# Dalton Transactions

Cite this: Dalton Trans., 2011, 40, 6645



# Gold(I) complexes bearing mixed-donor ligands derived from N-heterocyclic carbenes<sup>†</sup>

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*Received 19th November 2010, Accepted 12th January 2011* DOI: 10.1039/c0dt01613f

The new 2-phenylthiocarbamoyl-1,3-dimesitylimidazolium inner salt (IMes-CSNPh) reacts with [AuCl(L)] in the presence of NH<sub>4</sub>PF<sub>6</sub> to yield  $[(L)Au(SCNPh \cdot IMes)]^+$  (L = PMe<sub>3</sub>, PPh<sub>3</sub>, PCy<sub>3</sub>, CNBu<sup>+</sup>). The carbene-containing precursor [(IDip)AuCl] reacts with IMes CSNPh under the same conditions to afford the complex  $[(IDip)Au(SCNPh \cdot IMes)]^+$  (IDip = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene). Treatment of the diphosphine complex [(dppm)(AuCl)<sub>2</sub>] with one equivalent of IMes·CSNPh yields the digold metallacycle, [(dppm)Au2(SCNPh·IMes)]2+, while reaction of  $[L_2(AuCl)_2]$  with two equivalents of IMes·CSNPh results in  $[(L_2){Au(SCNPh \cdot IMes)}_2]^{2+}$  ( $L_2 = dppb$ , dppf, or dppa; dppb = 1,4-bis(diphenylphosphino)butane, dppf = 1,1'-bis(diphenylphosphino)ferrocene, dppa = 1,4-bis(diphenylphosphino)acetylene). The homoleptic complex  $[Au(SCNPh \cdot IMes)_2]^+$  is formed on reaction of [AuCl(tht)] (tht = tetrahydrothiophene) with two equivalents of the imidazolium-2-phenylthiocarbamoyl ligand. This product reacts with AgOTf to yield the mixed metal compound [AuAg(SCNPh·IMes)<sub>2</sub>]<sup>2+</sup>. Over time, the unusual trimetallic complex [Au(AgOTf)<sub>2</sub>(SCNPh·IMes)<sub>2</sub>]<sup>+</sup> is formed. The sulfur-oxygen mixed-donor ligands IMes·COS and SIMes COS (SIMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene) were used to prepare  $[(L)Au(SOC \cdot IMes)]^+$  and  $[(L)Au(SOC \cdot SIMes)]^+$  from  $[(L)AuCl] (L = PPh_3, CN^{\dagger}Bu)$ . The bimetallic examples  $[(dppf){Au(SOC \cdot IMes)}_2]^{2+}$  and  $[(dppf){Au(SOC \cdot SIMes)}_2]^{2+}$  were synthesized from the reaction of [(dppf)(AuCl)<sub>2</sub>] with the appropriate ligand. Reaction of [(tht)AuCl] with one equivalent of IMes COS or SIMes COS yields  $[Au(SOC \cdot IMes)_2]^+$  and  $[Au(SOC \cdot SIMes)_2]^+$ , respectively. The compounds [(Ph<sub>3</sub>P)Au(SCNPh·IMes)]PF<sub>6</sub>, [(Cy<sub>3</sub>P)Au(SCNPh·IMes)]PF<sub>6</sub> and [Au(AgOTf)<sub>2</sub>(SCNPh·IMes)<sub>2</sub>]OTf were characterized crystallographically.

# Introduction

Over the past twenty years, *N*-heterocyclic carbenes (NHCs) have become firmly established as electron-rich and versatile donor ligands for transition metals.<sup>1</sup> They have challenged or replaced phosphines in many spheres due to their stronger  $\sigma$ -donating properties and potential for steric tuning.<sup>2</sup> Thus far, research on NHCs has mostly focused on derivatives of imidazole, triazole, or thiazole, of which imidazol-2-ylidene and its saturated analogue imidazolin-2-ylidene have been the subject of the most in-depth studies.<sup>3</sup> The potential for a wide variety of substituents on the nitrogen atoms, including unsymmetrical combinations, helped maintain the sustained interest in these divalent carbon species, since the first representatives of this family were isolated and characterized in the late  $1980s.^4$ 

Perhaps the most notable examples of complexes with NHCs employed as ancillary ligands are the Grubbs-type secondgeneration ruthenium–alkylidene catalysts for olefin metathesis (Fig. 1).<sup>5</sup> NHCs have also been applied to gold(I) chemistry,<sup>6</sup> first by Burini<sup>7</sup> and then by Raubenheimer and co-workers,<sup>8</sup> who pioneered the synthesis of gold–NHC complexes. The straightforward preparation of [(NHC)AuCl] derivatives devised by Nolan and co-workers further contributed to the widespread use of these compounds in organometallic catalysis.<sup>9</sup> In addition to all of the transition metals, NHCs form stable complexes with main group elements, such as lithium or beryllium,<sup>10</sup> as well as lanthanides



Fig. 1 Notable examples of complexes bearing NHC ligands.

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and actinides.<sup>11</sup> They have also found applications on their own as nucleophilic reagents and organocatalysts.<sup>12</sup>

Despite their high profile, NHCs have scarcely been used as starting materials for the synthesis of other ligands. Upon reaction with carbon dioxide, they form inner salts, which can be stored and handled with no particular precautions.<sup>13</sup> Such NHC·CO<sub>2</sub> zwitterions are rather labile in solution and may be used as surrogates to free carbenes for organometallic synthesis and catalytic applications.<sup>14</sup> Betaines are also obtained when carbon disulfide reacts with NHCs or precursors thereof.<sup>15</sup> The NHC·CS<sub>2</sub> adducts differ from the NHC·CO<sub>2</sub> series in that the dithiocarboxylate moiety shows no significant lability upon reaction with metals.<sup>16</sup> The coordination chemistry of these stable zwitterions remained almost unexplored<sup>17</sup> previous to recent work based on rutheniumarene<sup>18</sup> or vinyl complexes.<sup>19</sup> These latter reports built on a contemporary study of five imidazol(in)ium-2-dithiocarboxylates, whose stereoelectronic properties were thoroughly investigated.<sup>20</sup> Recently we have extended the study of this ligand set to the synthesis of gold(I) complexes and gold nanoparticles,<sup>21</sup> as part of a program to explore multimetallic compounds and the surface functionalisation of nanoparticles.22

Our interest in mixed-donor ligands<sup>23</sup> led us to examine a similarly underused class of zwitterions of the type NHC·CSNR, obtained by reaction of NHCs with aryl isothiocyanates.<sup>16,24</sup> The asymmetry and the choice of donor atom introduce options lacking in the NHC·CS<sub>2</sub> ligands, as well as an additional site of steric modification on the nitrogen donor. In this contribution, we investigate the coordination chemistry of the new 2-phenylthiocarbamoyl-1,3-dimesitylimidazolium inner salt (IMes·CSNPh) with various gold(1) precursors. We also report the first gold(1) complexes of the O,S-mixed-donor ligands, IMes·COS and SIMes·COS, formed upon treatment of the corresponding free NHCs with carbon oxysulfide.

### **Results and discussion**

#### Complexes with a sulfur-nitrogen mixed-donor ligand

The ligand used in this study is the 1,3-bis(2,4,6-trimethylphenyl)-2-N-phenylthiocarbamoyl imidazolium inner salt, IMes-CSNPh (1). Although a number of NHC·CSNR zwitterions are known in the literature,16,24 this particular compound had not been described. It was isolated in 81% yield using a one-pot procedure involving deprotonation of 1,3-dimesitylimidazolium chloride (IMes·HCl) with sodium hydride to generate the corresponding free imidazol-2-ylidene carbene in situ, followed by reaction with phenyl isothiocyanate. Somewhat surprisingly, this betaine was unstable in deuterated chloroform, so <sup>1</sup>H NMR analysis was carried out in acetone- $d_6$  or CD<sub>2</sub>Cl<sub>2</sub>. Seven distinct proton environments were observed with the mesityl methyl substituents resonating at ca. 2.35 and 2.39 ppm in a 1:2 ratio. This observation suggests that the protons of the ortho-methyl groups are rendered equivalent on the NMR timescale. In acetone- $d_6$ , the N-phenyl protons gave rise to a triplet at 6.79 ppm, a doublet at 6.89 ppm, and a triplet in the 7.03–7.07 ppm region, overlapping with a sharp singlet assigned to the meta-C<sub>6</sub>H<sub>2</sub> protons at 7.05 ppm. The deshielded imidazole HC=CH protons were observed as a sharp singlet at 7.66 ppm. Further evidence for the composition of the ligand was provided by electrospray mass spectrometry (ESI-MS),

which gave a molecular ion at m/z 440, and good agreement of elemental analysis with calculated values.

A dichloromethane solution of the archetypal gold(I) phosphine complex, [AuCl(PPh<sub>3</sub>)], was treated with a small excess of the IMes CSNPh ligand (1) in the presence of ammonium hexafluorophosphate in methanol for 1 h at room temperature (Scheme 1). After work up, a light yellow crystalline solid was obtained in 61% yield. Only one phosphorus-containing product was detected by <sup>31</sup>P NMR spectroscopy (singlet at 37.3 ppm). The <sup>1</sup>H NMR spectrum of complex 2 showed two closely spaced resonances at 2.32 and 2.35 ppm for the mesityl aliphatic protons, while the NPh protons resonated between 6.16 and 6.84 ppm with the ortho component showing the greatest shift with respect to the value recorded for the free ligand. This is not surprising given that the NPh protons are closest to the AuPPh<sub>3</sub> unit, the coordination of which also results in an increase in N-C double bond character. The meta protons of the mesityl groups were observed at 7.05 ppm, slightly upfield of the imidazole HC=CH protons at 8.19 ppm, which showed the largest shift compared to the free ligand. <sup>13</sup>C NMR data were recorded for 2, including an HSQC (Heteronuclear Single Quantum Coherence) experiment. The most deshielded signal at 153.4 ppm was assigned to the imidazolium C2 carbon, while the CSN carbon at 145.1 ppm resonated as a doublet due to a 4.1 Hz coupling with the phosphorus nucleus. The overall chemical composition of  $[(Ph_3P)Au(SCNPh \cdot IMes)]PF_6(2)$ was corroborated by ESI-MS, which gave an abundant molecular ion at m/z 898, as well as good agreement of elemental analysis with calculated values. Single crystals of 2 were grown by vapour diffusion of diethyl ether into a dichloromethane solution of the complex. A suitable crystal was chosen for X-ray diffraction analysis (Fig. 2). The results of this study are discussed below (see Structural discussion).



Fig. 2 Molecular structure of the cation in 2. Selected bond lengths (Å) and angles (°): Au–P(41) 2.2670(4), Au–S(1) 2.3021(4), S(1)–C(2) 1.7423(15), C(2)–C(4) 1.489(2), C(2)–N(3) 1.2659(19), C(4)–N(5) 1.3357(19), C(4)–N(8) 1.3452(19); P(41)–Au–S(1) 167.432(14), C(2)–S(1)–Au 112.15(5). Hydrogen atoms and the hexafluorophosphate counteranion were omitted for clarity.



Scheme 1 Preparation of gold(I)–(2-*N*-phenylthiocarbamoyl-1,3-dimesitylimidazolium) complexes 2–12.

Substantial steric effects are expected within complexes of generic formula [(L)Au(SCNPh·IMes)]<sup>+</sup> given the proximity of the thiocarbamoyl ligand NPh moiety to the gold(1) centre. The greater steric encumbrance introduced by the tricyclohexylphosphine ligand compared to triphenylphosphine was investigated using the complex [AuCl(PCy<sub>3</sub>)] as starting material instead of [AuCl(PPh<sub>3</sub>)] (Scheme 1). The colourless product obtained was formulated as [(Cy<sub>3</sub>P)Au(SCNPh·IMes)]PF<sub>6</sub> (**3**) on the basis of a new singlet at 58.6 ppm in the <sup>31</sup>P NMR spectrum and multiplets between 1.20 and 1.84 ppm in <sup>1</sup>H NMR spectroscopy attributed to the phosphine ligand. A molecular ion at m/z 916 was observed in 100% abundance. Single crystals of this product were obtained (Fig. 3) and a structural study undertaken (*vide infra*). The trimethylphosphine analogue, [(Me<sub>3</sub>P)Au(SCNPh·IMes)]PF<sub>6</sub> (**4**),

was prepared in the same manner (Scheme 1). Spectroscopic data due to the IMes CSNPh ligand were similar to those found for **2** and **3**, whereas the retention of the PMe<sub>3</sub> ligand was confirmed by the presence of a doublet at 1.37 ppm in the <sup>1</sup>H NMR spectrum, showing coupling of 11.5 Hz to the phosphorus nucleus.

In order to extend our investigations of the gold(1) fragments beyond gold–phosphine units, the *tert*-butyl isocyanide precursor [AuCl(CN<sup>1</sup>Bu)] was treated with IMes·CSNPh in the presence of NH<sub>4</sub>PF<sub>6</sub> to provide [('BuNC)Au(SCNPh·IMes)]PF<sub>6</sub> (**5**) in moderate yield (Scheme 1). The CN<sup>1</sup>Bu substituent exerts a low steric demand and has been used previously to form thiolate complexes possessing distinctive solid-state structures.<sup>25</sup> The presence of the 'Bu substituent in the complex was confirmed by a sharp singlet at 1.58 ppm due to its nine equivalent protons.



Fig. 3 Molecular structure of the cation in 3. Selected bond lengths (Å) and angles (°): Au–P(41) 2.2731(6), Au–S(1) 2.3084(6), S(1)–C(2) 1.748(3), C(2)–C(4) 1.493(3), C(2)–N(3) 1.271(3), C(4)–N(5) 1.338 (3), C(4)–N(8) 1.331(3); P(41)–Au–S(1) 169.04(2), C(2)–S(1)–Au 107.71(8). Hydrogen atoms and the hexafluorophosphate counteranion were omitted for clarity.

As mentioned above (cf. Fig. 1), NHC ligands have entered the arena of gold(I) chemistry, challenging the ubiquity of  $[AuCl(PR_3)]$ complexes. The compound [AuCl(IDip)], featuring the 1,3-bis(2,6diisopropylphenyl)imidazol-2-ylidene ligand, was used to prepare  $[(IDip)Au(SCNPh \cdot IMes)]PF_{6}$  (6), again in moderate yield due to partial solubility of the product in the ethanol used for work up (Scheme 1). <sup>1</sup>H NMR analysis of the product showed signals arising from the IDip moiety in addition to those due to the IMes-CSNPh ligand. Two sets of doublets at 1.14 and 1.16 ppm were observed for the isopropyl methyl protons, while the adjacent methine unit gave a septet at 2.49 ppm. Both signals show mutual coupling of  ${}^{3}J_{HH} = 6.9$  Hz. The overall chemical composition of [(IDip)Au(SCNPh·IMes)]PF<sub>6</sub> (6) was confirmed by ESI-MS and good agreement of elemental analysis with calculated values. Unfortunately, neither complex 5 nor 6 formed crystals of sufficient quality for X-ray diffraction.

The next stage in our investigations was to explore the synthesis of digold complexes with IMes-CSNPh (1). Previous studies have shown that the length of the bridging hydrocarbon chain in the diphosphine compounds [ $\{Ph_2P(CH_2)_nPPh_2\}(AuCl)_2$ ] is often the source of their structural diversity in the solid state.<sup>26</sup> For longer hydrocarbon chain lengths, such as butylene in [(dppb)(AuCl)\_2], intramolecular aurophilic interactions<sup>27</sup> are not observed;<sup>28</sup> whereas for a single methylene bridge in [(dppm)(AuCl)\_2], 'A-frame' configurations with short contacts between neighbouring gold(1) centres are favoured.<sup>29</sup> For this reason the dppm motif has been utilized in earlier work on dithio ligands, *e.g.* [(dppm)Au\_2(S\_2CNR\_2)]<sup>+</sup>, to access metallacycles.<sup>30</sup>

The reaction of  $[(dppb)(AuCl)_2]$  with two equivalents of IMes·CSNPh in the presence of NH<sub>4</sub>PF<sub>6</sub> yielded  $[(dppb){Au(SCNPh·IMes)}_2](PF_6)_2$  (7) in 62% yield (Scheme 1). The protons of the chelating diphosphine butylene bridge gave rise to <sup>1</sup>H NMR signals at 1.38 and 2.10 ppm corresponding to four protons each as unresolved multiplets, while a single resonance at 34.2 ppm in the <sup>31</sup>P NMR spectrum confirmed the presence of only one phosphorus environment. Fast atom bombardment (FAB) mass spectrometry revealed a molecular ion at m/z 1844. Elemental analysis supported the proposed composition.

A less usual diphosphine variant is found in the 1,2-bis(diphenylphosphino)acetylene complex, [(dppa)(AuCl)<sub>2</sub>], which exhibits a rigid, linear configuration within the Ph<sub>2</sub>P-C=C-PPh<sub>2</sub> unit.<sup>31</sup> This starting material was used to synthesize  $[(dppa){Au(SCNPh \cdot IMes)}_2](PF_6)_2$  (8) (Scheme 1). The <sup>31</sup>P NMR spectrum of the product showed a single resonance at 9.1 ppm. The twenty protons from the four phenyl groups gave rise to a broad multiplet between 7.63 and 7.65 ppm in the <sup>1</sup>H NMR spectrum, while FAB-MS analysis revealed a molecular ion at m/z 1812. A further metal centre was introduced into this type of assembly through the use of  $[(dppf)(AuCl)_2]$  as a precursor to  $[(dppf){Au(SCNPh \cdot IMes)}_2](PF_6)_2$  (9), which exhibited two broad singlets at 3.97 and 4.45 ppm in <sup>1</sup>H NMR spectroscopy. The flexibility of the dppf unit could in theory allow a metallacycle to form.32 However, reaction with one or two equivalents of IMes CSNPh resulted in 9, which displayed spectroscopic features consistent with the coordination of two IMes-CSNPh units (no change in the chemical shift of the NPh protons). This stoichiometry was further supported by FAB mass spectrometry and elemental analysis.

The reaction of [(dppm)(AuCl)<sub>2</sub>] with one equivalent of IMes CSNPh led to the formation of a light yellow solid (Scheme 1). Integration of the triplet resonance observed at 3.38 ppm ( ${}^{2}J_{\rm HP}$  11.8 Hz) for the methylene protons of the dppm ligand indicated the formation of the metallacycle  $[(dppm)Au_2(SCNPh \cdot IMes)](PF_6)_2$  (10). Based on literature precedent, it is likely that the close proximity of the gold centres in 10 permits aurophilic interactions to guide the formation of a cyclic product, as found in many dithiocarbamate compounds of the form [(dppm)Au<sub>2</sub>(S<sub>2</sub>CNR<sub>2</sub>)]<sup>+</sup>,<sup>30</sup> or in the more closely related compound [(dppm)Au<sub>2</sub>(S<sub>2</sub>C·IMes)](PF<sub>6</sub>)<sub>2</sub>.<sup>21</sup> A second route giving access to the bis(triflate) salt of 10 instead of the bis(hexafluorophosphate) compound was also investigated (see Experimental section). It involved removal of the chloride ligands in [(dppm)(AuCl)<sub>2</sub>] by AgOTf and yielded a product of greater purity.

With many 1,1-dithio ligands, such as dithiocarbamate anions, homoleptic, metallacyclic, digold complexes of generic formula  $[Au_2(S_2CNR_2)_2]$  are commonly formed, typically with a short separation of gold(I) centres.<sup>26,33</sup> This trend was further supported when [AuCl(tht)] (tht = tetrahydrothiophene) was treated with the dithiocarboxylate betaine IMes  $CS_2$ , yielding [Au<sub>2</sub>(S<sub>2</sub>C·IMes)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>.<sup>21</sup> In contrast, the reaction between the same gold precursor and either one or two equivalents of IMes CSNPh (1) resulted in the formation of the monogold species  $[Au(SCNPh \cdot IMes)_2](PF_6)$  (11), in which the gold centre bears a formal negative charge, thereby requiring only a single hexafluorophosphate counteranion (Scheme 1). This formulation was based on elemental analysis and mass spectrometry data, with the latter displaying a 100% abundant molecular ion at m/z 1075. Monovalent gold has a greater affinity for sulfur compared to nitrogen, but the outcome was still surprising, given that many cyclic species are known with similar mixed-donor ligands, such as 2-mercaptopyridine in  $[Au_2(S, N-Spy)_2]$ .<sup>34</sup> The steric demand of the NPh groups might explain the different coordination behaviour exhibited by 11. Indeed, the most significant chemical shift change



Scheme 2 Addition of silver triflate to gold(1)–(2-phenylthiocarbamoyl-1,3-dimesitylimidazolium) complex 11.

in <sup>1</sup>H NMR spectroscopy was shown by the *ortho*-NPh protons, which resonated at 5.68 ppm in the complex compared to 6.89 ppm in the free ligand.

In order to ascertain whether or not coordination to the pendant nitrogen donors in compound 11 was possible, this complex was treated with one equivalent of AgOTf (Scheme 1 and 2). The <sup>1</sup>H NMR spectrum of the product exhibited resonance patterns similar to 11 with some significant changes in their chemical shifts. All five protons of the N-phenyl substituent were shifted downfield (consistent with deshielding due to the effect of coordination), with the largest displacements (+0.2 ppm) being observed for the para and meta protons to 6.98 and 7.12 ppm, respectively. There was also a significant change in the resonance attributed to the imidazole HC=CH protons from 7.37 to 7.62 ppm. Mass spectrometry (FAB) displayed a molecular ion at m/z 1183, as well as signals for  $[M + OTf]^+$  at 1333 and  $[M - Ag]^+$  at 1075. The overall composition was further supported by elemental analysis data to be  $[AuAg(SCNPh \cdot IMes)_2](PF_6)(OTf)$  (12). The formulation shown in Scheme 1 is the most likely one in terms of bonding mode for the silver ion (the triflate may or may not be coordinating).

Laguna and co-workers have investigated the contacts formed between gold(I) centres and other metals (particularly those of groups 11–13), revealing some fascinating motifs in the solid state.<sup>35</sup> Attempts to grow crystals of **12** in order to determine unambiguously its structure were frustrated continually by poor crystal quality or unsuitable morphology (very thin needles). Eventually, leaving a solution of the complex in dichloromethane layered with diethyl ether over a period of a week yielded a significant number of crystals of the same type. One of them was used for X-ray diffraction analysis. However, the molecular structure obtained did not belong to the expected complex **12**, but rather to a new trimetallic species, [Au(AgOTf)<sub>2</sub>(SCNPh·IMes)<sub>2</sub>]OTf **(13**), bearing two silver triflate units bonded to the gold and sulfur atoms (Scheme 2 and Fig. 4). The most surprising features of this structure are the presence of two silver units and the fact that they are not associated with the nitrogen donors. The triflate ions bridge the silver units, while the silver ions themselves occupy a triangular arrangement with the gold centre and the sulfur donors. The remaining crystals from those grown were collected and analyzed by mass spectrometry and <sup>1</sup>H NMR spectroscopy. In the former case, a molecular ion for the AuAg<sub>2</sub> assembly was observed at m/z 1589, as well as loss of a triflate anion at m/z1333. The <sup>1</sup>H NMR spectrum obtained, on the other hand, was identical to that recorded for 12. It is probable that the structure of 13 is not retained in solution and that one silver triflate unit dissociates to reform 12. The structure of 13 raises the possibility that the AgOTf unit in 12 may be coordinated to one sulfur rather than to both nitrogen donors, however, this is undermined by the simplicity of the <sup>1</sup>H NMR spectrum, in which no inequivalence is observed for the IMes-CSNPh resonances. Attempts to obtain 13 on a preparative scale remained unsuccessful. Addition of excess AgOTf to 11 only yielded 12 and no further reaction was observed.

#### Complexes with sulfur-oxygen mixed-donor ligands

Although the reactions of NHCs with  $CO_2$  and  $CS_2$  are well documented,<sup>16</sup> no reports exist of the formation of zwitterions with COS. However, exploratory work indicated that the thiocarboxylate betaines display a stability intermediate between those of the NHC·CO<sub>2</sub> and NHC·CS<sub>2</sub> adducts when used as mixed-donor ligands for ruthenium(II) complexes.<sup>36</sup> These results prompted us to examine the coordination chemistry of gold(I) with two representative NHC·COS inner salts, *viz.*, 1,3-dimesitylimidazolium-2-thiocarboxylate (IMes·COS) and its saturated heterocycle analogue SIMes·COS.

Treatment of  $[AuCl(PPh_3)]$  with IMes·COS resulted in a pale yellow product, which was analyzed by multinuclear NMR spectroscopy to be the new compound  $[(Ph_3P)Au(SOC \cdot IMes)]PF_6$ (14) (Scheme 3). Only one singlet appeared at 37.8 ppm in <sup>31</sup>P



**Fig. 4** Molecular structure of the  $C_2$ -symmetric cation in **13**. Selected bond lengths (Å) and angles (°): Au(1)–S(1) 2.3095(13), S(1)–C(2) 1.755(6), C(2)–N(3) 1.276(7), C(2)–C(4) 1.496(7), S(1)–Au(1)–S(1A) 173.92(7). Hydrogen atoms and the trifluoromethanesulfonate counteranion were omitted for clarity.

NMR spectroscopy, while the <sup>1</sup>H NMR spectrum of compound 14 displayed signals at similar chemical shift values to those observed in 2 minus the aromatic signals due to the NPh group. The overall chemical composition was supported by electrospray mass spectrometry (+ve mode), which showed a 100% abundance for the molecular ion at m/z 823, together with good agreement of elemental analysis with calculated values. The analogous compound  $[(Ph_3P)Au(SOC \cdot SIMes)]PF_6$  (15) was formed in a similar manner from [AuCl(PPh<sub>3</sub>)] and SIMes·COS (Scheme 3). Spectroscopic data were found to be almost identical, apart from the resonance at 4.72 ppm in the <sup>1</sup>H NMR spectrum due to the four ethylene protons of the SIMes ligand heterocyclic backbone. Again, the overall chemical composition was confirmed by mass spectrometry and elemental analysis. Unsatisfactory yields were partly due to significant electrostatic behaviour, which prevented all the solids being transferred successfully from the filtration apparatus. In addition, the yield from the actual reactions was also low and this could be due to partial loss of gaseous COS in a similar manner to that observed for elimination of carbon dioxide from NHC·CO<sub>2</sub> adducts in solution. Indeed, recrystallisation of the NHC·COS ligands themselves resulted in reduced yields.<sup>36</sup> However, from spectroscopic investigations, complexes **14** and **15** did not appear to be unstable once isolated.

In order to explore the range of co-ligands supported by the NHC·COS units, the isocyanide compound [('BuNC)AuCl] was treated with IMes·COS and SIMes·COS to yield the colourless complexes [('BuNC)Au(SOC·IMes)]PF<sub>6</sub> (16) and [('BuNC)Au(SOC·SIMes)]PF<sub>6</sub> (17), respectively (Scheme 3). In addition to typical resonances for the methyl protons of the mesityl groups, a new singlet was observed at 1.63 ppm in both 16 and 17, which was attributed to the tertiary butyl unit. The presence of the isocyanide ligand was also apparent in the solid-state infrared spectrum with strong absorptions at 2240 (16) and 2239 (17) cm<sup>-1</sup>. The overall formulation was supported by molecular ions in the mass spectra and good agreement of elemental analysis with calculated values. Unfortunately, no crystals could be obtained to ascertain the solid-state implications of the slim steric profile conferred by the isocyanide ligand.

In a similar manner to the synthesis of 9,  $[dppf(AuCl)_2]$  was treated with two equivalents of either IMes·COS or SIMes·COS



Scheme 3 Preparation of gold(I)-(1,3-dimesitylimidazol(in)ium-2-thiocarboxylate) complexes. Monometallic complexes: NHC·COS = IMes·COS, L = PPh<sub>3</sub> (14), CNBu<sup>t</sup> (16); NHC·COS = SIMes·COS, L = PPh<sub>3</sub> (15), CNBu<sup>t</sup> (17). Bimetallic complexes: IMes·COS (18), SIMes·COS (19). Homoleptic complexes: IMes·COS (20), SIMes·COS (21).

to provide the complexes  $[(dppf){Au(SOC \cdot IMes)}_2](PF_6)_2$ (18) and  $[(dppf){Au(SOC \cdot SIMes)}_2](PF_6)_2$  (19), respectively (Scheme 3). The retention of the ferrocenyl unit was indicated by broad resonances at 3.89 and 4.13 ppm (for 18), while typical features were observed for the NHC ·COS ligands. Again the overall composition was confirmed by mass spectrometry and elemental analysis.

Given that the betaines IMes·CS<sub>2</sub> and IMes·CSNPh reacted very differently with [ClAu(tht)] to yield either the digold cyclic compound  $[Au_2(S_2C \cdot IMes)_2](PF_6)_2^{21}$  or the monogold complex  $[Au(SCNPh \cdot IMes)_2](PF_6)$  (11), the products from the corresponding reactions with IMes COS and SIMes COS were investigated (Scheme 3). While characteristic resonances of the thiocarboxylate ligands were observed in the <sup>1</sup>H NMR spectra, this did not provide any evidence beyond that of successful reaction to give the homoleptic complexes. However, the mass spectra (FAB positive mode) of the compounds revealed molecular ions at m/z 925 and m/z 929 for  $[Au(SOC \cdot IMes)_2](PF_6)_2$  (20) and  $[Au(SOC \cdot SIMes)_2](PF_6)_2$  (21), respectively. These monogold formulations were supported by elemental analysis and are perhaps unsurprising given the hard/soft mismatch between the gold(I) centre and the oxygen donors. Indeed, very few compounds of gold(I) bearing oxygen donors are known. To the best of our knowledge, alkoxide analogues of [(R<sub>3</sub>P)Au(SR)] are unknown and examples of carboxylate analogues of [(R<sub>3</sub>P)Au(S<sub>2</sub>CR)] are rare.37

#### Structural discussion

The geometry at the gold centre in the structure of  $[(Ph_3P)-Au(SCNPh\cdot IMes)]PF_6$  (2) is significantly bent with a P–Au–S angle of 167.432(14)° (see Fig. 2). Compared to the 178.94(3)° value determined previously for  $[(Ph_3P)Au(S_2C\cdot IMes)]PF_6$ ,<sup>21</sup> the deviation from linearity is more significant and can be traced to the greater steric demand of the NPh unit. The Au–P distances of 2.2670(4) Å in 2 and 2.2622(7) Å in the literature compound,<sup>21</sup> are

similar and longer than that of 2.2447(10) Å reported for the piperidine dithiocarbamate complex  $[(Ph_3P)Au(S_2CNC_4H_8)]$ .<sup>38</sup> The Au–S distance of 2.3021(4) in **2** is shorter than that found in either the IMes·CS<sub>2</sub> analogue [2.3223(7) Å]<sup>21</sup> or the dithiocarbamate complex [2.3344(11) Å].<sup>38</sup> With a value of 169.04(2)°, the P–Au–S linkage in  $[(Cy_3P)Au(SCNPh\cdotIMes)]PF_6$  (3) is approximately linear (see Fig. 3), though the angle is again clearly influenced by the steric requirements of the NPh unit. The Au–P distance of 2.2731(6) Å in **3** is slightly longer than the corresponding distance of 2.2670(4) Å found in **2**, while the Au–S distances are similar in both structures.

Space-filling diagrams of complexes 2, 3 and the analogous dithiocarboxylate derivative are shown in Fig. 5. They illustrate the change in coordination environment of the gold centre caused by replacing a sulfur atom in the 1,1-dithio ligand with an Nphenyl substituent. One approach to the metal centre is rendered inaccessible by the steric bulk of the aromatic ring, a feature that could be exploited for catalytic purposes in the appropriate setting. Comparison between Fig. 5b and 5c shows that the greater steric requirement of tricyclohexylphosphine compared to triphenylphosphine results in the gold centre being enclosed even more substantially by the neighbouring atoms, allowing access only from the exposed face shown in Fig. 5d. While these complexes are not expected to show catalytic activity themselves, these observations illustrate the potential for fine-tuning the access to metal centres to which the ligand is attached through alteration of the steric demands of the substituents.

The complex cation  $[Au(AgOTf)_2(SCNPh\cdot IMes)_2]^+$  in 13 has  $C_2$ symmetry about an axis that passes through the gold centre and bisects the Ag(1)  $\cdots$  Ag(1A) vector (see Fig. 4). The Ag(1)  $\cdots$  Ag(1A) separation is 3.417(3) Å. There is, however, significant disorder in the Ag<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> unit, making the bond lengths and angles, particularly those of the triflate ions, and even the conformations of this area somewhat uncertain. The bond data relating to the IMes·CSNPh ligand are comparable to those found in the structures of **2** and **3**, with the Au–S(1) distance of 2.3095(13) Å being



Fig. 5 Space-filling representations of a)  $[(Ph_3P)Au(S_2C \cdot IMes)]PF_6;^{21} b) [(Ph_3P)Au(SCNPh \cdot IMes)]PF_6 (2); c) [(Cy_3P)Au(SCNPh \cdot IMes)]PF_6 (3) with phosphorus obscured; d) rotated view of <math>[(Cy_3P)Au(SCNPh \cdot IMes)]PF_6 (3)$ .

close to the distance found in 3 but marginally longer than the corresponding bond length in 2. The S(1)-Au-S(1A) angle is almost linear at 173.92(7)°. Most of the disorder is concentrated on the triflate bridges, leaving the Ag(1)-S(1) distance of 2.5675(18) Å and the Ag(1A)–S(1A) length of 2.486(5) Å as relatively reliable. There are two Au(1)-Ag(1) distances corresponding to orientations of 77% occupancy [2.9064(12) Å] and 23% occupancy [2.960(4) Å]. These are well below the sum of the van der Waals radii for the elements (3.38 Å).<sup>39</sup> Although no directly analogous structures have been reported, these distances may be compared with some pertinent literature values. In the metallacyclic diphenylpyridylphosphine complex [AuAg(PPh<sub>2</sub>py)(OClO<sub>3</sub>)<sub>2</sub>] reported by Schmidbaur and co-workers,40 the Au-Ag distance is 2.820(1) Å, while a longer distance of 2.9314(5) Å is reported in [AuAg(PPh<sub>2</sub>CH<sub>2</sub>SPh)<sub>2</sub>](OTf)<sub>2</sub>], which is also an 8-membered cyclic species.<sup>41</sup> The diphenylmethylenedithiophosphinate complex  $[AuAg(CH_2PPh_2S)_2]$  has the gold centres coordinated through carbon while the silver is bonded to the sulfur centres, resulting in a distance between the metals of 2.9124(13) Å.<sup>42</sup> Even in non-metallacyclic systems, such as  $[Ag(\mu-dppm)_2(AuMes)_2]ClO_4$ (Mes = 2,4,6-trimethylphenyl), the Au–Ag distances are considerably below the sum of the van der Waals radii [2.944(2) and 2.946(2) Å].<sup>43</sup> These short distances have been interpreted in terms of metallophilic interactions, the like of which are commonly observed between gold(I) centres.35

## Conclusion

The gold(I) complexes described in this report demonstrate the great potential of NHC CSNR and NHC COS zwitterions

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as mixed-donor ligands. Like the related NHC·CS<sub>2</sub> betaines, their steric profile can be tailored through variation of the imidazol(in)ium substituents, while additional control over the coordination sphere of the metal can be exerted by the NR unit in the case of the NHC·CSNR adducts. In some instances, the reactivity of the *N*-phenylthiocarbamoyl and thiocarboxylate inner salts reflected that of the dithiocarboxylate betaines but in others, as in the case of the homoleptic compound (11), the reaction took a different course. As a result, new coordination behaviour was observed, allowing a further metal centre to be incorporated into the system. Work is currently underway to explore the hemilabile properties of the NHC·CSNPh and NHC·COS ligands as bidentate chelates in catalysis.

#### **Experimental section**

**General comments.** Unless otherwise stated, all experiments were carried out under aerobic conditions and the complexes obtained appear relatively stable towards the atmosphere, whether in solution or in the solid state. Some decomposition to gold colloid was occasionally observed, indicated by a purple colouration. Reagents and solvents were used as received from commercial sources. Petroleum ether is the fraction boiling in the 40–60 °C range. The following complexes and ligands were prepared as described elsewhere: [AuCl(PR<sub>3</sub>)], (R = Me,<sup>44</sup> Cy,<sup>45</sup> Ph<sup>29</sup>), [dppf(AuCl)<sub>2</sub>],<sup>46</sup> [dppm(AuCl)<sub>2</sub>],<sup>47</sup> [dppb(AuCl)<sub>2</sub>],<sup>28</sup> [dppa(AuCl)<sub>2</sub>],<sup>29</sup> [AuCl(tht)],<sup>48</sup> [AuCl(IDip)],<sup>12</sup> [AuCl(CN<sup>1</sup>Bu)],<sup>49</sup> IMes·HCl,<sup>50</sup> IMes·COS,<sup>36</sup> and SIMes·COS.<sup>36</sup> Electrospray and Fast Atom Bombardment (FAB) mass data were obtained using

Micromass LCT Premier and Autospec Q instruments, respectively. Infrared data were obtained using a Perkin Elmer Paragon 1000 FT-IR spectrometer. NMR spectroscopy was performed at 25 °C using Varian Mercury 300 and Bruker AV400 spectrometers in CDCl<sub>3</sub> unless otherwise indicated. All coupling constants are in Hertz. The <sup>31</sup>P NMR spectra of all complexes exhibited a septet resonance due to the hexafluorophosphate counteranion at -144.3 ppm ( $J_{PF} = 708$  Hz). Elemental analysis data were obtained from London Metropolitan University. The procedures given provide materials of sufficient purity for synthetic and spectroscopic purposes.

IMes-CSNPh (1). All glassware for this reaction was ovendried before use. Phenyl isothiocyanate (0.481 g, 3.56 mmol) and 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (1.21 g, 3.56 mmol) were dissolved in anhydrous THF (30 mL). Sodium hydride (0.214 g, 5.34 mmol, 60% dispersion in mineral oil) was added in portions over 15 min to the mixture cooled at 10-15 °C under N<sub>2</sub>. The suspension was stirred at 10-15 °C for 18 h. It was then quenched by adding water (10 mL) dropwise, after which all the solvents were removed. The residue was extracted with dichloromethane (30 mL), dried over anhydrous MgSO<sub>4</sub>, and the solvent removed to give the crude imidazolium inner salt. Recrystallisation from dichloromethane and petroleum ether yielded 1 as pale yellow powder (1.26 g, 81%). IR (neat): 3139, 2917, 1607, 1512, 1483, 1379, 1227, 1182, 1170, 1033, 1015, 957, 853, 768 cm<sup>-1</sup>. <sup>1</sup>H NMR (acetone-d<sub>6</sub>): 2.35 (s, 6H, p-CH<sub>3</sub>), 2.39 (s, 12H, *o*-CH<sub>3</sub>), 6.79 (t, 1H, *p*-NPh,  $J_{HH} = 7.2$  Hz), 6.89 (d, 2H, o-NPh,  $J_{\rm HH} = 9.7$  Hz), 7.03–7.07 (m, 2H + 4H, m-NPh + m-C<sub>6</sub>H<sub>2</sub>), 7.66 (s, 2H, HC=CH) ppm. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 2.39 (s, 12H, o- $CH_3$ ), 2.41 (s, 6H, *p*-CH<sub>3</sub>), 6.60 (d, 2H, *o*-NPh,  $J_{HH}$  = 7.2 Hz), 6.88 (t, 1H, *p*-NPh,  $J_{\rm HH} = 7.3$  Hz), 7.09 (s, 4H, *m*-C<sub>6</sub>H<sub>2</sub>), 7.13 (t, 2H, *m*-NPh, J<sub>HH</sub> unresolved), 7.15 (s, 2H, HC=CH) ppm. MS (ES +ve; abundance): m/z 440 (100) [M]<sup>+</sup>. Analysis: Calcd for C<sub>28</sub>H<sub>29</sub>N<sub>3</sub>S: C, 76.5; H, 6.6; N, 9.6%. Found: C, 76.7; H, 6.5; N, 9.6%.

[(Ph<sub>3</sub>P)Au(SCNPh·IMes)]PF<sub>6</sub> (2). A dichloromethane solution (10 mL) of [AuCl(PPh<sub>3</sub>)] (50 mg, 0.101 mmol) was treated with a solution of 1 (67 mg, 0.151 mmol) in dichloromethane (10 mL).  $NH_4PF_6$  (33 mg, 0.202 mmol) in methanol (10 mL) was added and the light yellow reaction mixture was stirred for 1 h at room temperature. All the solvents were removed and the crude product was dissolved in dichloromethane (10 mL). The suspension was filtered through Celite to remove NH4Cl and excess NH<sub>4</sub>PF<sub>6</sub>. Ethanol (15 mL) was added and the solvent volume was reduced until precipitation of the product was complete. The product was filtered, washed with ethanol (10 mL), petroleum ether (10 mL) and dried to give a light yellow crystalline solid (66 mg, 62%). IR (neat): 3172, 1599, 1496, 1482, 1383, 1238, 1103, 1072, 1030, 999, 912, 832 ( $v_{P-F}$ ), 760 cm<sup>-1</sup>. <sup>31</sup>P NMR (acetone- $d_6$ ): 37.3 (s, PPh<sub>3</sub>) ppm. <sup>1</sup>H NMR (acetone- $d_6$ ): 2.32 (s, 6H, p-CH<sub>3</sub>), 2.35 (s, 12H, o-CH<sub>3</sub>), 6.16 (d, 2H, o-NPh,  $J_{HH} = 7.3$  Hz), 6.54 (t, 1H, *p*-NPh,  $J_{\rm HH}$  = 7.5 Hz), 6.84 (t, 2H, *m*-NPh,  $J_{\rm HH}$  = 7.5 Hz), 7.19 (s, 4H, m-C<sub>6</sub>H<sub>2</sub>), 7.27-7.69 (m, 15H, C<sub>6</sub>H<sub>5</sub>), 8.19 (s, 2H, HC=CH) ppm. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 2.30 (s, 12H, *o*-CH<sub>3</sub>), 2.37 (s, 6H, *p*-CH<sub>3</sub>), 6.09 (d, 2H, *o*-NPh,  $J_{\text{HH}} = 7.2$  Hz), 6.40 (t, 1H, p-NPh,  $J_{\rm HH} = 7.5$  Hz), 6.77 (t, 2H, m-NPh,  $J_{\rm HH} = 7.6$  Hz), 7.11 (s, 4H, m-C<sub>6</sub>H<sub>2</sub>), 7.15–7.64 (m, 15H, C<sub>6</sub>H<sub>5</sub>), 7.53 (s, 2H, HC=CH) ppm. <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): 18.1 (s, *o*-CH<sub>3</sub>), 21.3 (s, *p*-CH<sub>3</sub>), 118.8 (s, o-NPh), 123.5 (s, HC=CH), 125.0 (s, p-NPh), 128.7 (d, ipsoPPh<sub>3</sub>,  $J_{PC} = 58.9$  Hz), 129.5 (d, *m*-PPh<sub>3</sub>,  $J_{PC} = 11.8$  Hz), 129.8 (s, *m*-NPh), 130.0 (s, *m*-Mes), 131.0 (s, *p*-Mes), 132.4 (s, *p*-PPh<sub>3</sub>), 134.5 (d, *o*-PPh<sub>3</sub>,  $J_{PC} = 13.8$  Hz), 135.7 (s, *o*-Mes), 142.0 (s, *ipso*-Mes), 145.1 (d, N=C-S,  $J_{PC} = 4.1$  Hz), 149.8 (s, *ipso*-NPh), 153.4 (s, Im NCN) ppm. MS (ES +ve; abundance): m/z 898 (100) [M]<sup>+</sup>, 440 (18) [M – AuPPh<sub>3</sub>]<sup>+</sup>. Analysis: Calcd for C<sub>46</sub>H<sub>44</sub>AuF<sub>6</sub>N<sub>3</sub>P<sub>2</sub>S: C, 52.9; H, 4.2; N, 4.0. Found: C, 53.0; H, 4.2; N, 3.9%.

 $[(Cy_3P)Au(SCNPh \cdot IMes)]PF_6$  (3). A dichloromethane solution (10 mL) of [AuCl(PCy<sub>3</sub>)] (42 mg, 0.083 mmol) was treated with a solution of 1 (40 mg, 0.091 mmol) in dichloromethane (10 mL).  $NH_4PF_6$  (27 mg, 0.166 mmol) in methanol (10 mL) was added and the light yellow reaction mixture was stirred for 1 h at room temperature. All the solvents were removed and the crude product was dissolved in dichloromethane (10 mL). The suspension was filtered through Celite to remove NH<sub>4</sub>Cl and excess  $NH_4PF_6$ . Diethyl ether (20 mL) was added and the crude solid triturated ultrasonically to give the product. The precipitate was filtered, washed with diethyl ether (10 mL), petroleum ether (10 mL) and dried to give a colourless solid (38 mg, 43%). IR (neat): 2923, 2852, 1580, 1556, 1493, 1445, 1234, 1177, 918, 834  $(v_{P-F})$ , 771, 757, 741, 726, 695 cm<sup>-1</sup>. <sup>31</sup>P NMR (acetone- $d_6$ ): 58.6 (s, PCy<sub>3</sub>) ppm. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>): 1.20–1.36 and 1.70–1.84 (m, 33H, Cy), 2.34 (s, 12H, o-CH<sub>3</sub>), 2.43 (s, 6H, p-CH<sub>3</sub>), 6.40 (d, 2H, o-NPh,  $J_{\rm HH}$  = 8.3 Hz), 7.15 (t, 1H, p-NPh,  $J_{\rm HH}$  = 8.6 Hz), 7.21 (s, 4H, m-C<sub>6</sub>H<sub>2</sub>), 7.36 (t, 2H, m-NPh,  $J_{HH} = 7.9$  Hz), 8.14 (s, 2H, HC=CH) ppm. MS (ES +ve; abundance): m/z 916 (100) [M]<sup>+</sup>, 440 (45)  $[M - AuPCy_3]^+$ . Analysis: Calcd for  $C_{46}H_{62}AuF_6N_3P_2S$ : C, 52.0; H, 5.9; N, 4.0. Found: C, 52.0; H, 5.9; N, 3.9%.

 $[(Me_3P)Au(SCNPh \cdot IMes)]PF_6$  (4). A dichloromethane solution (10 mL) of [AuCl(PMe<sub>3</sub>)] (30 mg, 0.097 mmol) was treated with a solution of 1 (47 mg, 0.107 mmol) in dichloromethane (10 mL).  $NH_4PF_6$  (32 mg, 0.194 mmol) in methanol (10 mL) was added and the light yellow reaction mixture was stirred for 1 h at room temperature. All the solvents were removed and the crude product was dissolved in dichloromethane (10 mL). The suspension was filtered through Celite to remove NH4Cl and excess NH<sub>4</sub>PF<sub>6</sub>. Ethanol (15 mL) was added and the solvent volume was reduced until precipitation of the product was complete. The precipitate was filtered, washed with ethanol (10 mL), petroleum ether (10 mL) and dried to give a light yellow solid (40 mg, 48%). IR (neat): 1491, 1447, 1417, 1383, 1227, 1188, 1164, 1104, 955, 920, 831 ( $v_{P-F}$ ), 764 cm<sup>-1</sup>. <sup>31</sup>P NMR (acetone- $d_6$ ): -2.7 (s, PMe<sub>3</sub>) ppm. <sup>1</sup>H NMR (acetone- $d_6$ ): 1.37 (d, 9H, CH<sub>3</sub>,  $J_{HP} = 11.5$  Hz), 2.33 (s, 12H, *o*-CH<sub>3</sub>), 2.44 (s, 6H, *p*-CH<sub>3</sub>), 6.07 (d, 2H, *o*-NPh,  $J_{HH}$  = 11.5 Hz), 7.13 (t, 1H, *p*-NPh,  $J_{\rm HH}$  = 8.0 Hz), 7.24 (s, 4H, *m*-C<sub>6</sub>H<sub>2</sub>), 7.45 (t, 2H, *m*-NPh,  $J_{HH}$  = 8.0 Hz), 8.17 (s, 2H, HC=CH) ppm. MS (ES +ve; abundance): m/z 712 (100) [M]<sup>+</sup>. Analysis: Calcd for C<sub>31</sub>H<sub>38</sub>AuF<sub>6</sub>N<sub>3</sub>P<sub>2</sub>S: C, 43.4; H, 4.5; N, 4.9. Found: C, 43.5; H, 4.4; N, 4.8%.

[('BuNC)Au(SCNPh-IMes)]PF<sub>6</sub> (5). A dichloromethane solution (10 mL) of [AuCl(CN'Bu)] (26 mg, 0.083 mmol) was treated with a solution of 1 (40 mg, 0.091 mmol) in dichloromethane (10 mL).  $NH_4PF_6$  (27 mg, 0.166 mmol) in methanol (10 mL) was added and the light yellow reaction mixture was stirred for 1 h at room temperature. All the solvents were removed and the crude product was dissolved in dichloromethane (10 mL). The suspension was filtered through Celite to remove  $NH_4Cl$  and

excess NH<sub>4</sub>PF<sub>6</sub>. Pentane (20 mL) was added and the crude solid triturated ultrasonically to give the product. The precipitate was filtered, washed with pentane (10 mL) and dried to give a light yellow solid (34 mg, 48%). IR (neat): 3323, 2234 ( $v_{\rm CN}$ ), 1588, 1557, 1493, 1376, 1232, 1186, 918, 831 ( $v_{\rm P-F}$ ), 761, 739, 696 cm<sup>-1</sup>. <sup>1</sup>H NMR (acetone- $d_6$ ): 1.58 (s, 9H, <sup>1</sup>Bu), 2.29 (s, 12H, *o*-CH<sub>3</sub>), 2.42 (s, 6H, *p*-CH<sub>3</sub>), 5.96 (d, 2H, *o*-NPh,  $J_{\rm HH} = 7.3$  Hz), 7.20–7.24 (m, 1H + 4H, *p*-NPh + *m*-C<sub>6</sub>H<sub>2</sub>), 7.47 (t, 2H, *m*-NPh,  $J_{\rm HH} = 7.9$  Hz), 8.23 (s, 2H, HC==CH) ppm. MS (ES +ve; abundance): m/z 719 (100) [M]<sup>+</sup>, 440 (40) [M – Au(CN<sup>1</sup>Bu)]<sup>+</sup>. Analysis: Calcd for C<sub>33</sub>H<sub>38</sub>AuF<sub>6</sub>N<sub>4</sub>PS: C, 45.8; H, 4.4; N, 6.5. Found: C, 46.0; H, 4.6; N, 6.3%.

 $[(IDip)Au(SCNPh \cdot IMes)]PF_{6}$  (6). A dichloromethane solution (10 mL) of [AuCl(IDip)] (30 mg, 0.048 mmol) was treated with a solution of 1 (23 mg, 0.053 mmol) in dichloromethane (10 mL). NH<sub>4</sub>PF<sub>6</sub> (16 mg, 0.096 mmol) in methanol (10 mL) was added and the light yellow reaction mixture was stirred for 1 h at room temperature. All the solvents were removed and the crude product was dissolved in dichloromethane (10 mL). The suspension was filtered through Celite to remove NH<sub>4</sub>Cl and excess NH<sub>4</sub>PF<sub>6</sub>. Diethyl ether (20 mL) was added and the crude solid triturated ultrasonically. The product was filtered, washed with diethyl ether (10 mL), petroleum ether (10 mL) and dried to give a light yellow solid (31 mg, 55%). IR (neat): 3149, 2965, 2927, 1557, 1459, 1384, 1227, 1184, 1060, 833 ( $v_{P-F}$ ), 759 cm<sup>-1</sup>. <sup>1</sup>H NMR (acetone- $d_6$ ): 1.14, 1.16 (d × 2, 2 × 12H, Me<sub>IDip</sub>,  $J_{HH}$  = 6.9 Hz), 2.11 (s, 12H, *o*-CH<sub>3</sub>), 2.12 (s, 6H, *p*-CH<sub>3</sub>), 2.49 (sept, 4H, CHMe<sub>IDip</sub>,  $J_{HH} = 6.8$  Hz), 6.01 (d, 2H, o-NPh,  $J_{\rm HH}$  = 8.2 Hz), 6.70 (t, 1H, p-NPh,  $J_{\rm HH}$  = 6.8 Hz), 6.80 (t, 2H, *m*-NPh,  $J_{\rm HH}$  = 7.6 Hz), 7.09 (s, 4H, *m*-C<sub>6</sub>H<sub>2</sub>), 7.42 (d, 4H, m-C<sub>6</sub>H<sub>3</sub>,  $J_{HH}$  = 7.8 Hz), 7.65 (t, 2H, p-C<sub>6</sub>H<sub>3</sub>,  $J_{HH}$  = 7.8 Hz), 7.73 (s, 2H, HC=CH<sub>IDip</sub>), 7.99 (s, 2H, HC=CH<sub>IMes</sub>) ppm. MS (ES +ve; abundance): m/z 1024 (100) [M]<sup>+</sup>, 440 (83) [M -Au(IDip)]<sup>+</sup>. Analysis: Calcd for C<sub>55</sub>H<sub>65</sub>AuF<sub>6</sub>N<sub>5</sub>PS: C, 56.5; H, 5.6; N, 6.0. Found: C, 56.4; H, 5.5; N, 5.9%.

 $[(dppb){Au(SCNPh \cdot IMes)_2}](PF_6)_2$  (7). A dichloromethane solution (10 mL) of [(dppb)(AuCl)<sub>2</sub>] (30 mg, 0.034 mmol) was treated with a solution of 1 (37 mg, 0.084 mmol) in dichloromethane (10 mL). NH<sub>4</sub>PF<sub>6</sub> (16 mg, 0.098 mmol) in methanol (10 mL) was added and the light yellow reaction mixture was stirred for 1 h at room temperature. All the solvents were removed and the crude product was dissolved in dichloromethane (10 mL). The suspension was filtered through Celite to remove NH<sub>4</sub>Cl and excess NH<sub>4</sub>PF<sub>6</sub>. Ethanol (15 mL) was added and the solvent volume was reduced until precipitation of the product was complete. The precipitate was filtered, washed with ethanol (10 mL), petroleum ether (10 mL) and dried to give a light yellow solid (41 mg, 61%). IR (neat): 3162, 2920, 1585, 1491, 1437, 1382, 1233, 1185, 1105, 918, 834 ( $v_{P-F}$ ), 743 cm<sup>-1</sup>. <sup>31</sup>P NMR (acetone- $d_6$ ): 34.2 (s, dppb) ppm. <sup>1</sup>H NMR (acetone- $d_6$ ): 1.38, 2.10 (m × 2, 2 × 4H, CH<sub>2</sub>), 2.33 (s, 12H, *p*-CH<sub>3</sub>), 2.36 (s, 24H, *o*-CH<sub>3</sub>), 6.06 (d, 4H, o-NPh,  $J_{\rm HH}$  = 7.6 Hz), 6.68 (t, 2H, p-NPh,  $J_{\rm HH}$  = 7.2 Hz), 6.86 (t, 4H, *m*-NPh,  $J_{\rm HH}$  = 8.0 Hz), 7.20 (s, 8H, *m*-C<sub>6</sub>H<sub>2</sub>), 7.42 (m, 8H,  $m-C_6H_5$ , 7.54 (m, 8H,  $o-C_6H_5$ ), 7.62 (m, 4H,  $p-C_6H_5$ ), 8.19 (s, 4H, HC=CH) ppm. MS (FAB +ve; abundance): m/z 1844 (13) [M +  $PF_6^{\dagger}$ , 623 (100)  $[M - Au(SCNPh \cdot IMes)_2]^{\dagger}$ . Analysis: Calcd for C84H86Au2F12N6P4S2: C, 50.7; H, 4.4; N, 4.2. Found: C, 50.8; H, 4.3; N, 4.2%.

 $[(dppa){Au(SCNPh \cdot IMes)_2}](PF_6)_2$  (8). A dichloromethane solution (10 mL) of [(dppa)(AuCl)<sub>2</sub>] (35 mg, 0.041 mmol) was treated with a solution of 1 (40 mg, 0.091 mmol) in dichloromethane (10 mL). NH<sub>4</sub>PF<sub>6</sub> (20 mg, 0.123 mmol) in methanol (10 mL) was added and the colourless reaction mixture was stirred for 1 h at room temperature. All the solvents were removed and the crude product was dissolved in dichloromethane (10 mL). The suspension was filtered through Celite to remove NH<sub>4</sub>Cl and excess NH<sub>4</sub>PF<sub>6</sub>. Ethanol (15 mL) was added and the solvent volume was reduced until precipitation of the product was complete. The precipitate was filtered, washed with ethanol (10 mL), petroleum ether (10 mL) and dried to give a light yellow solid (39 mg, 48%). IR (neat): 1587, 1558, 1493, 1438, 1381, 1233, 1185, 1167, 1103, 1026, 1014, 998, 917, 830 ( $v_{P-F}$ ), 747 cm<sup>-1</sup>. <sup>31</sup>P NMR (acetone- $d_6$ ): 9.1 (s, dppa) ppm. <sup>1</sup>H NMR (acetone- $d_6$ ): 2.34 (s, 24H, o-CH<sub>3</sub>), 2.35 (s, 12H, p-CH<sub>3</sub>), 6.02 (d, 4H, o-NPh,  $J_{HH} =$ 7.3 Hz), 6.42 (t, 2H, *p*-NPh,  $J_{\rm HH}$  = 7.3 Hz), 6.85 (t, 4H, *m*-NPh,  $J_{\rm HH} = 7.8$  Hz), 7.19 (s, 8H, m-C<sub>6</sub>H<sub>2</sub>), 7.63–7.75 (m, 20H, C<sub>6</sub>H<sub>5</sub>), 8.23 (s, 4H, HC=CH) ppm. MS (FAB +ve; abundance): m/z 1812  $(100) [M + PF_6]^+, 1030 (100), [M - Au(SCNPh \cdot IMes)]^+.$  Analysis: Calcd for C<sub>82</sub>H<sub>78</sub>Au<sub>2</sub>F<sub>12</sub>N<sub>6</sub>P<sub>4</sub>S<sub>2</sub>: C, 50.3; H, 4.0; N, 4.3. Found: C, 50.4; H, 4.1; N, 4.2%.

 $[(dppf){Au(SCNPh \cdot IMes)_2}](PF_6)_2$  (9). A dichloromethane solution (10 mL) of [(dppf)(AuCl)<sub>2</sub>] (42 mg, 0.041 mmol) was treated with a solution of 1 (40 mg, 0.091 mmol) in dichloromethane (10 mL). NH<sub>4</sub>PF<sub>6</sub> (20 mg, 0.123 mmol) in methanol (10 mL) was added and the light orange reaction mixture was stirred for 1 h at room temperature. All the solvents were removed and the crude product was dissolved in dichloromethane (10 mL). The suspension was filtered through Celite to remove NH<sub>4</sub>Cl and excess NH<sub>4</sub>PF<sub>6</sub>. Ethanol (15 mL) was added and the solvent volume was reduced until precipitation of the product was complete. The precipitate was filtered, washed with ethanol (10 mL), petroleum ether (10 mL) and dried to give a light orange solid (35 mg, 40%). IR (neat): 1587, 1557, 1492, 1438, 1382, 1232, 1183, 1171, 1102, 1031, 999, 954, 918, 830 ( $v_{P-F}$ ), 748 cm<sup>-1</sup>. <sup>31</sup>P NMR (acetone- $d_6$ ): 31.8 (s, dppf) ppm. <sup>1</sup>H NMR (acetone- $d_6$ ): 2.32 (s, 24H, o-CH<sub>3</sub>), 2.35 (s, 12H, p-CH<sub>3</sub>), 3.97, 4.45 (s × 2, 2 × 4H,  $C_5H_4$ ), 6.14 (d, 4H, *o*-NPh,  $J_{HH}$  = 6.7 Hz), 6.52 (t, 2H, *p*-NPh,  $J_{\rm HH}$  = 7.1 Hz), 6.82 (t, 4H, *m*-NPh,  $J_{\rm HH}$  = 7.7 Hz), 7.18 (s, 8H, m-C<sub>6</sub>H<sub>2</sub>), 7.20-7.30, 7.54-7.68 (m × 2, 20H, C<sub>6</sub>H<sub>5</sub>), 8.19 (s, 4H, HC=CH) ppm. MS (FAB +ve; abundance): m/z 1972 (28) [M + PF<sub>6</sub>]<sup>+</sup>, 751 (100) [M - Au(SCNPh·IMes)<sub>2</sub>]<sup>+</sup>. Analysis: Calcd for C<sub>90</sub>H<sub>86</sub>Au<sub>2</sub>F<sub>12</sub>FeN<sub>6</sub>P<sub>4</sub>S<sub>2</sub>: C, 51.0; H, 4.1; N, 4.0. Found: C, 51.2; H, 4.0: N. 3.9%.

[(dppm)Au<sub>2</sub>(SCNPh-IMes)](PF<sub>6</sub>)<sub>2</sub>/(OTf)<sub>2</sub> (10). Procedure A: A dichloromethane solution (10 mL) of [(dppm)(AuCl)<sub>2</sub>] (35 mg, 0.042 mmol) was treated with a solution of 1 (20 mg, 0.045 mmol) in dichloromethane (10 mL). NH<sub>4</sub>PF<sub>6</sub> (20 mg, 0.124 mmol) in methanol (10 mL) was added and the colourless reaction mixture was stirred for 1 h at room temperature. All the solvents were removed and the crude product was dissolved in dichloromethane (10 mL). The suspension was filtered through Celite to remove NH<sub>4</sub>Cl and excess NH<sub>4</sub>PF<sub>6</sub>. Ethanol (15 mL) was added and the solvent volume was reduced until precipitation of the product was complete. The precipitate was filtered, washed with ethanol (10 mL), petroleum ether (10 mL) and dried to give a light yellow solid (29 mg, 47%). Repeated recrystallisation from

dichloromethane and ethanol was required to obtain a sample of good purity. Procedure B: [(dppm)(AuCl)<sub>2</sub>] (96.6 mg, 0.114 mmol) was dissolved in dry tetrahydrofuran (10 mL) and a solution of silver triflate (58.4 mg, 0.227 mmol) in dry tetrahydrofuran (5 mL) was added under nitrogen. The reaction mixture was stirred for 45 min in the dark at 0 °C. It was filtered into a tetrahydrofuran (5 mL) solution of 1 (50 mg, 0.114 mmol). Stirring was continued for 2 h at 0 °C and then all the solvent was removed. The crude product was dissolved in dichloromethane (5 mL) and filtered through Celite. Pentane was added until precipitation of the light yellow solid was complete (127 mg, 74%). IR (neat, triflate salt): 1606, 1587, 1485, 1437, 1382, 1254, 1152, 1102, 1028, 999, 952, 912, 892, 856 cm<sup>-1</sup>. <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>): 25.6, 32.8 (d × 2, dppm,  $J_{PP} = 56.9$  Hz) ppm. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 2.18 (br s, 6H, *o*-CH<sub>3</sub>), 2.29 (s, 6H, *o*-CH<sub>3</sub>), 2.35 (s, 3H, *p*-CH<sub>3</sub>), 2.43 (br s, 3H, *p*-CH<sub>3</sub>), 3.70 (t, 2H, CH<sub>2</sub>, *J*<sub>HP</sub> unresolved), 6.02 (d, 2H, o-NPh,  $J_{\rm HH} = 7.3$  Hz), 6.36 (t, 1H, p-NPh,  $J_{HH} = 7.4$  Hz), 6.67 (t, 2H, *m*-NPh,  $J_{HH} = 7.6$  Hz), 7.19 (s, 4H, *m*-C<sub>6</sub>H<sub>2</sub>), 7.35–7.56 (m, 20H, C<sub>6</sub>H<sub>5</sub>), 7.71 (s, 2H, HC=CH) ppm. MS (FAB +ve; abundance): m/z 1252 (50) [M + 2H<sub>2</sub>O]<sup>+</sup>, 1217 (5) [M]<sup>+</sup>. Analysis: Calcd for C<sub>53</sub>H<sub>51</sub>Au<sub>2</sub>F<sub>12</sub>N<sub>3</sub>P<sub>4</sub>S: C, 42.2; H, 3.4; N, 2.8. Found: C, 42.1; H, 3.3; N, 2.7%.

 $[Au(SCNPh \cdot IMes)_2](PF_6)$  (11). A dichloromethane solution (10 mL) of [AuCl(tht)] (20 mg, 0.062 mmol) was treated with a solution of 1 (60 mg, 0.137 mmol) in dichloromethane (10 mL). NH<sub>4</sub>PF<sub>6</sub> (30 mg, 0.186 mmol) in methanol (10 mL) was added and the light yellow reaction mixture was stirred for 1 h at room temperature. All the solvents were removed and the crude product was dissolved in dichloromethane (10 mL). The suspension was filtered through Celite to remove NH<sub>4</sub>Cl and excess NH<sub>4</sub>PF<sub>6</sub>. Ethanol (15 mL) was added and the solvent volume was reduced until precipitation of the product was complete. The precipitate was filtered, washed with ethanol (10 mL), petroleum ether (10 mL) and dried to give a light yellow solid (41 mg, 54%). IR (neat): 1556, 1492, 1233, 1188, 921, 878, 837 (*v*<sub>P-F</sub>), 759, 731, 691 cm<sup>-1</sup>. <sup>1</sup>H NMR (acetone-d<sub>6</sub>): 2.25 (s, 24H, o-CH<sub>3</sub>), 2.42 (s, 12H, p-CH<sub>3</sub>), 5.68 (d, 4H, o-NPh,  $J_{\text{HH}} = 7.8$  Hz), 6.75 (t, 2H, *p*-NPh,  $J_{HH} = 7.3$  Hz), 6.89 (t, 4H, *m*-NPh,  $J_{HH} = 7.7$  Hz), 7.17 (s, 8H, *m*-C<sub>6</sub>H<sub>2</sub>), 8.03 (s, 4H, HC=CH) ppm. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 2.22 (s, 24H, o-CH<sub>3</sub>), 2.45 (s, 12H, p-CH<sub>3</sub>), 5.68 (d, 4H, o-NPh,  $J_{\rm HH} = 7.2$  Hz), 6.75 (t, 2H, *p*-NPh,  $J_{\rm HH} = 7.4$  Hz), 6.92 (t, 4H, *m*-NPh,  $J_{\rm HH} = 7.8$  Hz), 7.12 (s, 8H, m-C<sub>6</sub>H<sub>2</sub>), 7.37 (s, 4H, HC=CH) ppm. MS (ES +ve; abundance): m/z 1075 (100) [M]<sup>+</sup>, 440 (34) [M - Au(SCNPh·IMes)]<sup>+</sup>. Analysis: Calcd for C<sub>56</sub>H<sub>58</sub>AuF<sub>6</sub>N<sub>6</sub>PS<sub>2</sub>: C, 55.1; H, 4.8; N, 6.9. Found: C, 55.0; H, 4.7; N, 6.8%.

[AuAg(SCNPh-IMes)<sub>2</sub>](PF<sub>6</sub>)(OTf) (12). Silver triflate (3 mg, 0.012 mmol) was added to a solution of [Au(SCNPh-IMes)<sub>2</sub>](PF<sub>6</sub>) (11) (13.5 mg, 0.011 mmol) in chloroform (10 mL) and the mixture was stirred for 1 h at room temperature. All the solvent was removed, diethyl ether (10 mL) was added and the product was triturated ultrasonically. The yellow solid was filtered and dried under vacuum. Yield: 13.8 mg (85%). IR (neat): 1590, 1491, 147, 1384, 1290, 1219, 1167, 1019, 909, 893, 837 ( $v_{P-F}$ ), 759 cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 2.21 (s, 24H, *o*-CH<sub>3</sub>), 2.47 (s, 12H, *p*-CH<sub>3</sub>), 5.70 (d, 4H, *o*-NPh,  $J_{HH} = 7.3$  Hz), 6.98 (t, 2H, *p*-NPh,  $J_{HH} = 7.3$  Hz), 7.12 (t, 4H, *m*-NPh,  $J_{HH} = 7.8$  Hz), 7.19 (s, 8H, *m*-C<sub>6</sub>H<sub>2</sub>), 7.62 (s, 4H, HC=CH) ppm. MS (FAB +ve; abundance) m/z: 1333 (3) [M + OTf]<sup>+</sup>, 1183 (2) [M]<sup>+</sup>, 1075 (5) [M – Ag]<sup>+</sup>. Analysis: Calcd for

 $C_{57}H_{58}AgAuF_9N_6O_3PS_3\cdot 2CHCl_3:$  C, 41.3; H, 3.5; N, 4.9. Found: C, 40.7; H, 3.4; N, 4.7%.

 $[(Ph_3P)Au(SOC \cdot IMes)]PF_6$  (14). A dichloromethane solution (10 mL) of [AuCl(PPh<sub>3</sub>)] (50 mg, 0.101 mmol) was treated with a solution of IMes COS (40 mg, 0.110 mmol) in dichloromethane (10 mL).  $NH_4PF_6$  (25 mg, 0.153 mmol) in methanol (10 mL) was added and the light yellow reaction mixture was stirred for 1 h at room temperature. All the solvents were removed and the crude product was dissolved in dichloromethane (10 mL). The suspension was filtered through Celite to remove NH4Cl and excess NH<sub>4</sub>PF<sub>6</sub>. Ethanol (15 mL) was added and the solvent volume was reduced until precipitation of the product was complete. The precipitate was filtered, washed with ethanol (10 mL), petroleum ether (10 mL) and dried to give a light yellow solid (62 mg, 63%). IR (neat): 3152, 1738, 1607, 1490, 1437, 1381, 1231, 1183, 1168, 1101, 1028, 1010, 999, 900, 831 ( $v_{P-F}$ ), 711 cm<sup>-1</sup>. <sup>31</sup>P NMR (acetoned<sub>6</sub>): 37.8 (s, PPh<sub>3</sub>) ppm. <sup>1</sup>H NMR (acetone-d<sub>6</sub>): 2.25 (s, 12H, o-CH<sub>3</sub>), 2.37 (s, 6H, *p*-CH<sub>3</sub>), 7.19 (s, 4H, *m*-C<sub>6</sub>H<sub>2</sub>), 7.54–7.69 (m,  $15H, C_6H_5$ , 8.15 (s, 2H, HC=CH) ppm. MS (ES +ve; abundance): m/z 823 (100) [M]<sup>+</sup>, 365 (100) [M – AuPPh<sub>3</sub>]<sup>+</sup>. Analysis: Calcd for C<sub>40</sub>H<sub>39</sub>AuF<sub>6</sub>N<sub>2</sub>OP<sub>2</sub>S: C, 49.6; H, 4.1; N, 2.9. Found: C, 49.6; H, 4.1; N, 2.8%.

[(Ph<sub>3</sub>P)Au(SOC·SIMes)]PF<sub>6</sub> (15). A dichloromethane solution (10 mL) of [AuCl(PPh<sub>3</sub>)] (50 mg, 0.101 mmol) was treated with a solution of SIMes·COS (40 mg, 0.109 mmol) in dichloromethane (10 mL).  $NH_4PF_6$  (25 mg, 0.153 mmol) in methanol (10 mL) was added and the colourless reaction mixture was stirred for 1 h at room temperature. All the solvents were removed and the crude product was dissolved in dichloromethane (10 mL) and filtered through Celite to remove NH<sub>4</sub>Cl and excess NH<sub>4</sub>PF<sub>6</sub>. Ethanol (15 mL) was added and the solvent volume was reduced until precipitation of the product was complete. The precipitate was filtered, washed with ethanol (10 mL), petroleum ether (10 mL) and dried to give a colourless solid (59 mg, 60%). IR (neat): 1739, 1612, 1573, 1481, 1437, 1381, 1289, 1217, 1101, 1029, 999, 877, 833 ( $v_{P-F}$ ), 711 cm<sup>-1</sup>. <sup>31</sup>P NMR (acetone- $d_6$ ): 37.4 (s, PPh<sub>3</sub>) ppm. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>): 2.28 (s, 6H, *p*-CH<sub>3</sub>), 2.53 (s, 12H, *o*-CH<sub>3</sub>), 4.72 (s, 4H, CH<sub>2</sub>CH<sub>2</sub>), 7.08 (s, 4H, m-C<sub>6</sub>H<sub>2</sub>), 7.51–7.69 (m, 15H,  $C_6H_5$ ) ppm. MS (ES +ve; abundance): m/z 825 (40) [M]<sup>+</sup>, 367 (100)  $[M - AuPPh_3]^+$ . Analysis: Calcd for  $C_{40}H_{41}AuF_6N_2OP_2S$ : C, 49.5; H, 4.3; N, 2.9. Found: C, 49.6; H, 4.2; N, 3.0%.

[('BuNC)Au(SOC·IMes)]PF<sub>6</sub> (16). A dichloromethane solution (10 mL) of [AuCl(CN<sup>t</sup>Bu)] (25 mg, 0.079 mmol) was treated with a solution of IMes COS (31.8 mg, 0.087 mmol) in dichloromethane (10 mL). NH<sub>4</sub>PF<sub>6</sub> (26 mg, 0.160 mmol) in methanol (10 mL) was added and the light yellow reaction mixture was stirred for 1 h at room temperature. All the solvents were removed and the crude product was dissolved in dichloromethane (10 mL). The suspension was filtered through Celite to remove NH<sub>4</sub>Cl and excess NH<sub>4</sub>PF<sub>6</sub>. All the solvent was again removed and diethyl ether (15 mL) added. Ultrasonic trituration produced a colourless product. This was filtered, washed with diethyl ether (10 mL) and dried (50 mg, 80%). IR: 2240 ( $v_{\rm CN}$ ), 1608, 1490, 1376, 1233, 1183, 1010, 900, 831 ( $v_{P-F}$ ), 730 cm<sup>-1</sup>. <sup>1</sup>H NMR (acetone $d_6$ ): 1.63 (s, 9H, <sup>t</sup>Bu), 2.22 (s, 12H, o-CH<sub>3</sub>), 2.40 (s, 6H, p-CH<sub>3</sub>), 7.20 (s, 4H, m-C<sub>6</sub>H<sub>2</sub>), 8.19 (s, 2H, HC=CH) ppm. MS (ES +ve; abundance): m/z 791 (39) [M + PF<sub>6</sub>]<sup>+</sup>, 365 (100) [M - IMes · COS]<sup>+</sup>.

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Analysis: Calcd for C<sub>27</sub>H<sub>33</sub>AuF<sub>6</sub>N<sub>3</sub>OPS: C, 41.1; H, 4.2; N, 5.3. Found: C, 41.2; H, 4.0; N, 5.2%.

 $[(BuNC)Au(SOC \cdot SIMes)]PF_6$  (17). A dichloromethane solution (10 mL) of [AuCl(CN<sup>t</sup>Bu)] (25 mg, 0.079 mmol) was treated with a solution of SIMes COS (32.0 mg, 0.087 mmol) in dichloromethane (10 mL). NH<sub>4</sub>PF<sub>6</sub> (26 mg, 0.160 mmol) in methanol (10 mL) was added and the light yellow reaction mixture was stirred for 1 h at room temperature. All the solvents were removed and the crude product was dissolved in dichloromethane (10 mL). The suspension was filtered through Celite to remove NH<sub>4</sub>Cl and excess NH<sub>4</sub>PF<sub>6</sub>. All the solvent was again removed and diethyl ether (15 mL) added. Ultrasonic trituration produced a colourless product. This was filtered, washed with diethyl ether (10 mL) and dried (58 mg, 93%). IR: 2239 (v<sub>CN</sub>), 1675, 1610, 1478, 1376, 1290, 1191, 1031, 877, 832 ( $v_{P-F}$ ), 738, 699 cm<sup>-1</sup>. <sup>1</sup>H NMR (acetone-d<sub>6</sub>): 1.63 (s, 9H, <sup>t</sup>Bu), 2.33 (s, 6H, p-CH<sub>3</sub>), 2.50 (s, 12H, o-CH<sub>3</sub>), 4.74 (s, 4H, CH<sub>2</sub>CH<sub>2</sub>), 7.10 (s, 4H, m-C<sub>6</sub>H<sub>2</sub>) ppm. MS (ES +ve; abundance): m/z 795 (34) [M + PF<sub>6</sub>]<sup>+</sup>, 646 (2) [M]<sup>+</sup>, 367 (100) [M – SIMes·COS]<sup>+</sup>. Analysis: Calcd for C<sub>27</sub>H<sub>35</sub>AuF<sub>6</sub>N<sub>3</sub>OPS: C, 41.0; H, 4.5; N, 5.3. Found: C, 41.0; H, 4.5; N, 5.5%.

 $[(dppf){Au(SOC \cdot IMes)}_2](PF_6)_2$  (18). A dichloromethane solution (10 mL) of [(dppf)(AuCl)<sub>2</sub>] (25 mg, 0.025 mmol) was treated with a solution of IMes COS (19.7 mg, 0.054 mmol) in dichloromethane (10 mL). NH<sub>4</sub>PF<sub>6</sub> (12 mg, 0.074 mmol) in methanol (10 mL) was added and the light yellow reaction mixture was stirred for 1 h at room temperature. All the solvents were removed and the crude product was dissolved in dichloromethane (10 mL). The suspension was filtered through Celite to remove NH<sub>4</sub>Cl and excess NH<sub>4</sub>PF<sub>6</sub>. All the solvent was again removed and diethyl ether (15 mL) added. Ultrasonic trituration produced a vellow product. This was filtered, washed with diethyl ether (10 mL) and dried (32 mg, 66%). IR: 1609, 1487, 1437, 1381, 1312, 1239, 1176, 1103, 1035, 998, 932, 828 ( $v_{P-F}$ ), 749, 695 cm<sup>-1</sup>.  $^{31}$ P NMR (acetone- $d_6$ ): 34.8 (s, PPh<sub>3</sub>) ppm.  $^{1}$ H NMR (acetone- $d_6$ ): 2.29 (s, 24H, o-CH<sub>3</sub>), 2.33 (s, 12H, p-CH<sub>3</sub>), 3.89 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 4.13 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 7.22 (s, 8H, m-C<sub>6</sub>H<sub>2</sub>), 7.17–7.19, 7.48–7.52, 7.61–7.66 (m  $\times$  3, 20H, C<sub>6</sub>H<sub>5</sub>), 7.97, 7.98 (s  $\times$  2, 4H, HC=CH) ppm. MS (ES +ve; abundance): m/z 1964 (2) [M + 2PF<sub>6</sub>]<sup>+</sup>, 1822  $(15) [M + PF_6]^+, 1676 (5) [M]^+, 1115 (23) [M - Au(IMes \cdot COS)]^+.$ Analysis: Calcd for C<sub>78</sub>H<sub>76</sub>Au<sub>2</sub>F<sub>12</sub>FeN<sub>4</sub>O<sub>2</sub>P<sub>4</sub>S<sub>2</sub>: C, 47.6; H, 3.9; N, 2.9. Found: C, 47.8; H, 4.0; N, 3.1%.

 $[(dppf){Au(SOC \cdot SIMes)}_2](PF_6)_2$  (19). A dichloromethane solution (10 mL) of [(dppf)(AuCl)<sub>2</sub>] (25 mg, 0.025 mmol) was treated with a solution of SIMes·COS (19.8 mg, 0.054 mmol) in dichloromethane (10 mL). NH<sub>4</sub>PF<sub>6</sub> (12 mg, 0.074 mmol) in methanol (10 mL) was added and the light yellow reaction mixture was stirred for 1 h at room temperature. All the solvents were removed and the crude product was dissolved in dichloromethane (10 mL). The suspension was filtered through Celite to remove NH<sub>4</sub>Cl and excess NH<sub>4</sub>PF<sub>6</sub>. All the solvent was again removed and diethyl ether (15 mL) added. Ultrasonic trituration produced a yellow product. This was filtered, washed with diethyl ether (10 mL) and dried (29 mg, 60%). IR: 1611, 1568, 1480, 1385, 1288, 1215, 1199, 1182, 1173, 1101, 1031, 831 ( $v_{P-F}$ ), 750, 693 cm<sup>-1</sup>. <sup>31</sup>P NMR (acetone- $d_6$ ): 30.8 (s, PPh<sub>3</sub>) ppm. <sup>1</sup>H NMR (acetoned<sub>6</sub>): 2.20 (s, 12H, p-CH<sub>3</sub>), 2.48 (s, 24H, o-CH<sub>3</sub>), 4.26 (br s, 4H, C<sub>5</sub>H<sub>4</sub>), 4.45–4.47 (m, 4H, C<sub>5</sub>H<sub>4</sub>), 4.74 (s, 8H, CH<sub>2</sub>CH<sub>2</sub>), 7.22

(s, 8H, m-C<sub>6</sub>H<sub>2</sub>), 7.47–7.73 (m, 20H, C<sub>6</sub>H<sub>3</sub>) ppm. MS (ES +ve; abundance): m/z 1825 (10) [M + PF<sub>6</sub>]<sup>+</sup>, 1680 (2) [M]<sup>+</sup>, 1314 (21) [M – SIMes·COS]<sup>+</sup>, 1177 (3) [M – Au(SIMes·COS)]<sup>+</sup>. Analysis: Calcd for C<sub>78</sub>H<sub>80</sub>Au<sub>2</sub>F<sub>12</sub>FeN<sub>4</sub>O<sub>2</sub>P<sub>4</sub>S<sub>2</sub>: C, 47.5; H, 4.1; N, 2.8. Found: C, 47.6; H, 4.1; N, 2.7%.

 $[Au(SOC \cdot IMes)_2]PF_6$  (20). A dichloromethane solution (10 mL) of [AuCl(tht)] (25 mg, 0.078 mmol) was treated with a solution of IMes·COS (56.8 mg, 0.156 mmol) in dichloromethane (10 mL).  $NH_4PF_6$  (25.4 mg, 0.156 mmol) in methanol (10 mL) was added and the light yellow reaction mixture was stirred for 1 h at room temperature. All the solvents were removed and the crude product was dissolved in dichloromethane (10 mL). The suspension was filtered through Celite to remove NH<sub>4</sub>Cl and excess  $NH_4PF_6$ . All the solvent was again removed and diethyl ether (15 mL) added. Ultrasonic trituration produced a pale yellow product. This was filtered, washed with diethyl ether (10 mL) and dried (80 mg, 96%). IR: 1606, 1557, 1489, 1380, 1289, 1230, 1184, 1169, 1034, 1010, 952, 901, 832 (v<sub>P-F</sub>), 769, 733, 724, 684, 662 cm<sup>-1</sup>. <sup>1</sup>H NMR (acetone- $d_6$ ): 2.18 (s, 24H, o-CH<sub>3</sub>), 2.36 (s, 12H, *p*-CH<sub>3</sub>), 7.12 (s, 8H, *m*-C<sub>6</sub>H<sub>2</sub>), 8.09 (s, 4H, HC=CH) ppm. MS (FAB +ve; abundance): m/z 925 (86) [M]<sup>+</sup>. Analysis: Calcd for C<sub>44</sub>H<sub>48</sub>AuF<sub>6</sub>N<sub>4</sub>O<sub>2</sub>PS<sub>2</sub>: C, 49.3; H, 4.5; N, 5.2. Found: C, 49.5; H, 4.4; N, 5.2%.

 $[Au(SOC \cdot SIMes)_2]PF_6$  (21). A dichloromethane solution (10 mL) of [AuCl(tht)] (25 mg, 0.078 mmol) was treated with a solution of SIMes COS (57.1 mg, 0.156 mmol) in dichloromethane (10 mL).  $NH_4PF_6$  (25.4 mg, 0.156 mmol) in methanol (10 mL) was added and the light yellow reaction mixture was stirred for 1 h at room temperature. All the solvents were removed and the crude product was dissolved in dichloromethane (10 mL). The suspension was filtered through Celite to remove NH4Cl and excess NH<sub>4</sub>PF<sub>6</sub>. All the solvent was again removed and diethyl ether (15 mL) added. Ultrasonic trituration produced a pale yellow product. This was filtered, washed with diethyl ether (10 mL) and dried (68 mg, 81%). IR: 1667, 1610, 1568, 1481, 1379, 1350, 1216, 1199, 1156, 1115, 1030, 879, 832 ( $v_{P-F}$ ), 738, 702, 667 cm<sup>-1</sup>. <sup>1</sup>H NMR (acetone-d<sub>6</sub>): 2.29 (s, 12H, p-CH<sub>3</sub>), 2.44 (s, 24H, o-CH<sub>3</sub>), 4.67 (s, 8H, CH<sub>2</sub>CH<sub>2</sub>), 7.00 (s, 8H, m-C<sub>6</sub>H<sub>2</sub>) ppm. MS (FAB +ve; abundance): m/z 929 (100) [M]<sup>+</sup>. Analysis: Calcd for C44H50AuF6N4O2PS2: C, 49.3; H, 4.7; N, 5.2. Found: C, 49.3; H, 4.7; N, 5.0%.

#### Crystallography

Single crystals of **2**, **3** and **13** were grown by vapour diffusion of diethyl ether onto a dichloromethane solution of the complex. Further details are given below and in the Supplementary Information. The structures were refined using the SHELXTL and SHELX-97 program systems.<sup>51</sup>

Crystal data for **2**.  $[C_{46}H_{44}AuN_3PS](PF_6)$ , M = 1043.81, triclinic,  $\bar{P}(no. 2)$ , a = 13.3686(3), b = 13.7657(3), c = 14.6220(4) Å,  $\alpha = 111.492(2)$ ,  $\beta = 115.794(2)$ ,  $\gamma = 90.1070(17)^\circ$ , V = 2212.12(11) Å<sup>3</sup>, Z = 2,  $D_c = 1.567$  g cm<sup>-3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 3.506 mm<sup>-1</sup>, T = 173 K, pale yellow blocks, Oxford Diffraction Xcalibur 3 diffractometer; 14763 independent measured reflections ( $R_{int} = 0.0194$ ),  $F^2$  refinement,  $R_1(obs) = 0.0213$ , w $R_2(all) = 0.0375$ , 11951 independent observed absorption-corrected reflections [ $|F_o| > 4\sigma(|F_o|)$ ,  $2\theta_{max} = 66^\circ$ ], 538 parameters. CCDC 773283. Crystal data for **3**. [C<sub>46</sub>H<sub>62</sub>AuN<sub>3</sub>PS](PF<sub>6</sub>), M = 1061.95, triclinic,  $\bar{P}$  (no. 2), a = 10.9296(2), b = 13.9751(3), c = 17.0449(3) Å,  $\alpha = 105.2760(19)$ ,  $\beta = 103.2896(18)$ ,  $\gamma = 101.5936(18)^{\circ}$ , V = 2347.48(9) Å<sup>3</sup>, Z = 2,  $D_c = 1.502$  g cm<sup>-3</sup>,  $\mu$ (Cu-K $\alpha$ ) = 7.439 mm<sup>-1</sup>, T = 173 K, colourless blocks, Oxford Diffraction Xcalibur PX Ultra diffractometer; 9279 independent measured reflections ( $R_{int} = 0.0309$ ),  $F^2$  refinement,  $R_1$ (obs) = 0.0242, w $R_2$ (all) = 0.0602, 8743 independent observed absorption-corrected reflections [ $|F_o| > 4\sigma(|F_o|), 2\theta_{max} = 145^{\circ}$ ], 539 parameters. CCDC 773284.

Crystal data for **13**. [C<sub>58</sub>H<sub>58</sub>Ag<sub>2</sub>AuF<sub>6</sub>N<sub>6</sub>O<sub>6</sub>S<sub>4</sub>](CF<sub>3</sub>SO<sub>3</sub>)·CH<sub>2</sub>Cl<sub>2</sub>, M = 1824.05, monoclinic, P2/c (no. 13), a = 10.31542(15), b = 16.59529(19), c = 20.2361(3) Å,  $\beta = 102.4511(14)^{\circ}$ , V = 3382.69(8)Å<sup>3</sup>, Z = 2 [C<sub>2</sub> symmetry],  $D_c = 1.791$  g cm<sup>-3</sup>,  $\mu$ (Cu-K $\alpha$ ) = 11.489 mm<sup>-1</sup>, T = 173 K, yellow plates, Oxford Diffraction Xcalibur PX Ultra diffractometer; 6557 independent measured reflections ( $R_{int} = 0.0353$ ),  $F^2$  refinement,  $R_1$ (obs) = 0.0524, w $R_2$ (all) = 0.1531, 5989 independent observed absorption-corrected reflections [| $F_o$ | >  $4\sigma$ (| $F_o$ |),  $2\theta_{max} = 145^{\circ}$ ], 513 parameters. CCDC 784174.

#### Acknowledgements

We are grateful to Johnson Matthey Ltd for a generous loan of hydrogen tetrachloroaurate. We thank Mr. Morgan Hans (University of Liège, Belgium) for his help with the synthesis of IMes·COS and SIMes·COS.

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