4CF_3$–2 (YILMEM). In contrast, related $[Pt(SR)_2(PPh_3)_2]$ (PIDMIZ, PINDEV, PIDNEW, PIGJAR, SEKSIL, XEYJIV) and $[Pt(SR)_2(dppm)]$ (VUPCOY) have S–Pt–S angles closer to 90°. The Pt–S distance in $[PtS^*_2(dppe)]$, 2.3558(14) Å, is similar to those in the related examples.

The crystal lattice contains two H_2O molecules (derived adventitiously) for each molecule of the complex, and these form an H-bonded chain parallel to the *c*-axis, with every second one H-bonded to oxygen of $MeOC_6H_4S^-$ from two adjacent molecules,

linking them together in the crystal. The tendency for the thiolate ligands to H-bond to water molecules in this way contrasts with the relatively poor proton affinity in solution evident from the ESI MS discussed above.

4. Conclusion

The thiolate ligand S^{*-} derived from 4-methoxybenzenethiol appears to have limited utility (based on the relatively small set of complexes studied), with only the dppe Pt complex forming an $[M+H]^+$ ion. The thiolate ligand derived from 4-mercaptopyridine can be considered as an electrospray-friendly thiolate ligand, promoting the formation of protonated $[M+H]^+$ and $[M+2H]^{2+}$ ions in ESI MS, although the known ability of the coordinated pyridinethiolate ligand to act as a metalloligand toward other metal centers may place limitations on the ability of the ionization site to be an inert spectator. To address this we are investigating the chemistry of thiolate ligands with alternative charge providers.

Supplementary material

Crystallographic data (excluding structure factors) for the structure described in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 772482. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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