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Coordination chemistry of the metalloligand [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] with nickel(II) complexes - an electrospray mass spectrometry directed synthetic study

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Synopsis

Reactions of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] with a range of nickel(II) substrates have been explored using electrospray mass spectrometry, coupled with synthesis and characterization in

selected systems. The X-ray crystal structure of $[Pt_2(\mu-S)_2(PPh_3)_4Ni(NCS)(PPh_3)]^+PF_6^-$ is reported.

Abstract

The reactivity of $[Pt_2(\mu-S)_2(PPh_3)_4]$ towards a range of nickel(II) complexes has been probed using electrospray ionisation mass spectrometry (ESMS) coupled with synthesis and characterisation in selected systems. Reaction of $[Pt_2(\mu-S)_2(PPh_3)_4]$ with $Ni(NCS)_2(PPh_3)_2$ gives $[Pt_2(\mu-S)_2(PPh_3)_4Ni(NCS)(PPh_3)]^+$, isolated as its BPh_4^- salt; the same product is obtained in the reaction of $[Pt_2(\mu-S)_2(PPh_3)_4]$ with $[NiBr_2(PPh_3)_2]$ and KNCS. An X-ray structure determination reveals the expected sulfide-bridged structure, with an N-bonded thiocyanate ligand and a square-planar coordination geometry about nickel. A range of nickel(II) complexes NiL_2, containing β-diketonate, 8-hydroxyquinolinate, or salicylaldehyde oximate ligands react similarly, giving $[Pt_2(\mu-S)_2(PPh_3)_4NiL]^+$ cations.

1. Introduction

The metalloligand $[Pt_2(\mu-S)_2(PPh_3)_4]$ **1** contains highly nucleophilic sulfur atoms, and has been used to assemble a wide variety of sulfide-bridged homo- and hetero-metallic aggregates.[1,2] Complexes containing other phosphine ligands such as dppe ($Ph_2PCH_2CH_2PPh_2$) also show similar behaviour, but have been less studied to date.[3] Recently, we have been using the technique of electrospray ionisation mass spectrometry (ESMS) to probe reactions of $[Pt_2(\mu-S)_2(PPh_3)_4]$ [2,4] and the selenium analogue $[Pt_2(\mu-Se)_2(PPh_3)_4]$ [5] towards metal halides and related substrates, and some of these results

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have been summarised in a review.[6] The results from these mass spectrometry studies can then be used to direct subsequent macroscopic syntheses to the more promising reaction systems, thus providing an efficiency of operation, and conserving precious metals.

In this paper we report the application of this methodology to the study of the reactivity of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** towards a range of nickel(II) complexes. Little work has been done to date in this area; while derivatives of the $\{Pt_2S_2\}$ core are known for many metals, the only nickel species known to date is $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ni(dppe)]^{2+}$.[7] Indeed, all other compounds containing the Pt-S-Ni-S four-membered ring system are complexes of thiolate ligands, where each S is alkylated.[8] As will be demonstrated, the $\{Pt_2S_2\}$ core supports nickel substrates bearing a wide range of ancillary ligands.

2. Results and discussion

2.1 Reactivity with nickel(II) phosphine complexes

As an initial entry into the chemistry of the $\{Pt_2S_2\}$ core with nickel(II), complexes containing bidentate phosphines were investigated, since the only known nickel adduct of the $\{Pt_2S_2\}$ core is of the dppeNi^{2+} fragment.[7] Reactions involving a 1:1 molar ratio of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with the various nickel complexes were probed by electrospray mass spectrometry (ESMS), as a convenient and established method for monitoring the coordination chemistry of the $\{Pt_2S_2\}$ system.[2,4,6]   [NiCl$_2$(dppe)] was studied, together with related complexes [NiCl$_2$(dppp)] [dppp = Ph$_2$P(CH$_2$)$_3$PPh$_2$] and [NiCl$_2$(dppf)] [dppf = 1,1'-Fe(C$_5$H$_5$PPh$_2$)$_2$], for comparative purposes. In all cases, the common ion observed was the dicationic $[Pt_2(\mu\text{-}S)_2(PPh_3)_4NiL]^{2+}$ ion (L = bidentate ligand). In the case of the dppf system, the orange $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ni(dppf)]^{2+}$ (*m/z* 1058) ion was the only one observed. The reaction with [NiCl$_2$(bipy)$_2$].MeOH likewise gave solely yellow-orange $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ni(bipy)]^{2+}$ (*m/z* 858.5). Confirmation was readily achieved by examining the

isotopic envelopes of these ions, which display the expected patterns, with a 0.5 m/z separation between adjacent peaks, the characteristic signature of a dication. For [NiCl$_2$(dppe)] and [NiCl$_2$(dppp)] the ions [[Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$NiL]$^{2+}$ (L = dppe, m/z 980; L = dppp, m/z 987) were observed as major ions, but other species were also observed with significant intensity, such as [PtCl(PPh$_3$)(dppe)]$^+$ (m/z 891) and [PtCl(PPh$_3$)(dppp)]$^+$ (m/z 905), and [Pt(dppe)$_2$]$^{2+}$ (m/z 495.5).

The reactivity of a series of triphenylphosphine-nickel complexes was then determined. In these experiments the products formed are influenced by the greater lability of a triphenylphosphine ligand, compared with a bidentate ligand. Reactions of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] with the complexes [NiX$_2$(PPh$_3$)$_2$] (X = Cl, Br, I) in methanol were followed by ESMS, and gave very similar spectra. The common major ions, summarised in Table 1, are [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Ni(PPh$_3$)]$^{2+}$ (m/z 912), [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Ni(PPh$_3$)(MeCN)]$^{2+}$ (m/z 932.5), [PtX(PPh$_3$)$_3$]$^+$ (the latter formed by disintegration of the platinum starting complex), and the monocationic adduct [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$NiX(PPh$_3$)]$^+$ common to all three complexes. Acetonitrile is commonly used as a mobile phase solvent in the electrospray mass spectrometer used in this study, and some contamination of the methanol mobile phase used is possible. The observation of a coordinated acetonitrile ligand clearly indicates an affinity of nickel(II) for this ligand. It is noteworthy that the relative intensity of the ion [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$NiI(PPh$_3$)]$^+$ was somewhat greater than those of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$NiX(PPh$_3$)]$^+$ (X = Cl, Br), which were of roughly equal intensity. When the methanolic solutions were evaporated to dryness and the products redissolved in acetonitrile, the monocations [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$NiX(PPh$_3$)]$^+$ disappeared (presumably due to solvolysis of the halide by MeCN) and the major ions observed in all three systems were [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Ni(PPh$_3$)]$^{2+}$ and [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Ni(PPh$_3$)(MeCN)]$^{2+}$, with the [PtX(PPh$_3$)$_3$]$^+$ ions also observed.

In contrast to the range of species observed in the halide systems, the reaction of [Ni(NCS)$_2$(PPh$_3$)$_2$] with [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] yielded a single product ion at m/z 1882, identified as [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Ni(NCS)(PPh$_3$)]$^+$. This product was subsequently synthesised

on the macroscopic scale and isolated by addition of either $NaBPh_4$ or NH_4PF_6 to the reaction solution, giving **2a** and **2b** respectively. The infrared spectrum of the diamagnetic complex **2a** shows a CN stretching frequency at 2092 cm^{-1}, which is consistent with an N-bonded thiocyanate ligand.[**9**] The reaction of the related pyridine (py) complex $[Ni(NCS)_2(py)_4]$ with $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ was also investigated, and gave a brown solution containing the $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ni(NCS)(py)]^+$ ion (*m/z* 1699).

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **2a** in CDCl$_3$ shows two inequivalent PPh$_3$ ligands bonded to platinum, at δ 17.8 and 15.7 (*syn* and *anti* to the NCS ligand on Ni), with superposition of a singlet at δ 17.8 due to the triphenylphosphine on Ni. The two $^1J(PtP)$ coupling constants are fairly similar, at 3235 and 3190 Hz. When the complex is dissolved in d^6-DMSO, there is a slight change in chemical shifts, such that the resonances no longer overlap (δ PPh$_3$-Pt 17.2, 14.8; δ PPh$_3$-Ni 15.3). Variable-temperature ^1H NMR in this solvent resulted in coalescence of the PPh$_3$-Ni resonance with one set of Pt-PPh$_3$ resonances (at 360 K), followed by coalescence of all resonances at 400 K. On cooling back to 298 K the complex was largely unchanged, except for a small amount of Ph$_3$PO decomposition product (δ 43) (air was not excluded). Room temperature fluxional behaviour in a related {Pd$_3$S$_2$} aggregate was reported previously [**10**]; in this case, the greater lability of palladium compared to platinum is expected to be a significant factor. The PPh$_3$ ligand on nickel does not appear to be labile on the NMR timescale at room temperature, since addition of free PPh$_3$ to a CDCl$_3$ solution of **2a** did not broaden the ^{31}PPh$_3$-Ni resonance, and a sharp peak for free PPh$_3$ (δ -5) was observed.

An attempt was made to find an alternative route to $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ni(NCS)(PPh_3)]^+$, by substitution of a halide by thiocyanate. Thus, the reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with one equivalent of $[NiBr_2(PPh_3)_2]$, followed by addition of KNCS gives an orange solution in which the desired cation $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ni(NCS)(PPh_3)]^+$ was identified by ESMS as the base peak, with a small ion due to $[Pt(NCS)(PPh_3)_3]^+$ (*m/z* 1040) also observed.

Displacement of the thiocyanate ligand of **2a** by other anions can also be readily probed using ESMS. Thus, addition of excess NaBr to a methanol solution of **2a** yielded (even after standing for 48 h) only a minor ion at *m/z* 1904 assigned as the bromide complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4NiBr(PPh_3)]^+$. Reaction of **2a** with NaNO$_2$ also resulted in displacement of the thiocyanate ligand giving $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ni(NO_2)(PPh_3)]^+$ (*m/z* 1870) as a medium intensity ion. Greater reactivity was shown with NaN$_3$ which yielded (in addition to the starting material) the species $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ni(N_3)(PPh_3)]^+$ (*m/z* 1866), as well as an unidentified species at *m/z* 827. On standing overnight, the intensity of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ni(N_3)(PPh_3)]^+$ increased relative to $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ni(NCS)(PPh_3)]^+$, though the base peak was now $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ni(N_3)]^+$ (*m/z* 1603) formed by loss of PPh$_3$ (presumably by reaction with azide ions). Electrospray mass spectrometry clearly provides a rapid and informative technique for monitoring such exchange reactions.

*2.2 X-ray crystal structure of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Ni(NCS)(PPh$_3$)]PF$_6$ **2b***

Since no crystal structures have been previously carried out on nickel adducts of the {Pt$_2$S$_2$} core, and to confirm the square-planar geometry at nickel, the molecular structure of the title complex was determined. Crystals were grown from acetone-hexane, and the complex crystallises with three molecules of acetone per cation. Selected bond lengths and angles for the structure are summarised in Table 2. The molecular structure, Figure 1, shows a triangular {NiPt$_2$} core capped on both sides by symmetrical μ$_3$-sulfido ligands. The d^8 platinum centres exhibit square-planar coordination environments, while the nickel(II) centre also adopts a square-planar geometry, chelated by the two sulfides and coordinated to a PPh$_3$ ligand and a thiocyanate. No significant metal-metal interactions occur [Pt(1)....Ni(1) 2.9440(8), Pt(2)....Ni(1) 2.9651(8) Å] and the Pt(1)....Pt(2) distance of 3.300 Å lies beyone the expected range for a metal-metal bond. The dihedral angle that the {Pt$_2$S$_2$} butterfly makes along the S(1)....S(2) axis is 128.3°, with the two sulfides chelated

to the nickel at an angle of 83.22(6)°. As might be expected from the greater steric bulk of a PPh$_3$ ligand compared to NCS, the P(5)-Ni-S(2) bond angle, 96.30(7)°, is larger than N(1)-Ni-S(1), 91.9(2)°. The P(5)-Ni-N(1) bond angle in **2b** [89.0(2)°] is slightly smaller than that in *trans*-[Ni(NCS)$_2$(PPh$_3$)$_2$] [92.1(1)°] [**11**] probably reflecting the greater steric bulk in the {Pt$_2$S$_2$} system.

The thiocyanate ligand is N-bonded, as is observed in all other structures of nickel(II) complexes containing phosphine and thiocyanate ligands, which, like **2b**, also have square-planar geometries.[**12**] The Ni-N distance in **2b** [1.865(6) Å] is notably longer than in other triphenylphosphine-nickel-thiocyanate complexes, such as *trans*-[Ni(NCS)$_2$L$_2$] [L = 1'-(diphenylphosphino)ferrocenecarboxylic acid] which has Ni-N 1.819(5) Å [**13**] and *trans*-[Ni(NCS)$_2$(PPh$_3$)$_2$] where the Ni-N distance is 1.819(3) Å [**11**]. The Ni-P distance in **2b** [2.198(2) Å] is somewhat shorter than in both *trans*-[Ni(NCS)$_2$L$_2$] [L = 1'-(diphenylphosphino)ferrocenecarboxylic acid] [Ni-P 2.263 Å] [**13**] and *trans*-[Ni(NCS)$_2$(PPh$_3$)$_2$] [2.245 Å] [**11**]. This is presumably because in **2b** the PPh$_3$ on Ni is *trans* to a triply-bridging sulfido ligand (with presumably a lower *trans*-influence than another PPh$_3$ ligand), thus shortening the Ni-P bond in **2b**. Likewise, in **2b** the NCS ligand is also *trans* to a sulfido ligand, but this presumably has a **higher** *trans* influence than another NCS ligand present in the *trans*-[Ni(NCS)$_2$(phosphine)$_2$] type complexes compared above, so the Ni-N bond in **2b** is longer.

It is worth commenting on the nature of the product observed in **2b**, i.e. a monocation with one phosphine and one NCS ligand, and a square-planar nickel(II). Presumably, the species [{Pt$_2$S$_2$}Ni(PPh$_3$)$_2$]$^{2+}$ is disfavoured because of steric bulk of the PPh$_3$ ligands, and the relatively short Ni-S and Ni-P bonds which accentuate this. (By comparison, species of the type [{Pt$_2$S$_2$}Pt(phosphine)$_2$]$^{2+}$ are well-known, and stable [**7**,**14**]) In addition, due to the much greater lability of nickel(II) compared with platinum(II), a PPh$_3$ ligand can be lost from the former metal more easily, thereby reducing steric congestion.

It might be initially expected that the nickel might adopt a tetrahedral geometry to minimise steric interactions with the bulky PPh$_3$ ligands. Indeed, nickel(II) complexes can adopt square-planar, tetrahedral or octahedral geometries, depending on the ligands. However, nickel(II) thiocyanate complexes invariably have a square-planar geometry, and the same electronic effect also appears to direct the square-planar nickel geometry in **2a**.

2.3 Reactivity with nickel(II) complexes containing bidentate monoanionic nitrogen/oxygen donor ligands

With the success in the nickel-thiocyanate system discussed in the preceding Sections, other nickel(II) complexes containing chelating monoanionic ligands (L) were trialed, with the expectation of obtaining stable, monocationic NiL$^+$ adducts of the {Pt$_2$S$_2$} core. We recently described ESMS-monitored reactions of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] with various transition metal acetylacetonate complexes, though nickel(II) was not investigated.[**2**,**4**] Reaction of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] with [Ni(acac)$_2$(H$_2$O)$_2$] (acac = CH$_3$COCHCOCH$_3$) gave a brown solution for which ESMS showed only the [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Ni(acac)]$^+$ ion (*m/z* 1660). In analogous fashion, the related nickel(II) β-diketonate complexes derived from thenoyltrifluoroacetone [Ni(tta)$_2$(H$_2$O)$_2$] and ethyl benzoylacetate [Ni(PhCOCHCOOEt)$_2$(H$_2$O)$_2$] gave solely [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Ni(diketonate)]$^+$ ions. The attempted 'one-pot' synthesis of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Ni(acac)]$^+$ starting from [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$], one equivalent of NiCl$_2$.6H$_2$O and excess Hacac in methanol was unsuccessful, with the major species being [Pt(acac)(PPh$_3$)$_2$]$^+$ (*m/z* 818) in addition to a small amount of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Ni(acac)]$^+$, as shown by ESMS.

The nickel(II)-diketonate complexes **3** - **5** were subsequently isolated on the macroscopic scale by addition of NaBPh$_4$ to the filtered reaction solutions, and fully characterised. The ^{31}P-{^{1}H} NMR spectra show single ^{31}P environments. This is as expected for the acac complex, and in the case of the unsymmetrical complexes (*viz.* **4** and

5) the different substituents on the diketonate ligand are presumably too distant from the PPh$_3$ ligands on platinum to effect any inequivalence between them (or, less likely, the system is fluxional at room temperature). Magnetic susceptibility measurements on complexes **3** and **5** indicate that they are diamagnetic in the solid state, and therefore contain square-planar nickel(II). Because sharp NMR spectra can be obtained on these complexes they are also diamagnetic in solution, and so it is possible to rule out a tetrahedral nickel(II) centre, which would render all platinum-coordinated phosphines equivalent.

Other NiL$_2$ complexes also gave clean reactions with [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$]. Reaction with [Ni(hq)$_2$].2H$_2$O (hq = anion of 8-hydroxyquinoline) gave yellow [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Ni(hq)]$^+$ (*m/z* 1706). The complex was isolated as a yellow solid **6** by addition of NaBPh$_4$ to the reaction mixture. When excess nickel complex is used, there is a small ion due to [Pt(hq)(PPh$_3$)$_2$]$^+$ at *m/z* 863, which is removed when the [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Ni(hq)]$^+$ ion is precipitated with BPh$_4$$^-$. The ^{31}P-{^{1}H} NMR spectrum shows two sets of inequivalent PPh$_3$ ligands [^{1}J(PtP) coupling constants 3163, 3245 Hz], as a result of the different (N,O) donor atoms at the nickel centre. In a similar fashion, reaction of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] with the nickel(II) complex of salicylaldehyde oximate [Ni(salox)$_2$] gave the corresponding monocation [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Ni(salox)]$^+$, which was also isolated and characterised as its BPh$_4$$^-$ salt **7**. Complexes **6** and **7** were found to be diamagnetic, indicating the presence of square-planar nickel(II) centres.

In contrast to the reactivity of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] with the nickel(II) complexes described above, no reaction was observed with the dimethylglyoximate complex [Ni(dmg)$_2$]; this highly insoluble nickel complex is used in gravimetric determinations of nickel, [**15**] and this, together with its pronounced stability are the most likely reasons for its lack of reactivity.

The possibility of exchange reactions on the {Pt$_2$S$_2$} core can easily be demonstrated by ESMS. When **2a** was stirred for 24 h with an excess of [Ni(acac)$_2$(H$_2$O)$_2$] in MeOH-

CH$_2$Cl$_2$, the ESMS spectrum revealed that the complex [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Ni(acac)]$^+$ (*m/z* 1661) is largely formed, with a small amount of residual [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Ni(NCS)(PPh$_3$)]$^+$ (*m/z* 1882).

2.4 Reactivity with nickel(II) complexes containing bidentate monoanionic sulfur donor ligands

Nickel(II) forms NiL$_2$ complexes with chelating sulfur donor ligands L, such as dithiophosphinate (R$_2$PS$_2^-$) and dithiocarbamate (R$_2$NCS$_2^-$). Complexes [Ni(S$_2$PR$_2$)$_2$] and [Ni(S$_2$CNR$_2$)$_2$] have been investigated with [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$], since it is of interest to see if a simple reaction occurs in this case. The liberated R$_2$PS$_2^-$ or R$_2$NCS$_2^-$ ions are good ligands towards platinum(II), and might effect fragmentation of the {Pt$_2$S$_2$Ni} aggregate, ligand substitution (of the triphenylphosphine ligands), or the formation of more complex products.

Reaction of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] with [Ni(S$_2$CNEt$_2$)$_2$] results in dissolution of the starting materials and formation of a brown solution which contains mainly [Pt(S$_2$CNEt$_2$)(PPh$_3$)$_2$]$^+$ (*m/z* 868) together with a small amount of the desired [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Ni(S$_2$CNEt$_2$)]$^+$ (*m/z* 1710). Likewise, reaction with [Ni(S$_2$PBu$^i_2$)$_2$] gave mainly [Pt(S$_2$PBu$^i_2$)(PPh$_3$)$_2$]$^+$ (*m/z* 929) plus some [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Ni(S$_2$PBu$^i_2$)]$^+$ (*m/z* 1771). No attempt was made to isolate the {Pt$_2$S$_2$} adducts in these cases.

2.5 Conclusions

We have successfully used electrospray mass spectrometry to probe the reactivity of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] with a wide range of nickel(II) complexes. This mass spectrometry-directed approach allows identification of those reaction systems which give single products worthy of macroscopic isolation and characterisation. The dominant theme in this area is

the formation of monocationic products, either through use of a monoanionic chelating ligand (e.g. acetylacetonate or 8-hydroxyquinolinate anions, and related ligands) or, in the case of triphenylphosphine complexes, through retention of a coordinated monodentate anion (such as thiocyanate). Dicationic products $[Pt_2(\mu-S)_2(PPh_3)_4NiL]^{2+}$ are confirmed [7] when L is a neutral bidentate phosphine ligand (such as dppf) or 2,2'-bipyridine. In these cases, the reduced lability results in retention of this ligand in preference to an anion.

3. Experimental

3.1 General procedures

Reactions were carried out in LR grade methanol, with no precautions taken to exclude air or moisture. Products were recrystallised 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. Water was double distilled prior to use.

^1H and $^{13}C-\{^1H\}$ NMR spectra were recorded on a Bruker DRX400 instrument (^1H 400.13 MHz; ^{13}C 100.62 MHz) and $^{31}P-\{^1H\}$ NMR spectra were recorded on a Bruker AC300P instrument at 121.51 MHz. NMR spectra were typically recorded in $CDCl_3$ solution, and referenced relative to residual $CHCl_3$ or (for ^{31}P spectra) external H_3PO_4. Electrospray mass spectra were recorded in positive-ion mode, in MeCN-H_2O (1:1 v/v) solvent, and cone voltages were varied between 20 and 50 V to explore fragmentation of the various ions. Assignment of ions was assisted by comparison of experimental and calculated isotope patterns, the latter obtained by means of the *Isotope* program.[16] Melting points were recorded on a Reichert Thermopan apparatus and are uncorrected. Infrared spectra were recorded on a BIO-RAD FTS-40 Spectrometer. Microanalytical data were obtained from the Campbell Microanalytical Laboratory, University of Otago, New

Zealand, or the Microanalytical Laboratory, Department of Chemistry, National University of Singapore. Magnetic susceptibility measurements were carried out using a Gouy balance.

The complexes $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** [**17**], $[Ni(acac)_2(H_2O)_2]$ [**18**], $[Ni(tta)_2(H_2O)_2]$ [**19**], $[Ni(PhCOCHCOOEt)_2(H_2O)_2]$ [**20**], $[Ni(hq)_2].2H_2O$ [**21**], $[Ni(salox)_2]$ [**22**], $[NiCl_2(PPh_3)_2]$ [**23**], $[NiBr_2(PPh_3)_2]$ [**23**], $[NiI_2(PPh_3)_2]$ [**23**], $[Ni(NCS)_2(PPh_3)_2]$ [**11**], $[Ni(NCS)_2(py)_4]$ [**24**], $[NiCl_2(dppe)]$ [**25**], $[NiCl_2(dppp)]$ [**25**], $[NiCl_2(dppf)]$ [**26**], $[NiCl_2(bipy)_2].MeOH$ [**27**], and $[Ni(S_2PBu^i_2)_2]$ [**28**] were prepared by minor modifications of the literature procedures. $NaBPh_4$, KNCS, nickel(II) chloride hexahydrate and acetylacetone were used as supplied from BDH, and NH_4PF_6 was used as supplied by Aldrich.

3.2 Mass spectrometry experiments

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ **1** (25 mg) and the nickel substrate (e.g $NiX_2(PPh_3)_2$, X = Cl, Br, I, NCS; 1 mole equivalent) were suspended in *ca.* 20 mL methanol, and stirred for 24 h. A small sample (*ca.* 5 drops) of the reaction solution was withdrawn, diluted with methanol (2 mL), centrifuged (to remove any traces of insoluble matter) and injected directly into the mass spectrometer.

3.3 Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ni(NCS)(PPh_3)]^+BPh_4^-$ **2a**

The complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (301 mg, 0.200 mmol) and $[Ni(NCS)_2(PPh_3)_2]$ (88 mg, 0.126 mmol) were suspended in methanol (20 mL) and stirred for 24 hours, giving a red-brown solution. After filtration, $NaBPh_4$ (80 mg, 0.234 mmol) in methanol (5 mL) was added with stirring, immediately giving a light brown precipitate. This was filtered, washed with water (5 mL), methanol (5 mL), diethyl ether (5 mL) and dried under vacuum to give **2a** (225 mg, 51%). IR, ν(CN) 2092 cm^{-1} (s). A sample for elemental analysis was

recrystallised as red-orange needles by vapour diffusion of diethyl ether into a dichloromethane solution of the complex. Found: C, 62.2; H, 4.4; N, 0.9. $C_{115}H_{95}NBNiP_5Pt_2S_3$ requires C, 62.7; H, 4.4; N, 0.6%. $^{31}P-\{^1H\}$ NMR, δ 17.8 [d, $^1J(PtP)$ 3235, $^2J(PP)$ 11], 15.7 [d, $^1J(PtP)$ 3190, $^2J(PP)$ 11] and 15.8 [s, PPh_3-Ni]. The complex was found to be diamagnetic by Gouy balance measurements.

3.4 Alternative synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ni(NCS)(PPh_3)]^+BPh_4^-$ 2a

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (200 mg, 0.133 mmol) and $[NiBr_2(PPh_3)_2]$ (99 mg, 0.133 mmol) in methanol (30 mL) were stirred for 1 h, giving a slightly cloudy brown solution. A solution of KNCS (20 mg, 0.206 mmol) in methanol (3 mL) was added, resulting in a colour change to a bright orange solution. The reaction mixture was stirred for 48 h, and analysis by ESMS showed $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ni(NCS)(PPh_3)]^+$ (m/z 1882, 100%) and $[Pt(NCS)(PPh_3)_3]^+$ (m/z 1039, 30%). The solution was filtered, and solid $NaBPh_4$ (100 mg, 0.292 mmol) added to the clear orange filtrate with stirring, giving an orange precipitate which was filtered off, washed with water (10 mL), methanol (5 mL) and diethyl ether (5 mL), and dried under vacuum to give an orange-brown solid (155 mg) which was identified as pure 2a by ESMS and $^{31}P-\{^1H\}$ NMR spectroscopy.

3.5 Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ni(NCS)(PPh_3)]^+PF_6^-$ 2b

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (71 mg, 0.0472 mmol) and $[Ni(NCS)_2(PPh_3)_2]$ (33 mg, 0.0472 mmol) were suspended in methanol (20 mL) and stirred for 24 h, giving a red-brown solution. After filtration, and washing of the filter with additional methanol (2 x 5 mL) excess NH_4PF_6 (10 mg, 0.0613 mmol) was added. After stirring for a further 1 h, a red solid precipitated. Distilled water (10 mL) was added to complete precipitation. The red solid was filtered, and washed with water (2 x 10 mL), ethanol (5 mL), diethyl ether (5 mL) and

dried under vacuum giving a red powder of **2b** (82 mg, 79%). Found: C, 53.9; H, 3.7; P, 9.2; S, 4.7. $C_{91}H_{75}F_6NNiP_6Pt_2S_3$ requires C, 53.9; H, 3.7; P, 9.2; S, 4.7%.

3.6 Synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ni(acac)]^+BPh_4^-$ **3**

The complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (300 mg, 0.200 mmol) and $[Ni(acac)_2(H_2O)_2]$ (58 mg, 0.198 mmol) were suspended in methanol (20 mL) and stirred for 24 hours, giving a brownish solution. After filtration, $NaBPh_4$ (80 mg, 0.234 mmol) in methanol (5 mL) was added to the filtrate with stirring, giving a light brown precipitate. This was filtered, washed with water (5 mL), methanol (5 mL), ether (5 mL) and dried under vacuum to give **3** (207 mg, 53%). A sample for elemental analysis was recrystallised as deep red rosettes by vapour diffusion of diethyl ether into a dichloromethane solution of the complex. Found: C, 60.8; H, 4.6. $C_{101}H_{87}BNiO_2P_4Pt_2S_2$ requires C, 61.3; H, 4.4%. ESMS [M]$^+$, *m/z* 1660 (100%). $^{31}P\text{-}\{^1H\}$ NMR, δ 21.1 [s, $^1J(PtP)$ 3180]. ^1H NMR, δ 7.50 - 6.89 (m, 80H, PPh_3 and BPh_4^-), 5.12 (s, CH) and 1.72 (s, 6H, CH_3).

3.7 Attempted alternative synthesis of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ni(acac)]^+BPh_4^-$ **3**

To a suspension of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (50 mg, 0.033 mmol) in methanol (10 mL) was added $NiCl_2.6H_2O$ (8 mg, 0.033 mmol) and acetylacetone (3 drops, excess) and the mixture stirred for 45 hours. The resulting cloudy light green solution was analysed by ESMS which revealed $[Pt(acac)(PPh_3)_2]^+$ (*m/z* 818) as the major species, together with a trace of the desired $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ni(acac)]^+$ (*m/z* 1660).

3.8 Synthesis of [Pt₂(μ-S)₂(PPh₃)₄Ni(tta)]⁺BPh₄⁻ **4**

Following the method for **3**, [Pt₂(μ-S)₂(PPh₃)₄] (201 mg, 0.134 mmol) with [Ni(tta)₂(H₂O)₂] (72 mg, 0.142 mmol) and NaBPh₄ (46 mg, 0.135 mmol) gave a light brown powder of **4** (109 mg, 39%). A sample for elemental analysis was recrystallised as deep red rosettes by vapour diffusion of diethyl ether into a dichloromethane solution of the complex. Found: C, 59.7; H, 3.9. $C_{107}H_{91}BNNiO_3P_4Pt_2S_2$ requires C, 59.4; H, 4.0%. $^{31}P\text{-}\{^1H\}$ NMR, δ 19.4 [s, $^1J(PtP)$ 3200]. ^1H NMR, δ 7.49 - 6.89 (m, 83H, PPh₃, BPh₄⁻ and thienyl H) and 6.20 (s, CH).

3.9 Synthesis of [Pt₂(μ-S)₂(PPh₃)₄Ni(PhCOCHCOOEt)]⁺BPh₄⁻ **5**

Following the method for **3**, [Pt₂(μ-S)₂(PPh₃)₄] (200 mg, 0.133 mmol) with [Ni(PhCOCHCOOEt)₂(H₂O)₂] (65 mg, 0.136 mmol) and NaBPh₄ (130 mg, 0.380 mmol) gave an light brown powder of **5** (150 mg, 54%). Found: C, 61.8; H, 4.4. $C_{107}H_{91}BNNiO_3P_4Pt_2S_2$ requires C, 62.0; H, 4.4%. ESMS [M]⁺ *m/z* 1753, 100%. $^{31}P\text{-}\{^1H\}$ NMR, δ 18.5, [s, $^1J(PtP)$ 3190]. ^1H NMR, δ 7.50 - 6.90 (m, 85H, Ph), 5.50 (s, 1H, CH), 3.64 [q, CH₂, $^3J(HH)$ 5.3] and 1.13 [t, CH₃, $^3J(HH)$ 5.3].

3.10 Synthesis of [Pt₂(μ-S)₂(PPh₃)₄Ni(hq)]⁺BPh₄⁻ **6**

Following the method for **3**, [Pt₂(μ-S)₂(PPh₃)₄] (200 mg, 0.133 mmol) with [Ni(hq)₂].2H₂O (46 mg, 0.120 mmol) gave a cloudy, bright yellow solution. Filtration followed by addition of NaBPh₄ (120 mg, 0.351 mmol) to the filtrate gave yellow-orange **6** (150 mg, 62%). Found: C, 61.7; H, 4.2; N, 0.5. $C_{105}H_{86}BNNiOP_4Pt_2S_2$ requires C, 62.3; H, 4.3; N, 0.7%. ESMS [M]⁺ *m/z* 1706, 100%. $^{31}P\text{-}\{^1H\}$ NMR, δ 17.6 [s, br, $^1J(PtP)$ *ca.* 3163, $^2J(PP)$ not discernible] and 17.3 [s, br, $^1J(PtP)$ *ca.* 3245, $^2J(PP)$ not discernible].

*3.11 Synthesis of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Ni(salox)]$^+$BPh$_4^-$ **7***

[Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] (200 mg, 0.133 mmol) with [Ni(salox)$_2$] (44 mg, 0.133 mmol) in methanol (30 mL) was stirred for 22.5 h giving a slightly cloudy brown solution. After filtration to remove a small amount of insoluble green material, NaBPh$_4$ (120 mg, 0.351 mmol) was added with stirring to the clear orange-brown filtrate. The resulting orange-brown precipitate was filtered off, washed with methanol (10 mL) and diethyl ether (10 mL) and dried under vacuum to give 138 mg (51%) of **7**. Found: C, 61.1; H, 4.3; N, 0.6. C$_{103}$H$_{86}$BNNiO$_2$P$_4$Pt$_2$S$_2$ requires C, 61.3; H, 4.3; N, 0.7%. ESMS [M]$^+$ *m/z* 1698, 100%. ^{31}P-{^{1}H} NMR, δ 17.8, [s, ^{1}J(PtP) 3211].

*3.12 X-ray structure determination of [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Ni(NCS)(PPh$_3$)]$^+$PF$_6^-$ **2b**. 3Me$_2$CO.*

Red single crystals were grown by layering n-hexane over a red acetone solution at 4 °C. The crystals were quickly transferred from the sample vial onto a microscope containing Paratone N oil. Under the microscope, a red block (0.40 x 0.18 x 0.14 mm) was selected and quickly mounted on a glass fibre using wax.

A Bruker AXS SMART diffractometer equipped with a CCD detector was used, and Mo-Kα radiation (λ = 0.71073 Å). A total of 46826 reflections were collected (-25 ≤ *h* ≤ 21, -19 ≤ *k* ≤ 20, -34 ≤ *l* ≤ 48) in the θ range of 1.76 - 25.00°, at 223(2) K, of which 16429 were independent (R$_{int}$ = 0.0330). The structure was solved by direct methods in conjunction with standard difference Fourier techniques. Non-hydrogen atoms were refined anisotropically. There are three acetone solvent molecules per cation, and the F atoms in the PF$_6^-$ counterion are disordered. Common isotropic thermal parameters were refined for the solvent atoms. Hydrogen atoms were placed in calculated (dC-H = 0.96 Å) positions. The largest peak and hole in the difference map were 1.183 and -1.077 e Å^{-3} respectively.

The least-squares refinement converged normally with residuals of R (based on F) = 0.0444, wR (based on F^2) = 0.0970, and GOF = 1.138 [based on I > 2σ(I)]. The software SMART [29] was used for collection of frames of data, indexing reflections, and for determination of lattice parameters, SAINT [29] for integration of intensity of reflections and scaling, SADABS [30] for empirical absorption correction, and SHELXTL [31] for space group and structure determination, refinements, graphics and structure reporting.

Crystal data for $C_{100}H_{93}F_6NNiO_3P_6Pt_2S_3$: monoclinic, space group P2$_1$/n, Z = 4, a = 18.785(2), b = 14.8294(11), c = 34.665(4) Å, β = 102.032(9)°, V = 9444.7(15) Å^3, D$_{calc}$ = 1.548 g cm^{-3}, F(000) = 4400.

4. Supplementary information

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. ######. Copies of this information can be obtained free of charge from 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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Table 2. Selected bond lengths (Å) and angles (°) for [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$Ni(NCS)(PPh$_3$)]$^+$PF$_6^-$. 3Me$_2$CO (**2b**.3Me$_2$CO)

Pt(1)-S(1)	2.349(2)	Pt(1)-S(2)	2.353(1)
Pt(2)-S(1)	2.333(2)	Pt(2)-S(2)	2.356(2)
Ni(1)-S(1)	2.227(2)	Ni(1)-S(2)	2.188(2)
Pt(1)-P(1)	2.298(2)	Pt(1)-P(2)	2.284(2)
Pt(2)-P(3)	2.293(2)	Pt(2)-P(4)	2.280(2)
Ni(1)-N(1)	1.865(6)	Ni(1)-P(5)	2.198(2)
Pt(1)-S(1)-Pt(2)	89.63(5)	Pt(1)-S(2)-Pt(2)	88.98(5)
Pt(1)-S(1)-Ni(1)	80.02(5)	Pt(1)-S(2)-Ni(1)	80.74(5)
Pt(2)-S(1)-Ni(1)	81.08(5)	Pt(2)-S(2)-Ni(1)	81.37(5)
S(1)-Pt(1)-S(2)	77.15(5)	S(1)-Pt(2)-S(2)	77.41(5)
P(1)-Pt(1)-P(2)	98.80(6)	P(3)-Pt(2)-P(4)	98.88(6)
P(1)-Pt(1)-S(1)	89.37(5)	P(3)-Pt(2)-S(1)	168.52(6)
P(1)-Pt(1)-S(2)	165.64(5)	P(3)-Pt(2)-S(2)	91.99(5)
S(1)-Ni(1)-S(2)	83.22(6)	P(5)-Ni(1)-N(1)	89.0(2)
P(5)-Ni(1)-S(1)	174.77(7)	N(1)-Ni(1)-S(1)	91.9(2)
P(5)-Ni(1)-S(2)	96.30(7)	N(1)-Ni(1)-S(2)	172.9(2)

Caption for Figure

Fig 1. Molecular structure of the complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Ni(NCS)(PPh_3)]^+PF_6^-.3Me_2CO$ (**2b**.$3Me_2CO$) showing the atom numbering scheme. Thermal ellipsoids are shown at the 50% probability level. The phenyl rings of the platinum-bonded triphenylphosphine ligands and the PF_6^- counterion have been omitted for clarity.