Pergamon

S0277-5387(96)00133-7

Polyhedron Vol. 15, No. 22, pp. 4015–4024, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0277-5387/96 $15.00+0.00

SYNTHESIS AND ELECTROSPRAY MASS SPECTROMETRY OF PLATINUM(II) COMPLEXES DERIVED FROM THIOUREA DIANIONS AND THE X-RAY STRUCTURE OF [Pt{NMeC(=NCN)S}(COD)] (COD = CYCLO-OCTA-1,5-DIENE)

WILLIAM HENDERSON* and BRIAN K. NICHOLSON

Department of Chemistry, University of Waikato, Private Bag 3105, Hamilton, New Zealand

(*Received* 10 *October* 1995; *accepted* 26 *February* 1996)

Abstract—Platinum(II) complexes formally derived from the thiourea dianion $[MeNC(S)N(CN)]^{2-}$ have been synthesized from the platinum-halide complexes *cis*-$[PtCl_2L_2]$ [L = tertiary phosphine or L_2 = cyclo-octa-1,5-diene (COD)] by reaction with the sodium salt of N-methyl N-cyanothiourea. The complexes have been fully characterized, including an X-ray crystal structure determination of [Pt{NMeC(=NCN)S}(COD)]. The results of an electrospray mass spectrometry study on platinum(II) complexes of thiourea dianions are also reported, including the *in situ* coordination chemistry with silver(I) ions. Copyright © 1996 Elsevier Science Ltd

Thioureas are versatile ligands, the hybrid hard nitrogen/soft sulfur donor atom set yielding a multitude of possibilities for coordination to both hard and soft metal centres. Thioureas are able to coordinate as neutral ligands, monoanions or as dianions, with the first of these being by far the most extensively observed binding mode.[1] We recently reported the synthesis of a number of platinum(II) complexes (**1a**) formed from 1,3-diphenylthiourea, PhNHC(S)NHPh.[2] The complexes were synthesized from the platinum(II) halide complex *cis*-$[PtCl_2(PPh_3)_2]$, either by reaction with the dianion $[PhNC(S)NPh]^{2-}$ or more conveniently by reaction with PhNHC(S)NHPh in refluxing dichloromethane, mediated by excess silver(I) oxide. In the latter case anhydrous solvents and exclusion of oxygen are unnecessary. Silver(I) oxide has been recently employed in the synthesis of a range of metal–nitrogen, oxygen, carbon and sulfur-bonded four-, five- and six-membered ring metallacyclic complexes.[2,3]

Examples of metallacyclic complexes derived from thiourea dianions are relatively rare. A number of other platinum(II) complexes have been synthesized and an X-ray structure determination on the N,N-diethyl derivative **1b** has been reported.[4] A related molybdenum complex (**2**) has also been structurally characterized.[5] N,S-Chelated thiourea monoanions coordinated to rhodium(III)[6] and platinum(II)[4] have been reported. Four-membered ring M—N—C(N)—S metallacycles derived from related monoionic ligands, such as thiouracil,[7] and pyridine- or pyrimidine-2-thiolates and related ligands[8] are much more common, including complexes with such ligands bridging two or more metal centres.[9] A number of metal clusters containing monodeprotonated thiourea ligands on Ru_3 and Os_3 cluster cores are also known.[10] We now describe the preparation of thiourea dianion complexes of platinum(II) formed from the sodium salt of N-cyano-N′-methylisothiourea (**3**).

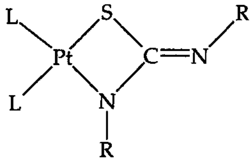
EXPERIMENTAL

General

The sodium salt of 1-cyano-3-methylisothiourea (**3**, Aldrich), triphenylphosphine (Pressure Chemi-

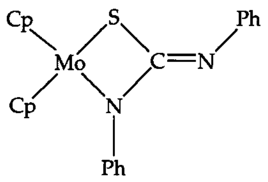
---

* Author to whom correspondence should be addressed.

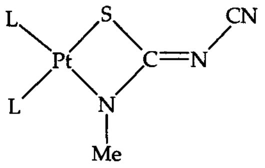


1

a; R = Ph, L = tertiary phosphine
b; R = Et, L = Ph_3P

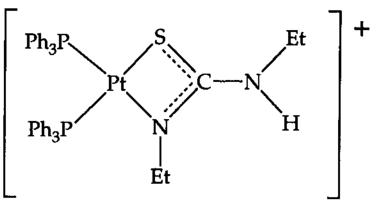


2

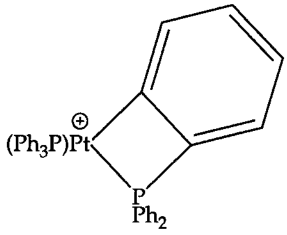


4

a; L-L = COD
b; L = PPh_3
c; L-L = DPPF
d; L-L = DPPE
e; L = $PBu^n{}_3$
f; L = $P(OPh)_3$



5



6

cal Co.), triphenylphosphite (BDH) and 1,1′-bis(diphenylphosphino)ferrocene (Aldrich) were used as supplied. The complexes *cis*-$[PtCl_2(PPh_3)_2]$ and $[PtCl_2(DPPE)]$ were prepared by ligand displacement of the COD ligand of $[PtCl_2(COD)]$[11] using the appropriate molar amount of phosphine in dichloromethane, as described previously.[12] $[\overline{Pt\{NPhC(=NPh)S}\}(PPh_3)_2]$ was prepared by the literature procedure.[2] All complexes described herein are air-stable and reactions were carried out in laboratory-grade solvents, without prior purification or exclusion of air.

Melting points were recorded on a Reichert hot-stage apparatus and are uncorrected. IR spectra were recorded on a Bio-Rad FTS-40 spectrophotometer as KBr discs. ^1H and $^{13}C[^1H]$ NMR spectra were recorded in $CDCl_3$ solution (unless otherwise specified) on a Bruker AC300P spectrometer at 300.13 and 75.47 MHz, respectively, referenced relative to $SiMe_2$ (δ 0.0). $^{31}P[^1H]$ NMR spectra were recorded in $CDCl_3$ solution on a JEOL FX90Q spectrometer at 36.23 MHz, with 85% H_3PO_4 (δ 0.0) as external reference.

Electrospray mass spectra were obtained in positive-ion mode with a VG Platform II mass spectrometer using a 1 : 1 v/v acetonitrile–water mobile phase. The compounds were dissolved in the mobile phase to give a solution typically of approximate concentration 0.1 mM. The diluted solution was injected into the spectrometer via a Rheodyne injector fitted with a 0.01 cm^3 sample loop. A Thermo Separation Products SpectraSystem P1000 LC pump delivered the solution to the mass spectrometer source (60°C) at a flow rate of 0.01 cm^3 min^{-1} and nitrogen was employed both as a drying and nebulizing gas. Cone voltages were typically varied from 10 to 100 V in order to investigate the effect of higher voltages on fragmentation of the parent ions. Typically, 10–12 scans were acquired, yielding an averaged spectrum. Excellent agreement between observed and calculated isotope distribution patterns was observed for all major peaks. Theoretical isotope patterns were calculated using the Isotope program.[13]

Synthesis of [Pt{NMEC(=CN)S}(COD)] (**4a**)

A mixture of [$PtCl_2$(COD)] (300 mg, 0.802 mmol), **3** (111 mg, 0.809 mmol) and silver(I) oxide (0.9 g, excess) was refluxed in dichloromethane (30 cm^3) for 4 h. Filtration to remove the silver salts afforded a pale yellow solution, to which was added petroleum spirit (60 cm^3) giving a pale yellow microcrystalline precipitate. This was filtered off and dried *in vacuo* to afford the title complex **4a** (253 mg, 76%). Found: C, 31.0; H, 3.6; N, 7.5. $C_{11}H_{15}N_3PtS$ requires: C, 31.7; H, 3.6; N, 10.1%; m.pt decomposed >210°C. IR: *ν*(C≡N) 2161, *ν*(C=N) 1560 cm^{-1}. NMR: ^{1}H *δ*H 5.46 [m, 2H, CH, COD, ^2J(Pt,H) = 61.0 Hz, 5.29 [s, 2H, CH, COD, ^2J(Pt,H) 58.8 Hz], 2.97 [s, 3H, PtNMe, ^3J(Pt,H) 39.2 Hz], 2.71 (m, 4H, CH_2 COD] and 2.36 (m, 4H, CH_2, COD); ^{13}C[^{1}H]: *δ*C 180.3 [s, C=N, ^2J(Pt,C) not discernible], 115.6 (s, CN), 100.0 [s, CH, COD, ^1J(Pt,C) = 117.4 Hz], 94.7 [s, CH, COD, ^1J(Pt,C) = 135.5 Hz], 34.9 [s, br, Me, ^2J(Pt,C) not resolved], 31.3 (s, CH_2, COD) and 30.2 (s, CH, COD).

Synthesis of [Pt{NMeC(=NCN)S}(PPh_3)$_2$] (**4b**)

A suspension of *cis*-[$PtCl_2(PPh_3)_2$] (200 mg, 0.253 mmol) and **3** (35 mg, 0.255 mmol) in methanol (30 cm^3) with triethylamine (0.5 cm^3) was refluxed for 1 h and then stirred at *ca* 30°C overnight to give a white suspension. Volatiles were removed under reduced pressure and a mixture of water (10 cm^3) and 2-propanol (70 cm^3) added. The white product was filtered off, washed with a small quantity of 2-propanol and then diethyl ether (5 cm^3) and dried *in vacuo* to give [Pt{NMeC(=NCN)S}(PPh_3)$_2$] (**4b**, 188 mg), m.pt 240–250°C (decomposed). IR: *ν*(C≡N) 2162, *ν*(C=N) 1541 cm^{-1}. NMR: ^{31}P[^{1}H], ($CDCl_3$/DMSO 3:1), *δ*P 15.2 [d, ^1J(Pt,P) = 3171, ^2J(P,P) = 19.5 Hz] and 10.9 [d, ^1J(Pt,P) = 3308 Hz]; ^{1}H ($CDCl_3$), *δ*H 7.46–7.20 (m, 30 H, PPh_3) and 2.16 [d, 3H, NMe, ^4J(P,H) = 4.0, ^3J(Pt,H) *ca* 31 Hz].

Alternative synthesis of [Pt{NMeC(=NCN)S}(PPh_3)$_2$] (**4b**)

To a solution of **4a** (80 mg, 0.192 mmol) in dichloromethane (2 cm^3) was added triphenylphosphine (100 mg, 0.382 mmol), to give a yellow solution. Petroleum spirit (4 cm^3) was added to give an off-white precipitate which was filtered off, washed with petroleum spirit (4 cm^3) and dried *in vacuo* to give **4b** (140 mg, 78%). The product was identical to that by the first route described, as evidenced by ^{31}P and ^{1}H NMR, and appeared to be pure. The complex crystallizes with both CH_2Cl_2 and H_2O of crystallization (the former confirmed by ^{1}H NMR). The best fit for the microanalytical data is given by the composition **4b**·CH_2Cl_2·H_2O. Found: C, 51.0; H, 3.9; N, 4.2. $C_{39}H_{33}N_3P_2PtS \cdot CH_2Cl_2 \cdot H_2O$ requires: C, 51.3; H, 4.0; N, 4.5%.

Synthesis of [Pt{NMeC(=NCN)S}(DPPF)] (**4c**).

To a solution of **4a** (50 mg, 0.120 mmol) in dichloromethane (2 cm^3) was added DPPF (67 mg, 0.121 mmol) to give a bright yellow solution. Petroleum spirit (4 cm^3) was added to give a yellow precipitate which was filtered off, washed with petroleum spirit (4 cm^3) and dried *in vacuo* to give **4c** (94 mg, 90%). Yellow needles for microanalysis were obtained by slow recrystallization from dichloromethane–petroleum spirit. Found: C, 52.3; H, 3.7; N, 4.9. $C_{37}H_{31}FeN_3P_2PtS$ requires: C, 51.5; H, 3.6; N, 4.9%; m.pt (decomposed) > 175°C. IR: *ν*(C≡N) 2177, *ν*(C=N) 1541 cm^{-1}. NMR: ^{31}P[^{1}H] ($CDCl_3$/DMSO 3:1), *δ*P 16.0 [d, ^1J(Pt,P) = 3259, ^2J(P,P) = 19.5 Hz] and 11.4 [d, ^1J(Pt,P) = 3347 Hz]; ^{1}H ($CDCl_3$), *δ*H 8.00–7.15 (m, 20H, Ph), 4.81 [d, 2H, Cp, *J*(H,H) = 1.8 Hz], 4.57 (s, br, 2H, Cp), 4.21 (s, br, 2H, Cp), 3.58 [d, 2H, Cp, *J*(H,H) = 1.8 Hz] and 2.17 [d, 3H, NMe, ^4J(P,H) = 4.0, ^3J(Pt,H) = *ca* 33 Hz].

Synthesis of [Pt{NMeC(=NCN)S}(DPPE)] (**4d**)

A suspension of [$PtCl_2$(DPPE)] (168 mg, 0.254 mmol) and **3** (35 mg, 0.255 mmol) in methanol (20 cm^3) with triethylamine (0.5 cm^3) was refluxed for 1 h and stirred overnight at *ca* 30°C to give a pale yellow suspension. Water (50 cm^3) was added and the product filtered off, washed with isopropanol (10 cm^3) and diethyl ether (10 cm^3), and dried *in vacuo* to give 120 mg (67%) of **4d**. Found: C, 48.8; H, 5.0; N, 6.0. $C_{29}H_{27}N_3P_2PtS$ requires: C, 49.3; H, 3.9; N, 6.0%; m.pt (decomposed) > 230°C. IR: *ν*(C≡N) 2163, *ν*(=N) 1539 cm^{-1}. NMR: ^{31}P[^{1}H] ($CDCl_3$/DMSO 3:1), *δ*P 43.8 [d, ^1J(Pt,P) = 3164, ^2J(P,P) = 7.4 Hz] and 36.7 [d, ^1J(Pt,P) = 3091 Hz]. The complex **4d** was also prepared by displacement of COD from **4a** by excess DPPE and found to be identical by ^{31}P NMR to that prepared as above.

In addition, the complexes **4e** and **4f** were synthesized for study by ESMS, by ligand displacement of COD from a small quantity (*ca* 10 mg) of **4a** dissolved in CH_2Cl_2 (*ca* 1 cm^3), followed by addition of petroleum spirit (*ca* 4 cm^3) to effect precipitation and removal of excess phosphine or phosphite ligand and displaced COD. The complexes were washed with petroleum spirit prior to vacuum drying and ESMS characterization.

Crystal structure determination of [Pt{NMeC(=NCN)S}(COD)] (**4a**)

Yellow crystals were obtained by allowing a concentrated $CDCl_3$ solution to stand for several days. A crystal of approximate dimensions $1.08 \times 0.70 \times 0.28$ mm was selected for the study. The space group and crystal quality were determined by precession photography.

Crystal data. $C_{11}H_{15}N_3PtS$, $M_r = 416.41$, monoclinic, space group $P2_1/c$, $a = 11.270(3)$, $b = 12.268(2)$, $c = 17.053(4)$ Å, $\beta = 96.00(2)°$, $U = 2344.8(9)$ Å^3 (from 26 reflections $9 < 2\theta < 29°$), $\lambda = 0.71073$ Å, $D_c = 2.359$ g cm^{-3}, $Z = 8$, $F(000) = 1568$, μ(Mo-K_α) = 12.1 mm^{-1}, $T = -143$°C.

Data collection. Nicolet R3 automatic diffractometer, ω scans. A total of 2567 reflections were measured, 2403 unique, 2091 $I > 2\sigma(I)$, in the range $4 < 2\theta < 50°, 0 < h < 6, 0 < k < 14, -20 < l < 20$. The data were corrected for absorption by a semi-empirical method with $T_{\max,\min}$ 0.425, 0.160, respectively.

Structure analysis and refinement. The structure was solved by Patterson methods and routinely developed. Full-matrix least-squares refinement was based on F^2. Only the Pt and S atoms were treated anisotropically since lighter atoms gave several "non-positive definite" ellipsoids. Hydrogen atoms were included in calculated positions with isotropic thermal parameters 1.2* U_{iso} of the carbon atom to which they are attached. The refinement converged with $R_1 = 0.0372$, $wR_2 = 0.0920$ (for 2σ data), 0.0467 and 0.0972, respectively (all data), where $w = [\sigma^2(F_o)^2 + (0.0645P)^2 + 10.91P]^{-1}$, where $P = 1/3(F_o^2 + 2F_c^2)$. Goodness of fit was 1.082. A final difference map showed no feature greater than $+1.18/-1.56$ e Å^{-3}. The SHELX programs were used for the crystallography.[14]

Additional material available from the Cambridge Crystallographic Data Centre comprises hydrogen atom coordinates, thermal parameters and bond lengths and angles for both independent molecules of the structure determination.

RESULTS AND DISCUSSION

Reaction of [$PtCl_2$(COD)] (COD = cyclo-octa-1,5-diene) with 1 mol equiv. of the monosodium salt of MeNHC(S)NHCN (**3**) in refluxing dichloromethane in the presence of excess silver(I) oxide gives the new complex **4a**. This is formally derived from the thiourea dianion [MeNC(S)N(CN)]$^{2-}$ and is analogous to previously reported examples of this relatively rare class of metallacycle, *viz.* **1** and **2**. The availability of the labile COD complex allows the potential synthesis of a wide variety of derivatives, *via* ligand displacement reactions, as illustrated by the reactions with triphenylphosphine, 1,1′-bis(diphenylphosphino)ferrocene (DPPF), 1,2-bis(diphenylphosphino)ethane (DPPE), tri-*n*-butylphosphine and triphenylphosphite, giving the complexes **4b–f**, respectively. Alternative syntheses for the triphenylphosphine **4b** and DPPE **4d** complexes utilized the reaction of *cis*-[$PtCl_2(PPh_3)_2$] or [$PtCl_2$(DPPE)] with **3** in refluxing methanol with added triethylamine base, giving the complexes as white microcrystalline solids. The complexes were found to be identical by $^{31}P[^1H]$ NMR and ESMS to those from the COD displacement reactions. All complexes **4** were air-stable, both in solution and in the solid state.

Only a small number of complexes derived from thiourea dianions have been structurally characterized. We therefore undertook a single crystal X-ray diffraction study on the COD complex **4a**. The complex crystallizes with two independent molecules in the unit cell, with relatively minor conformational differences in the COD ligands. The molecular structure of molecule 1, together with the crystallographic numbering scheme, is shown in Fig. 1. Selected intramolecular bond lengths for both independent molecules are given in Table 1, while bond angles are given in Table 2.

The complex contains the expected square-planar platinum atom, coordinated to a chelating COD ligand and to the formally dianionic thiourea ligand, via the nitrogen (with the attached methyl group) and the sulfur atom. The coordination environment is therefore similar to the other platinum(II) (**1**)[2,4] and molybdenum(IV) (**2**)[5] analogues structurally characterized previously. In molecule 1 the platinum atom and the entire thiourea ligand are essentially coplanar, with the greatest deviation from the least-squares plane being C(13) (0.19 Å). In molecule 2 the Pt—S—C(1)—N(1) metallacycle is planar, but the N—C—N unit is tilted significantly from this plane. For each molecule, the dihedral angles between the least-squares plane of the thiourea ligand and that defined by the four platinum-bound carbon atoms of the COD ligand is 87°.

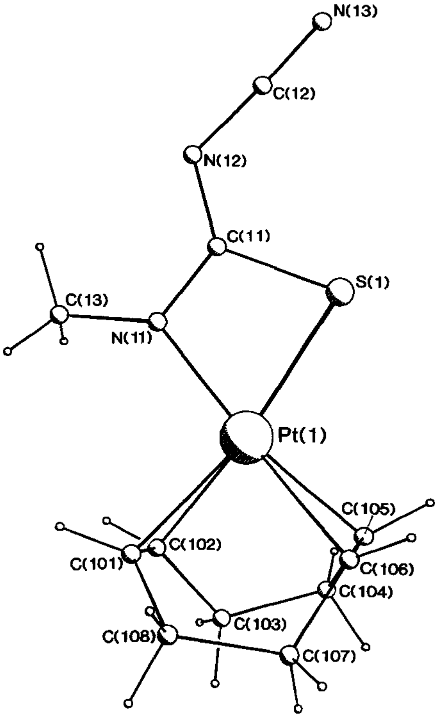


Fig. 1. Molecular structure of one of the independent molecules (molecule 1) of [Pt{NMeC(=NCN)S}(COD)] (**4a**) showing the atom numbering scheme. The other molecule has a comparable geometry.

The platinum–sulfur [average 2.311(3) Å] and platinum–nitrogen [average 2.01(1) Å] bond distances of **4a** are somewhat shorter than the corresponding values in **1a** (L = PPh$_3$)[2] [2.331(1) and 2.054(3) Å] and **1b**[4] [2.332(8) and 2.05(3) Å]. This is presumably a result of the higher *trans* influence

Table 2. Selected intramolecular bond angles (°) for [Pt{(NMeC(=NCN)S}(COD)] (**4a**) with estimated standard deviations in parentheses

	Molecule 1	Molecule 2[a]
N(11)—Pt(1)—C(105)	156.3(4)	155.7(5)
N(11)—Pt(1)—C(101)	99.2(5)	99.7(4)
C(101)—Pt(1)—C(106)	81.4(5)	81.3(5)
N(11)—Pt(1)—C(102)	99.9(4)	101.9(4)
C(105)—Pt(1)—C(102)	82.5(5)	81.4(5)
N(11)—Pt(1)—S(1)	70.7(3)	70.7(3)
C(105)—Pt(1)—S(1)	100.0(3)	98.8(3)
C(106)—Pt(1)—S(1)	103.1(3)	103.0(3)
C(11)—S(1)—Pt(1)	78.0(4)	79.1(4)
C(11)—N(11)—C(13)	124(1)	124(1)
C(11)—N(11)—Pt(1)	102.8(9)	102.3(8)
C(13)—N(11)—Pt(1)	132.0(7)	132.6(8)
C(12)—N(12)—C(11)	119(1)	117(1)
N(11)—C(11)—N(12)	126(1)	124(1)
N(11)—C(11)—S(1)	108.4(9)	107.8(8)
N(12)—C(11)—S(1)	125.7(9)	127.8(9)
N(13)—C(12)—N(12)	177(2)	172(1)
COD ligand		
C(102)—C(101)—C(108)	128(1)	129(1)
C(101)—C(102)—C(103)	123(1)	124(1)
C(102)—C(103)—C(104)	113(1)	113(1)
C(105)—C(104)—C(103)	114(1)	113(1)
C(106)—C(105)—C(104)	126(1)	125(1)
C(105)—C(106)—C(107)	125(1)	127(1)
C(106)—C(107)—C(108)	114(1)	113(1)
C(101)—C(108)—C(107)	112(1)	113(1)

[a] Equivalent bond angle to that in molecule 1.

Table 1. Intramolecular bond lengths (Å) for [Pt{NMeC(=NCN)S}(COD)](**4a**) with estimated standard deviations in parentheses

	Molecule 1	Molecule 2[a]		Molecule 1	Molecule 2[a]
Pt(1)—N(11)	2.00(1)	2.01(1)	Pt(1)—S(1)	2.318(3)	2.303(3)
Pt(1)—C(101)	2.17(1)	2.17(1)	Pt(1)—C(102)	2.20(1)	2.18(1)
Pt(1)—C(105)	2.15(1)	2.17(1)	Pt(1)—C(106)	2.19(1)	2.20(1)
S(1)—C(11)	1.78(1)	1.77(1)	N(11)—C(11)	1.29(1)	1.31(2)
N(11)—C(13)	1.46(2)	1.46(1)	N(12)—C(12)	1.32(2)	1.34(2)
N(12)—C(11)	1.34(2)	1.33(2)	N(13)—C(12)	1.16(2)	1.13(2)
COD ligand					
C(101)—C(102)	1.37(2)	1.33(2)	C(101)—C(108)	1.51(2)	1.54(2)
C(102)—C(103)	1.53(2)	1.49(2)	C(103)—C(104)	1.55(2)	1.53(2)
C(104)—C(105)	1.51(2)	1.50(2)	C(105)—C(106)	1.35(2)	1.39(2)
C(106)—C(107)	1.49(2)	1.50(2)	C(107)—C(108)	1.55(2)	1.54(2)
Pt(1)···C(11)	2.615(12)	2.63(1)			

[a] Equivalent bond distance to that in molecule 1.

of the triphenylphosphine ligands compared with that of COD.[15] Unfortunately, a detailed comparison of the relative *trans*-influences of the S and N donor atoms of the thiourea dianion ligand is precluded by the relatively large e.s.d.s for the Pt—C distances and the spread of values 2.15(1)–2.21(1) Å. The average Pt—C distance opposite S is 2.18 Å, the same as the average distance opposite the nitrogen atom.

Of the five C—N bond distances in the molecule, N(11)—C(13) is, as expected, the longest at 1.46(2) Å, while that for the cyanide group C(12)—N(13) is the shortest, at 1.16(2) Å. However, on examining the remaining C—N bonds, the metallacyclic C(11)—N(11), the exocyclic C(11)—N(12) (which is nominally a double bond) and the N(12)—C(12) bonds, these are found to be quite similar at 1.29(1), 1.34(2) and 1.32(2) Å, respectively. This suggests that there is a certain amount of conjugation occurring between the cyano and C=N moieties. The C—N bond lengths of the CNCN moiety of **4a** are overall very comparable with those of 2-cyano-1,3-dimethylguanidine.[16] The C—S bond of **4a** [1.78(1) Å] is the same as that in **1a** (L = PPh_3)[2] [1.782(5) Å] and has a substantial amount of single-bond character.

It is noteworthy that the complex exists as a single isomer for both independent molecules, with the cyano group directed away from the methyl substituent on the metallacyclic nitrogen, presumably for steric reasons. Other structurally characterized analogues show similar selectivity. No evidence was found in NMR studies for any other isomers. As far as we are aware, complexes **4** represent the first containing a chelating dianionic thiourea with two different substituents on the nitrogen atoms.

The $^{13}C[^1H]$, ^1H and, where appropriate, $^{31}P[^1H]$ NMR spectroscopic properties of complexes **4a–d** are consistent with their formulation as complexes of thiourea dianions. The olefinic CH carbons of the COD complex **4a** appear as two distinct singlets at δ 100.0 and 94.7, showing one-bond coupling to ^{195}Pt of 117.4 and 135.5 Hz, respectively. The relatively low solubility of **4a** precluded resolution of ^{195}Pt coupling to the C=N carbon atom. Such signals are ordinarily weak in ^{13}C NMR spectra in the absence of attached hydrogen atoms to provide relaxation effects. The N-methyl group in **4a** appeared as a broad singlet at δ 34.9 and ^{195}Pt coupling could not be resolved, while the nitrile carbon appeared in the expected region at δ 115.6.

The COD CH protons of **4a** also yield two resonances in the ^1H NMR spectrum, at δ 5.46 and 5.29, showing coupling to ^{195}Pt of 61.0 and 58.8 Hz, respectively. The spatial proximity of the N-methyl hydrogens to the COD CH protons on the same side of the molecule allows confirmation of the latter by nOe difference spectroscopy. Upon irradiation of the N-methyl protons at δ 2.97, a 1.4% nOe enhancement was observed to the COD CH protons at δ 5.46. Unfortunately, poor solubility of the complex in both $CDCl_3$ and $CDCl_3$–$(CD_3)_2SO$ mixtures did not allow assignment of the individual COD CH carbons via a ^{13}C—^1H correlation experiment. In the ^1H NMR spectra, the N-methyl group showed four-bond coupling (4.0 Hz in the PPh_3 complex **4b**) to one of the phosphines. This is presumably to the *trans*-phosphine ligand, since *cis* couplings in square-planar platinum(II) complexes are known to be substantially smaller than their *trans* counterparts. Three-bond coupling to ^{195}Pt was again observed, being 39 and 31 Hz in **4a** and **b**, respectively.

For the phosphine complexes **4b–d**, the $^{31}P[^1H]$ NMR spectra showed the expected doublet of doublets due to two inequivalent phosphine ligands, *trans* to differing *trans* influence donor atoms.

The IR spectra of **4a–d** show two strong C—N stretching bands, the nitrile group appearing in the region 2161–2177 cm^{-1} and the imine group in the region 1539–1560 cm^{-1}. For comparison, the diphenyl analogue **1a** (L = PPh_3) displays a ν(C=N) stretch at 1550 cm^{-1}.[2]

Electrospray mass spectrometry

The thiourea complexes described in this paper, together with the previously reported diphenyl analogue **1a**, have been investigated by electrospray mass spectrometry[17] (ESMS). This new technique is finding rapidly increasing applications in the analysis of organometallic and other coordination complexes.[18] Examples involving anionic thiolate ligands have also been reported.[19] ESMS provides soft ionization, transferring existing ions in solution into the gas phase and typically yielding strong molecular ions under conditions of low fragmentation (i.e. when low skimmer cone voltages are employed). Upon increasing the cone voltage, fragmentation can be induced, to provide additional structural information. The versatility of the ESMS technique accordingly lends itself to the study of the thiourea-derived metallacyclic complexes **4**.

Positive-ion ESMS spectra were recorded in aqueous acetonitrile (1 : 1 v/v) at a range of cone voltages; data for the major ions observed are summarized in Table 3. All of the complexes gave excellent spectra, with protonated $[M+H]^+$ ions at low cone voltages (20–30 V). Aggregates of the type $[2M+H]^+$ and $[2M+NH_4]^+$ were also observed in

Table 3. Positive-ion electrospray mass spectral data for the thiourea complexes **1a** and **4a–f**[a]

Complex (M)	Cone voltage (V)	Major ions (m/z)[b]
[Pt{NMeC(=NCN)S}(COD)] (**4a**)	20	$[M+H]^+$ (417, 100%), $[2M+H]^+$ (833, 11%), $[2M+NH_4]^+$ (850, 4%), $[3M+H]^+$ (1249, 5%)
	80	$[Pt(NCNH)(COD)]^+$ (344, 33%), $[M+H]^+$ (417, 100%), $[2M+H]^+$ (833, 20%), plus a number of unidentified species.
[Pt{NMeC(=NCN)S}(PPh$_3$)$_2$] (**4b**)	20	$[M+H]^+$ (833, 100%), $[2M+H]^+$ (1666, 19%)
	60	$[Pt\{Ph_2P(o\text{-}C_6H_4)\}(Ph_3P)]^+$ (**6**, 718, 6%), $[(Ph_3P)_2PtNCNH]^+$ (760, 100%), $[M+H]^+$ (833, 55%), $[2M+H]^+$ (1666, 20%)
[Pt{NMeC(=NCN)S}(DPPF)] (**4c**)	20	$[M+H]^+$ (863, 100%), $[2M+H]^+$ (1725, 12%)
	60	$[Pt(NCNH)(DPPF)]^+$ (790, 55%), $[M+H]^+$ (863, 100%), $[2M+H]^+$ (1725, 43%)
[Pt{NMeC(=NCN)S}(DPPE)](**4d**)	20	$[M+H]^+$ (707, 100%), $[2M+H]^+$ (1413, 18%)
[Pt{NMeC(=NCN)S}(PBu$^n_3$)$_2$] (**4e**)	20	$[M+H]^+$ (713, 100%), $[2M+H]^+$ (1425, 4%)
	40	$[(Bu_3P)_2PtNCNH]^+$ (640, 85%), 652 (unidentified), $[M+H]^+$ (713, 100%), $[M+Na]^+$ (735, 25%), $[2M+H]^+$ (1425, 28%), $[2M+Na]^+$ (1447, 8%)
[Pt{NMeC(=NCN)S}{P(OPh)$_3$}$_2$] (**4f**)	20	$[M+H]^+$ (929, 100%)
	80	$[Pt\{o\text{-}OC_6H_4P(OPh)_2\}\{P(OPh)_3\}]^+$ (814, 88%), $[M+H]^+$ (929, 100%)
[Pt{NPhC(=NPh)S}(PPh$_3$)$_2$] (**1a**)	20–60	$[M+H]^+$ (946, 100%)
	80	$[Pt\{Ph_2P(o\text{-}C_6H_4)\}(Ph_3P)]^+$ (**6**, 718, 18%), $[Pt(NHPh)(PPh_3)_2]^+$ (811, 48%), $[M+H]^+$ (946, 100%)
[Pt{NMeC(=NCN)S}(PPh$_3$)$_2$] (**4b**) + AgNO$_3$	20	$[2M+2Ag]^{2+}$ (940.5, 100%), $[2M+Ag]^+$ (1773, 30%) plus a number of minor unidentified species
[Pt{NMeC(=NCN)S}(COD)] (**4a**) + AgNO$_3$	20	361 (unidentified), 402 (unidentified), $[M+Ag(NCCH_3)]^+$ (565), + $[2M+Ag]^+$ (941)

[a] Recorded in $CH_3CN–H_2O$.

[b] Species are identified by the major peak in the isotope distribution pattern; M = parent complex.

many instances. The principal exception was the diphenylthiourea-derived complex **1a**, which showed only an $[M+H]^+$ peak at m/z 946. Figure 2 shows the positive-ion ESMS spectrum of the triphenylphosphine complex **4b**, recorded at a cone voltage of 20 V. The two peaks are unambiguously assigned as $[M+H]^+$ (m/z 833) and $[2M+H]^+$ (m/z 1666). There is excellent agreement between observed and calculated isotope distribution patterns, shown in the inset to Fig. 2. The protonated species $[M+H]^+$ formed in the ESMS experiment is of interest. The related platinum complex **1b** derived from 1,3-diethylthiourea has been reported to give the chelated thiourea monoanion **5** upon reaction with a molar equivalent of p-toluenesulfonic acid.[4] It is likely that the imine nitrogen is also the most basic centre in the complexes **1** and **4**, and protonation for ESMS is most likely to occur at this site. Protonation at either the N-methyl or nitrile nitrogen atoms is also possible, however, and ESMS cannot distinguish between these various possibilities. Ionization can also be achieved by alkali metal cations; addition of a small quantity of KCl to the solution of **4b** yielded additional peaks due to the potassium adducts $[M+K]^+$ (m/z 871) and $[2M+K]^+$ (m/z 1704). Potassium ions have been used previously as an ionization reagent in aprotic media.[20]

Increasing the cone voltage under which the ESMS spectra are recorded typically leads to fragmentation of the complexes **4**. The triphenylphosphite complex, however, showed little tendency for fragmentation, yielding a strong $[M+H]^+$ peak up to relatively high cone voltages (*ca* 100 V). At moderate cone voltages (40–60 V), fragmentation leads to identification of species nominally formed by loss of MeNCS (for complexes **4**) or PhNCS for complex **1a** (L = PPh_3). Thus, for **4a** the species $[(COD)PtNCNH]^+$ was observed at m/z 344, whilst for the phosphine complex **4b** the corresponding species $[(Ph_3P)_2PtNCNH]^+$ was observed at m/z 760. The

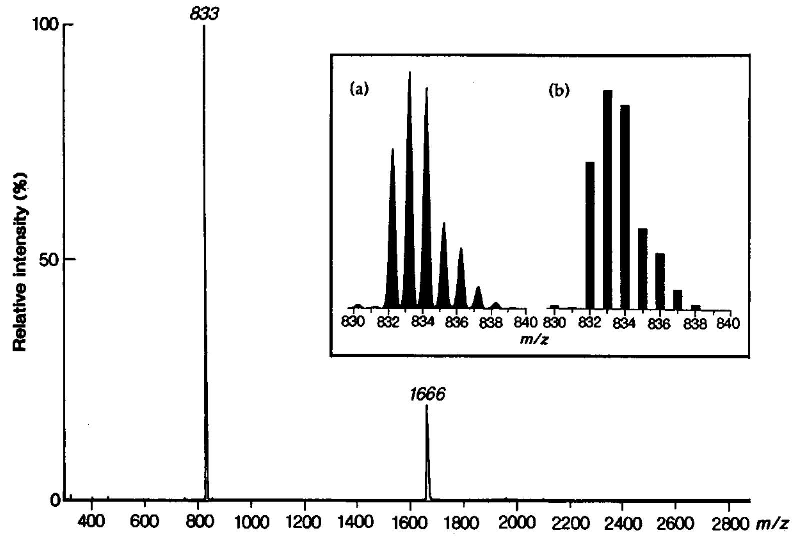


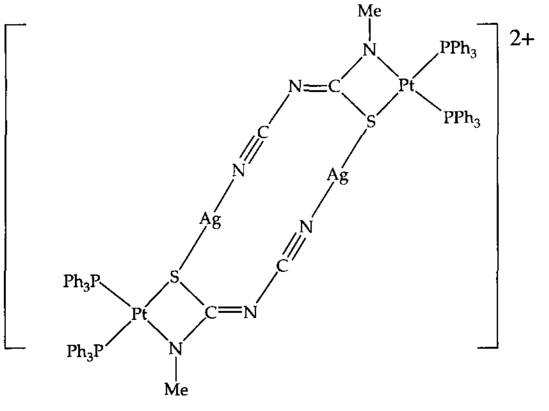
Fig. 2. Positive ion electrospray mass spectrum of $[\overline{\mathrm{Pt}\{\mathrm{NMeC}({=}\mathrm{NCN})\mathrm{S}}\}(\mathrm{PPh_3})_2]$ (**4b**) recorded at a cone voltage of 20 V. The inset shows the (a) observed and (b) calculated isotope distribution patterns for the principal ion $[\mathrm{M+H}]^+$.

nature of these species is uncertain, but may involve coordinated amido ligands, such as $[(\mathrm{Ph_3P})_2\mathrm{PtNH(CN)}]^+$. There was no evidence for fragment ions containing the PtNCMeH moiety. The loss of MeNCS clearly involves a major structural rearrangement of the complex.

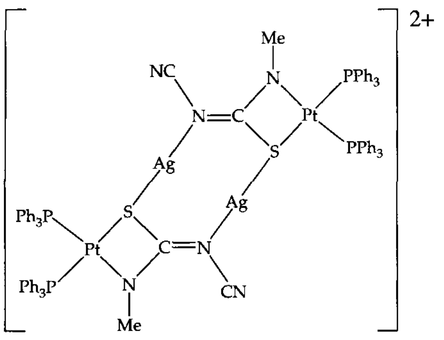
At yet higher high cone voltages (typically > 80 V), the complexes containing phosphine or triphenylphosphite ligands undergo orthometallation of the aryl groups, typified by the species **6** observed at *m*/*z* 718 for the triphenylphosphine complex **4b**. Confirmation was again assisted by the use of simulated isotope distribution patterns. Orthometallated triphenyl- and other aryl-phosphine ligands have been observed previously in ESMS spectra[21] and are well established as isolated species.[22]

The presence of the soft sulfur atom in complexes **4** suggested that it might be possible to use these complexes as "ligands" in the synthesis of heterobimetallic complexes. There is considerable literature precedent in the use of compounds containing metal–sulfur bonds in such reactions, including metal-sulfido and -thiolato complexes.[23] We have used ESMS in a preliminary study to investigate interactions between the complex **4b** and $\mathrm{Ag^+}$ ions. Excess aqueous $\mathrm{AgNO_3}$ solution was added to a solution of **4b** in $\mathrm{CH_3CN{-}H_2O}$. The peak due to $[\mathrm{M+H}]^+$ disappeared and was replaced by a number of new species. The major species, centred around *m*/*z* 940, was initially tentatively assigned as the monosilver adduct $[\mathbf{4b}\cdot\mathrm{Ag}]^+$. However, the isotope distribution pattern under high resolution conditions, shown in Fig. 3, indicated that the species is in fact a dication, *viz.* $[\mathbf{4b}\cdot\mathrm{Ag^+}]_2^{2+}$. Structural assignment of the species can only be tentative, based on the ESMS data alone. A species containing coordinated thiolate and either imine or nitrile nitrogen atoms in a dimeric structure is the most likely possibility, which would retain the preferred linear coordination at silver. The C≡N, C=N and S donor groups are the most likely to coordinate to the soft silver atom since the N—Me group is unlikely to have any donor characteristics, being essentially sp^2 hybridized, with the lone pair residing in a *p*-orbital. Molecular models suggest that the dimeric species **7** and **8** are both feasible structures, however the species **8** involving coordinated imine groups would require isomerization of the metallacycle, to place the nitrile group on the same side of the molecule as the N—Me group. The species **7** requires no such isomerization to occur prior to dimer formation and is thus the tentatively preferred structure. Silver has a strong tendency to coordinate to nitrile groups, as shown by the observation of the silver species $[\mathrm{Ag(NCCH_3)}]^+$ and $[\mathrm{Ag(NCCH_3)_2}]^+$ at *m*/*z* 148 and 189, respectively, in solutions containing $\mathrm{AgNO_3}$. The other main species detected in the ESMS spectrum of the mixture of **4b** and silver cations is the adduct $[(\mathbf{4b})_2\cdot\mathrm{Ag}]^+$, at *m*/*z* 1773.

Different ESMS behaviour was observed when excess $\mathrm{AgNO_3}$ solution was added to the COD complex **4a**. The two main platinum species identified are $[\mathbf{4a}\cdot\mathrm{Ag(NCCH_3)}]^+$ (*m*/*z* 565) and $[(\mathbf{4a})_2\cdot\mathrm{Ag}]^+$ (*m*/*z* 941), confirmed by excellent agreement



7



8

between the experimental and theoretical isotope patterns. For the diphenyl thiourea derivative **1a** (L = PPh_3), much less tendency to coordinate to Ag^+ was observed. Even in the presence of a large excess of $AgNO_3$ (evidenced by large peaks due to $[Ag(NCCH_3)]^+$ and $[Ag(NCCH_3)_2]^+$ as described above) a significant peak due to the protonated species $[M+H]^+$ (*m/z* 946) was observed. Another monocationic species at *m/z* 1116 is assigned as $[M+H+AgNO_3]^+$. These observations support the notion that the nitrile moiety of complex **4b** is involved in the coordination of this complex to Ag^+ ions.

In conclusion, ESMS provides a rapid means of screening coordination chemistry systems for complex formation, identifying promising combinations for more detailed preparative studies. Further detailed investigation of the synthesis of complexes derived from asymmetric thiourea dianions, together with their coordination chemistry, is currently in progress.

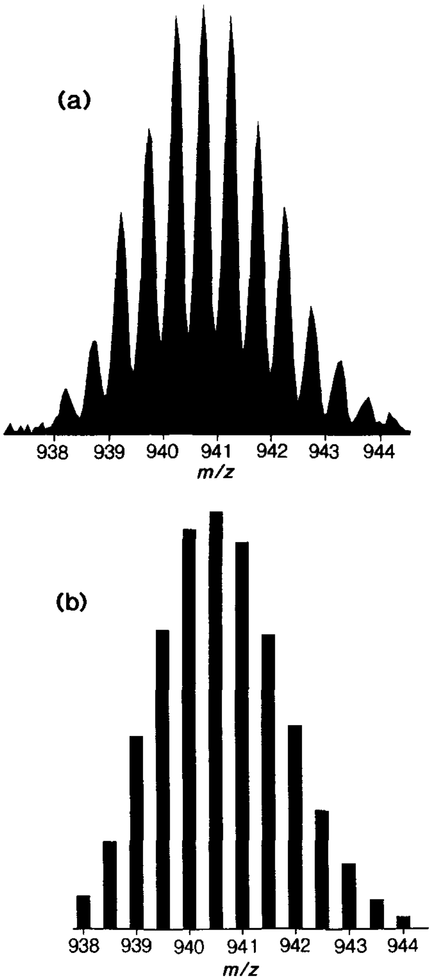


Fig. 3. (a) Observed and (b) calculated isotope distribution patterns for the species $[\mathbf{4b}\cdot Ag]_2^{2+}$, observed in the positive ion electrospray mass spectrum of a mixture of **4b** and $AgNO_3$. The 0.5 mass unit separation between adjacent peaks is characteristic of a dipositive ion.

Acknowledgements—We thank the University of Waikato for financial support, Professor Ward Robinson (University of Canterbury) for acquisition of the X-ray data set and Mrs A Upreti for recording IR spectra. The New Zealand Lottery Grants Board is acknowledged for a grant-in-aid towards the purchase of a mass spectrometer. Dr Ralph Thomson is thanked for the nOe experiments.

REFERENCES

1. S. E. Livingstone, in *Comprehensive Coordination Chemistry* (Edited by G. Wilkinson, R. D. Gillard and J. A. McCleverty), Vol. 2, section 16.6. Pergamon Press, Oxford (1987).
2. W. Henderson, R. D. W. Kemmitt, S. Mason, M. R. Moore, J. Fawcett and D. R. Russell, *J. Chem. Soc., Dalton Trans.* 1992, 59.
3. W. Henderson, B. K. Nicholson and A. G. Oliver, *J. Chem. Soc., Dalton Trans.* 1994, 1831; J. A. Daldy, J. Fawcett, W. Henderson, R. D. W. Kemmitt and D. R. Russell, *J. Chem. Soc., Dalton Trans.* 1994, 3383; W. Henderson, J. Fawcett, R. D. W. Kemmitt,

C. Proctor and D. R. Russell, *J. Chem. Soc., Dalton Trans.* 1994, 3085; W. Henderson, B. K. Nicholson and A. G. Oliver, *Polyhedron* 1994, **13**, 3099; W. Henderson, R. D. W. Kemmitt and A. L. Davis, *J. Chem. Soc., Dalton Trans.* 1993, 2247; R. D. W. Kemmitt, S. Mason, J. Fawcett and D. R. Russell, *J. Chem. Soc., Dalton Trans.* 1992, 851; R. D. W. Kemmitt, S. Mason, M. R. Moore and D. R. Russell, *J. Chem. Soc., Dalton Trans.* 1992, 409.

4. S. Okeya, Y. Fujiwara, S. Kawashima, Y. Hayashi, K. Isobe, Y. Nakamura, H. Shimomura and Y. Kushi, *Chem. Lett.* 1992, 1823.
5. R. S. Pilato, K. A. Eriksen, E. I. Stiefel and A. L. Rheingold, *Inorg. Chem.* 1993, **32**, 3799.
6. P. Piraino, G. Bruno, G. Tresoldi, G. Faraone and G. Bombieri, *J. Chem. Soc., Dalton Trans.* 1983, 2391.
7. K. Yamanari, Y. Kushi, A. Fuyuhiro and S. Kaizaki, *J. Chem. Soc., Dalton Trans.* 1993, 403; K. Yamanari, K. Okusako, Y. Kushi and S. Kaizaki, *J. Chem. Soc., Dalton Trans.* 1992, 1621.
8. See, for example: P. K. Baker, M. E. Harman, S. Hughes, M. B. Hursthouse and K. M. A. Malik, *J. Organomet. Chem.* 1995, **498**, 257; M. Gupta, R. E. Cramer, K. Ho, C. Pettersen, S. Mishina, J. Bell and C. M. Jensen, *Inorg. Chem.* 1995, **34**, 60; S. Wang, R. J. Staples and J. P. Fackler Jr, *Acta Cryst.* 1994, **C50**, 889; R. Castro, J. A. Garcia-Vazquez, J. Romero, A. Sousa, W. Hiller and J. Strähle, *Polyhedron* 1994, **13**, 273; K. Yamanari, S. Dogi, K. Okusako, T. Fujihara, A. Fuyuhiro and S. Kaikazi, *Bull. Chem. Soc. Jpn* 1994, **67**, 3004; E. S. Raper, A. M. Britton and W. Clegg, *J. Chem. Soc., Dalton Trans.* 1990, 3341; T. S. Lobana, P. K. Bhatia and E. R. T. Tiekink, *J. Chem. Soc., Dalton Trans.* 1989, 749.
9. M. Bardaji, N. G. Connelly, M. C. Gimeno, P. G. Jones, A. Laguna and M. Laguna, *J. Chem. Soc., Dalton Trans.* 1995, 2245; M. Gupta, R. E. Cramer, K. Ho, C. Pettersen, S. Mishina, J. Belli and C. M. Jensen, *Inorg. Chem.* 1995, **34**, 60; M. G. Davidson, S. C. Llewellyn, M.-I. L. Solera, P. R. Raithby, R. Snaith and D. S. Wright, *J. Chem. Soc., Chem. Commun.* 1992, 573; M. A. Ciriano, J. J. Perez-Torrente, F. Viguri, F. J. Lahoz, L. A. Oro, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Chem. Soc., Dalton Trans.* 1990, 1493.
10. U. Bodensieck, L. Hoferkamp, H. Stoeckli-Evans and G. Süss-Fink, *J. Chem. Soc., Dalton Trans.* 1993, 127; E. Boroni, G. Predieri, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Organomet. Chem.* 1993, **451**, 163; E. W. Ainscough, A. M. Brodie, S. L. Ingham, T. G. Kotch, A. J. Lees, J. Lewis and J. M. Waters, *J. Chem. Soc., Dalton Trans.* 1994, 1.
11. J. X. McDermott, J. F. White and G. M. Whitesides, *J. Am. Chem. Soc.* 1976, **98**, 6521.
12. D. L. Oliver and G. K. Anderson, *Polyhedron* 1992, **11**, 2415.
13. L. J. Arnold, *J. Chem. Educ.* 1992, **69**, 811.
14. G. M. Sheldrick, SHELXL-93, SHELXS-86 and SHELXLA-90 Programs. University of Göttingen (1986–1993).
15. T. G. Appleton, H. C. Clark and L. E. Manzer, *Coord. Chem. Rev.* 1973, **10**, 335.
16. R. V. Chastain, C. G. McCarty and D. M. Wieland, *Chem. Commun.* 1971, 198.
17. J. B. Fenn, M. Mann, C. K. Meng, S. F. Wu and C. M. Whitehouse, *Mass Spectrom. Rev.* 1990, **9**, 37.
18. For selected recent references see: R. Colton, A. D'Agostino, J. C. Traeger and W. Kläui, *Inorg. Chim. Acta* 1995, **233**, 51; R. Colton, K. L. Harrison, Y. A. Mah and J. C. Traeger, *Inorg. Chim. Acta* 1995, **231**, 65; R. Arakawa, T. Matsuo, K. Nozaki, T. Ohno and M. Haga, *Inorg. Chem.* 1995, **34**, 2464; L. A. P. Kane-Maguire, R. Kanitz and M. M. Sheil, *J. Organomet. Chem.* 1995, **486**, 243.
19. See for example: A. M. Bond, R. Colton, A. D'Agostino, A. J. Downard and J. C. Traeger, *Analyt. Chem.* 1995, **67**, 1691; W. Henderson, C. O. Miles and B. K. Nicholson, *J. Chem. Soc., Chem. Commun.* 1995, 889; A. M. Bond, R. Colton, Y. A. Mah and J. C. Traeger, *Inorg. Chem.* 1994, **33**, 2548; R. Colton, J. C. Traeger and V. Tedesco, *Inorg. Chim. Acta* 1993, **210**, 193; T. J. Cardwell, R. Colton, N. Lambropoulos, J. C. Traeger and P. J. Marriott, *Anal. Chim. Acta* 1993, **280**, 239; A. M. Bond, R. Colton, A. D'Agostino, J. Harvey and J. C. Traeger, *Inorg. Chem.* 1993, **32**, 3952.
20. R. Saf, C. Mirtl and K. Hummel, *Tetrahedron Lett.* 1994, **35**, 6653.
21. J. Fawcett, W. Henderson, R. D. W. Kemmitt, D. R. Russell and A. Upreti, *J. Chem. Soc., Dalton Trans.*, in press.
22. C. Scheffknecht, A. Rhomberg, E. P. Müller and P. Peringer, *J. Organomet. Chem.* 1993, **463**, 245, and references therein.
23. See for example: A. Castellanos, J. J. Garcia, H. Torrens, N. Bailey, C. O. R. de Barbarin, A. Gutierrez and F. del Rio, *J. Chem. Soc., Dalton Trans.* 1994, 2861; M. Zhou, Y. Xu, C.-F. Lam, P.-H. Leung, L.-L. Koh, K. F. Mok and T. S. A. Hor, *Inorg. Chem.* 1994, **33**, 1572; M. Zhou, Y. Xu, C.-F. Lam, L.-L. Koh, K. F. Mok, P.-H. Leung and T. S. A. Hor, *Inorg. Chem.* 1993, **32**, 4660; S. S. Chojnacki, Y.-M. Hsaio, M. Y. Darensbourg and J. H. Reibenspies, *Inorg. Chem.* 1993, **32**, 3573; Y. Huang, R. J. Drake and D. W. Stephan, *Inorg. Chem.* 1993, **32**, 3022; M. Zhou, Y. Xu, L.-L. Koh, K. F. Mok, P.-H. Leung and T. S. A. Hor, *Inorg. Chem.* 1993, **32**, 1875; D. M. Roundhill, *Inorg. Chem.* 1980, **19**, 557.