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# The Use of Imidazolium-2-dithiocarboxylates in the Formation of Gold(I) Complexes and Gold Nanoparticles[†]

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The imidazolium-2-dithiocarboxylate ligands $\mathrm{IPr\cdot CS_2}$, $\mathrm{IMes\cdot CS_2}$, and $\mathrm{IDip\cdot CS_2}$ react with $\mathrm{[AuCl(PPh_3)]}$ to yield $\mathrm{[(Ph_3P)Au(S_2C\cdot IPr)]^+}$, $\mathrm{[(Ph_3P)Au(S_2C\cdot IMes)]^+}$, and $\mathrm{[(Ph_3P)Au(S_2C\cdot IDip)]^+}$, respectively. The compounds $\mathrm{[(L)Au(S_2C\cdot IMes)]^+}$ are prepared from the reaction of $\mathrm{IMes\cdot CS_2}$ with $\mathrm{[AuCl(L)]}$ ($\mathrm{L = PMe_3, PCy_3, CN^tBu}$). The carbene-containing precursor $\mathrm{[(IDip)AuCl]}$ reacts with $\mathrm{IPr\cdot CS_2}$ and $\mathrm{IMes\cdot CS_2}$ to afford the complexes $\mathrm{[(IDip)Au(S_2C\cdot IPr)]^+}$ and $\mathrm{[(IDip)Au(S_2C\cdot IMes)]^+}$ with two carbene units, one bound to the metal center and the other to the dithiocarboxylate unit. Treatment of the diphosphine-gold complex $\mathrm{[(dppm)(AuCl)_2]}$ with 1 equiv of $\mathrm{IMes\cdot CS_2}$ yields $\mathrm{[(dppm)Au_2(S_2C\cdot IMes)]^{2+}}$, while the reaction of $\mathrm{[L_2(AuCl)_2]}$ ($\mathrm{L_2}$ = dppb, dppf) with 2 equiv of $\mathrm{IMes\cdot CS_2}$ results in $\mathrm{[(L_2)\{Au(S_2C\cdot IMes)\}_2]^{2+}}$. The homoleptic complexes $\mathrm{[Au(S_2C\cdot IPr)_2]^{2+}}$, $\mathrm{[Au(S_2C\cdot IMes)_2]^{2+}}$, and $\mathrm{[Au(S_2C\cdot IDip)_2]^{2+}}$ are obtained from the reaction of [AuCl(tht)] with 2 equiv of the appropriate imidazolium-2-dithiocarboxylate ligand. The compounds $\mathrm{[(Ph_3P)Au(S_2C\cdot NHC)]^+}$ (NHC = IMes, IDip) and $\mathrm{[(IDip)Au(S_2C\cdot NHC)]^+}$ (NHC = IPr, IMes) are characterized crystallographically. The $\mathrm{IMes\cdot CS_2}$ ligand is also used to prepare functionalized gold nanoparticles with diameters of 11.5 (±1.2) and 2.6 (±0.3) nm.

## Introduction

Along with phosphorus donors, gold(I) chemistry has traditionally been dominated by sulfur-based ligands, with many complexes finding applications in fields as diverse as medicine, electronics, and decoration.[1] Yet, compared to metal compounds of dithiocarbamate[2a−c] or even xanthate ligands,[2a,b,d] examples of dithiocarboxylate complexes ($\mathrm{L}_n\mathrm{MS_2CR}$, where R is a carbon-based substituent) are still scarce in the literature.[2a,b] This difference may be explained at least in part by the more challenging synthesis of dithiocarboxylate ligands compared to analogous dithiocarbamate or xanthate species. Extensive reviews of the chemistry of dithio ligands indicate that the situation has improved little over the years.[2]

The lack of exploration in the field of dithiocarboxylate ligands may be contrasted with the explosion of interest in N-heterocyclic carbenes (NHCs)[3] since the first representative of this new class of divalent carbon species was isolated and characterized in 1991[3a] (although earlier contributions were also important[3b,c]). Often seen as an excellent alternative to phosphines, imidazol-2-ylidene derivatives have been embraced by those involved in catalysis. Perhaps the most prominent examples of NHCs as ancillary ligands are found in second-generation alkene metathesis catalysts, such as the Grubbs benzylidene complexes $\mathrm{[Ru({=}CHPh)(NHC)Cl_2(PCy_3)]}$ (Scheme 1).[4] The tunable, electron-rich nature and steric bulk of these heterocycles, alongside their lack of lability, offer excellent catalytic attributes that have been successfully employed with many more transition metals than just ruthenium.[5] In gold(I) chemistry,[6] Burini et al.[7] and then Raubenheimer et al.[8] pioneered the preparation of (homoleptic) gold NHC complexes. Later, Nolan and coworkers provided straightforward syntheses of [(NHC)-AuCl] derivatives (Scheme 1)[9] and exploited the use of such

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[†] Dedicated to Prof. Dr. Hubert Schmidbaur on the occasion of his 75th birthday.

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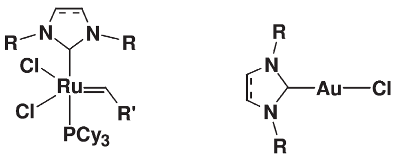
**Scheme 1.** Notable Examples of Complexes Bearing NHC Ligands

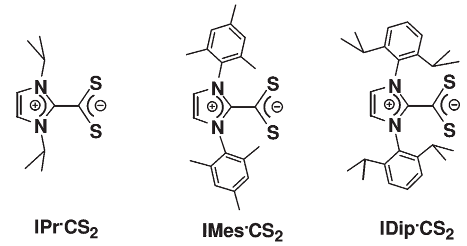


**Scheme 2.** Imidazoliumcarboxylate and -dithiocarboxylate Zwitterions Derived from NHCs

complexes in catalysis,[10] building on early work by Teles et al. on gold(I) compounds for the addition of alcohols to alkynes.[11]

The discovery that NHCs react with carbon dioxide to form carboxylate inner salts allowed the use of zwitterionic NHC·$CO_2$ adducts to generate carbene ligands within the coordination sphere of the metal, while permitting the easy storage and manipulation of otherwise oxygen- and moisture-sensitive carbene species (Scheme 2).[12] This approach has been extended very recently to the reaction of NHCs with carbon disulfide to yield zwitterionic imidazolium-2-dithiocarboxylate betaines.[13a] Unlike their carboxylate analogues, these species are not expected to readily eliminate carbon disulfide upon reaction with metals. Preliminary studies indicate that this is indeed the case with ruthenium and osmium compounds.[13b] In this report, we detail the first in-depth study of the coordination chemistry of NHC·$CS_2$ zwitterions with gold and we show that they are excellent ligands for monovalent gold complexes, whether homoleptic or with a range of phosphorus- or carbon-based coligands. Furthermore, we show that they are also able to function as surface units for nanoparticles of gold.

**Scheme 3.** Imidazolium-2-dithiocarboxylate Ligands Used in This Work



## Results and Discussion

**Formation of Gold(I) Complexes.** Our recent work on gold(I) complexes has centered on the incorporation of gold units into multimetallic systems using the zwitterionic dithiocarbamate $S_2CNC_4H_8NH_2$.[14] This led us to investigate similar reactions using betaines obtained from the reaction of NHCs (generated in situ) with carbon disulfide (Scheme 3).[15] The steric tunability of these ligands and their stability to loss of the $CS_2$ moiety made them attractive species with which to explore gold(I) chemistry. To date, the coordination behavior of NHC·$CS_2$ zwitterions has been investigated with only a few transition-metal salts (including one trivalent gold example),[16] and much of this work enjoyed only limited characterization, lacking NMR or structural studies, for example. A very recent example of chelation to ruthenium(II) arene complexes has also been published.[13b] To the best of our knowledge, no gold(I) complexes have been reported so far.

The most habitual starting point for gold(I) chemistry is the archetypal complex [AuCl($PPh_3$)]. Treatment of a dichloromethane solution of this compound with a slight excess of the least bulky imidazolium-2-dithiocarboxylate ligand used in this study, IPr·$CS_2$, in the presence of $NH_4PF_6$ led to a pale-brown solid in 73% yield (Scheme 4). Apart from the resonance due to the hexafluorophosphate counteranion, only one singlet in the $^{31}P$ NMR spectrum was observed at 36.0 ppm, indicating the formation of a single new product. The presence of the isopropyl-substituted dithiocarboxylate ligand was evidenced by a doublet at 1.55 ppm and a septet at 4.87 ppm, showing mutual coupling of 6.8 Hz. To lower field, in addition to resonances for the $PPh_3$ ligand, was a singlet at 7.36 ppm attributed to the HC=CH unit of the imidazole ring. The overall composition as

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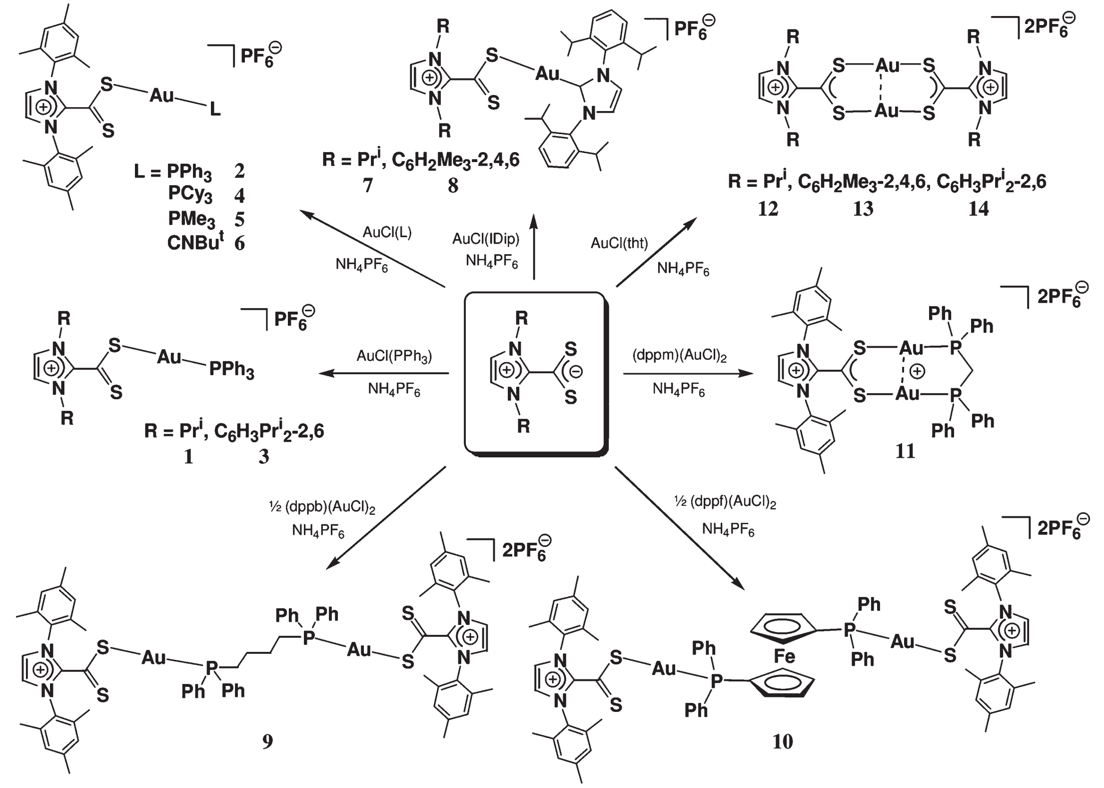
**Scheme 4.** Preparation of the Gold(I) Imidazolium-2-dithiocarboxylate Complexes



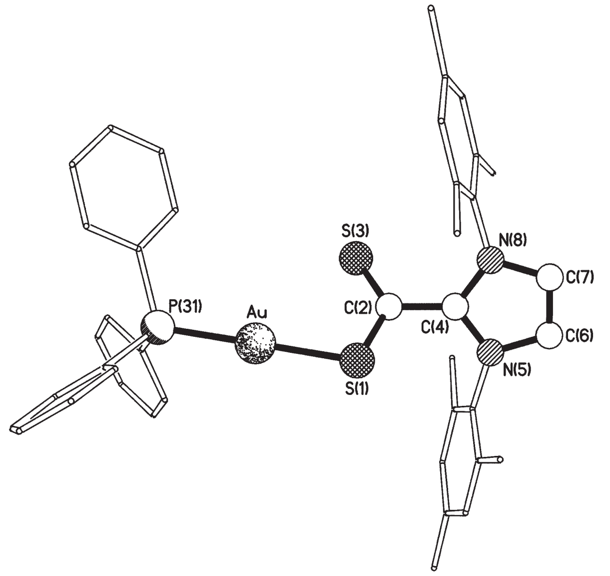


**Figure 1.** Molecular structure of **2**. Selected bond lengths (Å) and angles (deg; Au−P(31) 2.2622(7), Au−S(1) 2.3223(7), S(1)−C(2) 1.708(3), C(2)−C(4) 1.487(4), C(2)−S(3) 1.640(3), C(4)−N(5) 1.334(3), C(4)−N(8) 1.337(3); P(31)−Au−S(1) 178.94(3), C(2)−S(1)−Au 102.03(9). Hydrogen atoms and the hexafluorophosphate counteranion are omitted for clarity.

[(Ph$_3$P)Au(S$_2$C·IPr)]PF$_6$ (**1**) was based on an abundant molecular ion in the ES mass spectrum at *m*/*z* 687 and good agreement of elemental analysis. Although crystals suitable for X-ray diffraction analysis could not be obtained, linear coordination was assumed with the possibility of interaction with the other sulfur donor of the dithiocarboxylate ligand (i.e., anisobidentate coordination).

When the bulkier IMes·CS$_2$ betaine was allowed to react with [AuCl(PPh$_3$)] and NH$_4$PF$_6$ under the same experimental conditions, [(Ph$_3$P)Au(S$_2$C·IMes)]PF$_6$ (**2**) was isolated in 84% yield (Scheme 4). The new ligand was readily identified by singlets at 2.25 and 2.37 ppm for the *o*- and *p*-methyl substituents of the mesityl groups. The aromatic meta proton appeared as a singlet at 7.08 ppm, slightly upfield from the imidazole HC=CH proton at 7.41 ppm. Single crystals of the complex were grown, and a structural study was undertaken (Figure 1). The data obtained will be discussed in the context of the other structures bearing NHC·CS$_2$ ligands (vide infra).

The most sterically demanding ligand used in this work was the IDip·CS$_2$ zwitterion, which formed [(Ph$_3$P)-Au(S$_2$C·IDip)]PF$_6$ (**3**) with [AuCl(PPh$_3$)] and NH$_4$PF$_6$. $^1$H NMR analysis of this compound revealed doublets at 1.24 ($J_{HH}$ = 7.1 Hz) and 1.36 ($J_{HH}$ = 6.7 Hz) ppm for the methyl groups, while a septet for the C*H*Me$_2$ protons was noted at 2.66 ($J_{HH}$ = 6.8 Hz) ppm. The remaining aromatic resonances of the S$_2$C·IDip unit were obscured by features due to the triphenylphosphine ligand. In order to investigate the effect on the structure of an increase in steric bulk from IMes·CS$_2$ to IDip·CS$_2$, a structural investigation was carried out (Figure 2 and the Structural Discussion section).

The observation of the fascinating phenomenon of aurophilic interactions—bonding contacts between formally closed-shell d$^{10}$ gold(I) centers—depends on the steric profile of the ligand set in these (typically) linear compounds.[17] Adjustment of the steric attributes of the molecule was achieved by replacing the complex [AuCl(PPh$_3$)] with [AuCl(PCy$_3$)], which reacted smoothly

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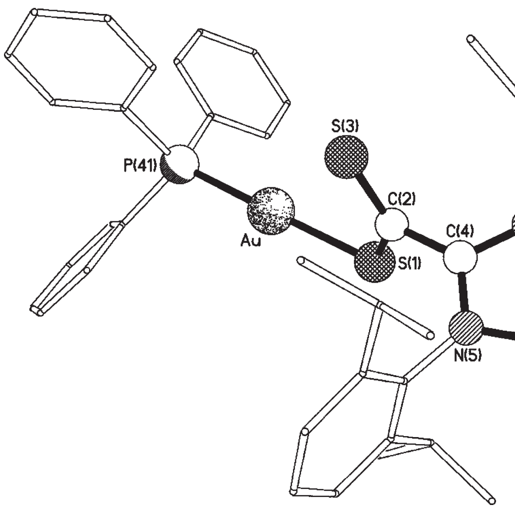

**Figure 2.** Molecular structure of **3**. Selected bond lengths (Å) and angles (deg); Au−P(41) 2.2595(5), Au−S(1) 2.3147(5), S(1)−C(2) 1.7027(14), C(2)−C(4) 1.483(2), C(2)−S(3) 1.6420(16), C(4)−N(8) 1.343(2), C(4)−N(5) 1.343(2); P(41)−Au−S(1) 173.63(2), C(2)−S(1)−Au 104.76(6). Hydrogen atoms and the hexafluorophosphate counteranion are omitted for clarity.

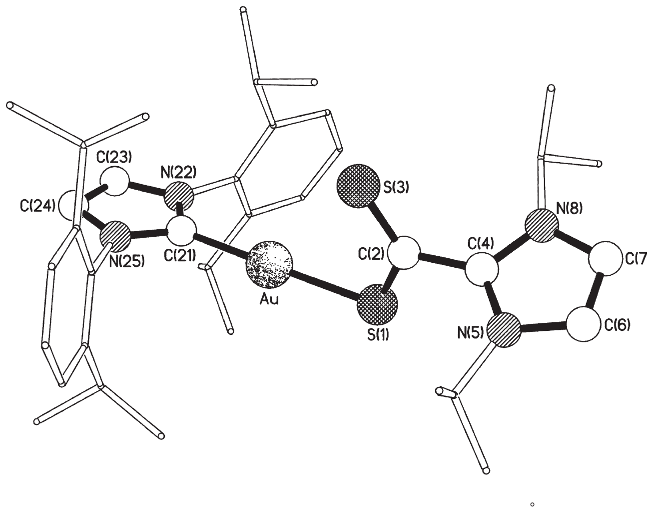

**Figure 3.** Molecular structure of **7**. Selected bond lengths (Å) and angles (deg); Au−C(21) 2.025(3), Au−S(1) 2.3047(8), S(1)−C(2) 1.701(4), C(2)−C(4) 1.495(5), C(2)−S(3) 1.639(4), C(4)−N(5) 1.336(5), C(4)−N(8) 1.345(5), C(21)−N(25) 1.341(4), C(21)−N(22) 1.347(4); C(21)−Au−S(1) 175.98(9), C(2)−S(1)−Au 106.99(12). Hydrogen atoms and the hexafluorophosphate counteranion are omitted for clarity.

with IMes·$CS_2$ to afford [$(Cy_3P)Au(S_2C$·IMes)]$PF_6$ (**4**) in 75% yield. This new compound displayed spectroscopic features similar to those of **2** apart from multiplets attributed to the cyclohexyl protons between 1.24 and 2.08 ppm in the $^1$H NMR spectrum. In order to provide a contrast to **4**, the precursor [$AuCl(PMe_3)$], bearing the smallest readily available phosphine, was employed to prepare [$(Me_3P)Au(S_2C$·IMes)]$PF_6$ (**5**). A doublet at 1.58 ppm in the $^1$H NMR spectrum, showing coupling to the phosphorus nucleus of 11.2 Hz, was assigned to the protons of the trimethylphosphine ligand. The precursor [AuCl(CN$^t$Bu)] also offers a low steric encumbrance at the gold center and has been used to generate thiolate complexes with unusual solid-state structures.[18] Its reaction with IMes·$CS_2$ in the presence of $NH_4PF_6$ led to the elimination of $NH_4Cl$ and formation of [($^t$BuNC)Au($S_2C$·IMes)]$PF_6$ (**6**) in 93% yield (Scheme 4). The retention of the isonitrile ligand was clearly indicated by the singlet observed at 1.54 ppm for the *tert*-butyl group in the $^1$H NMR spectrum. Unfortunately, no single crystals of complexes **4**−**6** could be obtained with which to ascertain the effect of the diverse steric profiles of these ligands on potential Au···Au contacts.

Although phosphine complexes of the general formula [$AuCl(PR_3)$] have long been the traditional starting point for much gold(I) chemistry, the development of NHCs as alternative ligands to phosphines has led to the incorporation of these excellent donors into gold complexes.[6,9] Thus, a dichloromethane solution of [AuCl(IDip)] was treated with the least bulky of the dithiocarboxylate ligands used in this study, IPr·$CS_2$, to afford a purple product in 71% yield (Scheme 4). In addition to resonances for the IPr·$CS_2$ ligand, $^1$H NMR analysis of the product showed doublets for the isopropyl methyl groups (1.31 and 1.38 ppm) and a septet (2.86 ppm) showing mutual coupling of 6.9 Hz for the isopropyl groups of the IDip ligand. The remaining protons of the metal-bonded carbene were observed at 7.24 (s, HC=CH), 7.40 (d, $J_{HH}$ = 7.8 Hz), and 7.62 (t, $J_{HH}$ = 7.8 Hz) ppm. An abundant molecular ion at *m*/*z* 813 in the electrospray (ES) mass spectrum and good agreement of the elemental analysis with calculated values supported the formulation as [(IDip)Au($S_2C$·IPr)]$PF_6$ (**7**). The pale-green complex [(IDip)Au($S_2C$·IMes)]$PF_6$ (**8**) was also prepared in a similar fashion (Scheme 4). Single crystals of complexes **7** and **8** were grown and their molecular structures determined by X-ray diffraction (Figures 3 and 4). These compounds provide fascinating examples of molecular architectures in which the carbene motif is bonded directly to the metal as well as via an intermediate dithiocarboxylate unit (see the Structural Discussion section).

The synthesis of digold compounds bearing the NHC·$CS_2$ ligands was then explored. The length of the hydrocarbon bridge in the compounds [$\{Ph_2P(CH_2)_nPPh_2\}(AuCl)_2$] has been shown to influence the diverse extended structures in the solid state.[1] Longer bridges such as those in [(dppb)$(AuCl)_2$] [dppb = 1,4-bis(diphenylphosphino)butane] do not display intramolecular aurophilic interactions, while shorter ones, especially [(dppm)$(AuCl)_2$] [dppm = 1,1-bis(diphenylphosphino)methane] favor “A-frame” complexes with short contacts between the neighboring gold centers. Incorporation of this motif in compounds with dithio ligands (e.g., [$(dppm)Au_2(S_2CNR_2)]^+$) has been reported.[19] The reaction of [(dppb)$(AuCl)_2$] or [(dppf)$(AuCl)_2$] [dppf = 1,1′-bis(diphenylphosphino)ferrocene] with 2 equiv of IMes·$CS_2$ led to the green, dicationic complexes [(dppb)$\{Au(S_2C$·IMes)$\}_2$]$(PF_6)_2$ (**9**) and [(dppf)$\{Au(S_2C$·IMes)$\}_2$]$(PF_6)_2$ (**10**) in 88% and 90% yields, respectively (Scheme 4). The dppb ligand gave rise

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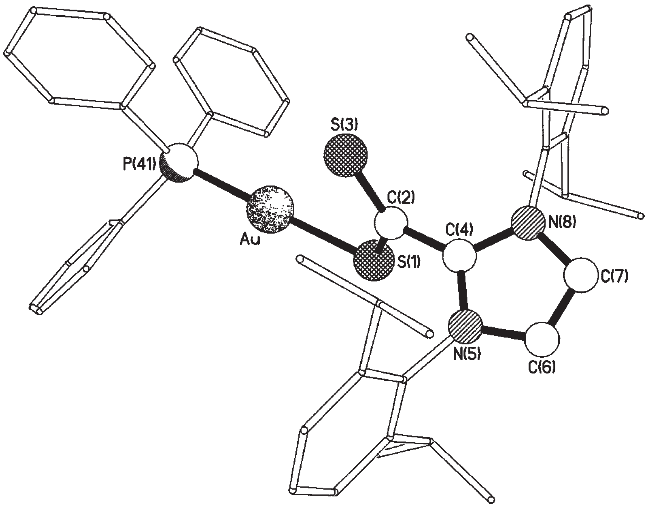

**Figure 4.** Molecular structure of **8**. Selected bond lengths (Å) and angles (deg); Au−C(31) 2.017(4), Au−S(1) 2.2912(10), S(1)−C(2) 1.702(5), C(2)−C(4) 1.494(5), C(2)−S(3) 1.643(4), C(4)−N(8) 1.333(6), C(4)−N(5) 1.339(6), C(31)−N(32) 1.341(5), C(31)−N(35) 1.348(5); C(31)−Au−S(1) 169.54(11), C(2)−S(1)−Au 105.30(15). Hydrogen atoms and the hexafluorophosphate counteranion are omitted for clarity.

to multiplets at 1.62 and 2.37 ppm in the $^1$H NMR spectrum of complex **9**, in addition to resonances for the IMes·$CS_2$ unit, which were similar to those observed in the spectra of the monometallic complexes **2**, **4**−**6**, and **8**. In complex **10**, the presence of the ferrocenyl unit was indicated by two broad singlets at 4.23 and 4.38 ppm in the $^1$H NMR spectrum. Integration of the spectra for both **9** and **10** clearly indicated that two dithiocarboxylate ligands were present, rather than a single ligand forming a metallacycle.[14b,20,21] This is in contrast to the product of IMes·$CS_2$ with [(dppm)($AuCl)_2$], which was formulated as [(dppm){$Au_2(S_2C$·IMes)}]$(PF_6)_2$ (**11**) on the basis of the ratio between the methylene protons at 3.72 (t, $J_{HP}$ = 12.3 Hz) ppm and the resonances of the IMes·$CS_2$ ligand. This composition was further supported by elemental analysis and mass spectrometry data.

Many dithio ligands, such as dithiocarbamates,[2c] form homoleptic digold complexes of the form [$Au_2(S_2CNR_2)_2$]. To investigate whether the dithiocarboxylate ligands examined in this study followed the same reactivity, [AuCl(tht)] (tht = tetrahydrothiophene) was treated with 1 equiv of each NHC·$CS_2$ betaine in the presence of $NH_4PF_6$ to give the brown digold complexes [$Au_2(S_2C$·NHC$)_2$]$(PF_6)_2$ [NHC = IPr (**12**), IMes (**13**), IDip (**14**); Scheme 4]. This formulation followed from spectroscopic and analytical data. The $^1$H NMR spectra (in $CD_2Cl_2$) of compound **14** and the free IDip·$CS_2$ ligand displayed similar resonances, with a few notable differences. One such divergence was the broad singlet observed in complex **14** for the isopropyl $CHMe_2$ protons at 2.52 ppm rather than the sharp septet seen in the spectrum of the ligand at 2.97 ($J_{HH}$ = 6.8 Hz) ppm. A similar broadening was also observed for the HC=CH imidazole proton at 7.46 ppm in contrast to the sharp singlet at 7.07 ppm observed in the spectrum of the free ligand. Related dithiocarbamate compounds, such as [$Au_2(S_2CNEt_2)_2$],[22] are notable for the very short gold−gold contacts seen in the solid state; however, no crystals suitable for X-ray diffraction of complexes **12**−**14** could be obtained.

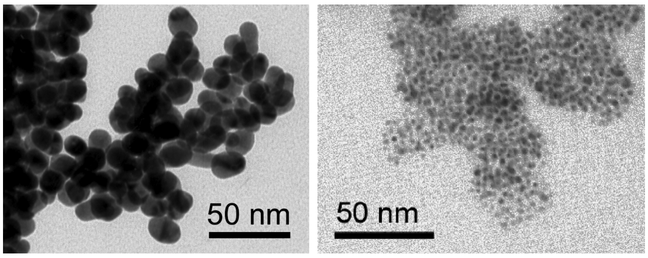

**Figure 5.** TEM images of (left) **NP1** and (right) **NP2**.

**Nanoparticle Preparation.** Since their early development,[23] monolayer-protected gold nanoparticles have been the focus of sustained interest.[24] In these materials, thiols are by far the most commonly used surface units, and only recently have alternative sulfur-based molecules, such as dithiocarbamates,[25] been used to protect the metal surface. We have recently investigated the use of metalladithiocarbamates to functionalize the surface of gold nanoparticles with ruthenium and nickel units.[14,26]

In order to broaden the scope of NHC·$CS_2$ ligands in gold chemistry, the potential of IMes·$CS_2$ for the preparation of gold nanoparticle materials was explored. Citrate-stabilized gold nanoparticles were generated[27] from $HAuCl_4$, and a dichloromethane−methanol solution of IMes·$CS_2$ was added to the resulting suspension. An instant darkening of the reaction mixture indicated the displacement of the citrate shell and the formation of IMes·$CS_2$-stabilized nanoparticles (**NP1**). The excess ligand present was removed by washing with dichloromethane, and the displaced citrate was eliminated by washing with water (Scheme 5). The material proved soluble in deuterated acetone, and a $^1$H NMR spectrum revealed broadened resonances at chemical shifts similar

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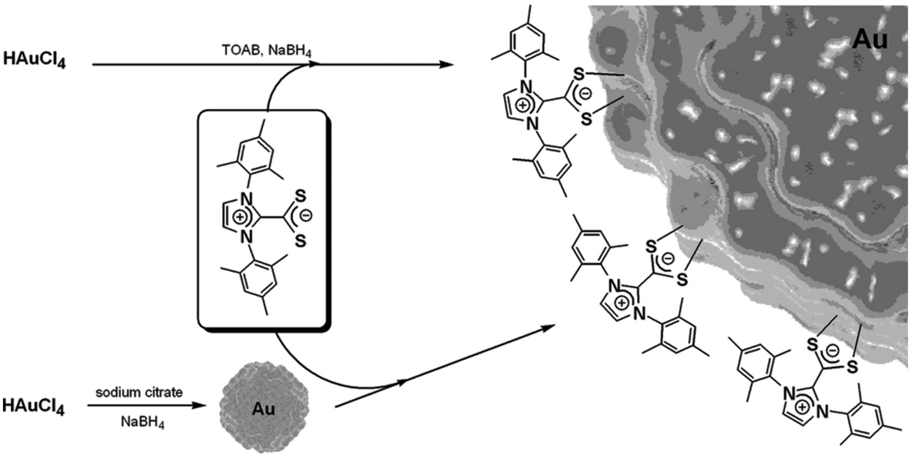
**Scheme 5.** Preparation of Gold Nanoparticles (**NP1** and **NP2**) with IMes·$CS_2$ Surface Units



to those found in free IMes·$CS_2$. IR spectroscopy showed peaks almost identical with those displayed by the ligand itself, including $\nu_{NCN}$ and $\nu_{SCS}$ absorptions at 1486 and 1049 $cm^{-1}$, respectively. The lack of change in the IR data upon coordination of these ligands has been commented on recently in a study on ruthenium arene complexes.[13b] Analysis of **NP1** using transmission electron microscopy (TEM) revealed nanoparticles of diameter 11.5 (±1.2) nm, as shown in Figure 5.

In a similar fashion, the more direct method pioneered by Brust et al.[23b] was used to form nanoparticles of smaller size (**NP2**) starting from $HAuCl_4$, tetraoctylammonium bromide (TOAB), IMes·$CS_2$, and sodium borohydride (Scheme 5). This material was washed with water; however, removal of free IMes·$CS_2$ proved more problematic because of its similar solubility to the nanoparticle material itself. Eventually, it was found that warming in acetonitrile dissolved all of the solid and cooling at −20 °C led to crystallization of the free IMes·$CS_2$ zwitterions. Repeating this procedure and removing the crystals formed allowed the unbound surface units to be separated. TEM imaging (Figure 5) indicated that the nanoparticles were of average diameter 2.6 (±0.3) nm and showed extensive interparticle agglomeration (Figure 5).

Nevertheless, the preparation of **NP1** and **NP2** illustrates that imidazolium-2-dithiocarboxylates are suitable protecting groups for gold nanoparticles and thereby extends the scope of dithio surface units in this arena beyond dithiocarbamates.

## Structural Discussion

The geometry at gold is almost linear in all four structurally characterized complexes with L−Au−S angles lying between 178.94(3)° for **2** and 169.54(11)° for **8**. The Au−P distances of 2.2622(7) (**2**) and 2.2595(5) (**3**) Å are comparable to that of 2.2447(10) Å reported for the dithiocarbamate compound $[(Ph_3P)Au(S_2CNC_4H_8)]$,[28] while the Au−C(Dip) bond distances of 2.025(3) Å for **7** and 2.017(4) Å for **8** are considerably greater than that of 1.942(3) Å found in the precursor, [(IDip)AuCl].[9] This suggests that IMes·$CS_2$ exerts a superior trans influence over chloride. There are no previously reported examples of NHC·$CS_2$ coordinated to gold(I), but the Au−S(1) distances of 2.3047(8) and 2.2912(10) Å in **7** and **8** are longer than those found in comparable isonitrilethiolate species, such as the 1,3,4-thiadiazole-2,5-disulfide compound, $[(C_2N_2S_3)(AuCN^tBu)_2]$ [2.279(2) and 2.272(2) Å][18a] or $[(^tBuNC)Au(SC_6H_4CO_2H\text{-}2)]$ [2.278(5) Å].[29] The Au−S distances of 2.3223(7) and 2.3147(5) Å found for **2** and **3**, respectively, are shorter than that of 2.3334(11) Å found for $[(Ph_3P)Au(S_2CNC_4H_8)]$.[28] The C(2)−S(3) bond lengths of 1.640(3), 1.6420(16), 1.639(4), and 1.643(4) Å are all substantially shorter than the C(2)−S(1) bond lengths [1.708(3), 1.7027(14), 1.701(4), and 1.702(5) Å] of the sulfur atom [S(1)] coordinated directly to the metal, indicating some multiple-bond character. The corresponding distances for the free ligand are between these values at 1.667(3) Å.[13a] Given that the sum of the van der Waals radii for gold and sulfur is 3.46 Å, the Au−S3 distance of 3.3549(8) Å in **2** indicates a weak interaction, although those of 3.4825(5) Å in **3**, 3.5612(9) Å in **7**, and 3.4817(11) Å in **8** are too long to be considered as significant bonding interactions. It is perhaps surprising that there is no more interaction between this arm of the chelate and the metal center (particularly for **3**), given the precedent for such anisobidentate coordination in gold dithiocarbamate compounds, such as $[(Ph_3P)Au(S_2CNC_4H_8)]$, which displays a corresponding Au−S distance of 3.0440(13) Å.[28] Despite the conducive planarity of the heterocyclic unit, the formation of intermolecular Au···Au contacts is prevented by the steric demands of the substituents. The cationic nature of the IMes·$CS_2$ unit is not reflected in any difference of the C(4)−N(8) or C(4)−N(5) bond lengths in the heterocycle compared to the Dip carbene unit; however, these distances are shorter than 1.374(6) and 1.387(6) Å found for the free ligand.[13a]

## Conclusions

The first examples of gold(I) complexes of dithiocarboxylate ligands derived from NHCs have been prepared and characterized (structurally in four cases). The NHC·$CS_2$ zwitterions act as excellent donors for a range of mono- and bimetallic gold complexes with phosphine, carbene, and isonitrile coligands. These complexes expand significantly the underexplored dithiocarboxylate class of sulfur donors,

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which has long remained a poor relation of the ubiquitous dithiocarbamate and numerous xanthate ligands. Furthermore, imidazolium-2-dithiocarboxylate betaines can be used to form monolayers on the surface of gold nanoparticles in a manner similar to that of dithiocarbamates.

## Experimental Section

**General Comments.** All experiments were carried out under aerobic conditions, and the complexes obtained appear relatively stable toward the atmosphere, whether in solution or in the solid state. Some decomposition to the gold colloid was occasionally observed, indicated by a purple coloration. Reagents and solvents were used as received from commercial sources. The following complexes and ligands were prepared as described elsewhere: [AuCl($PR_3$)] (R = Me,[30] Cy,[31] Ph[32]), [dppf($AuCl)_2$],[33] [dppm($AuCl)_2$],[34] [dppb($AuCl)_2$],[35] [AuCl(tht)],[36] [AuCl(IDip)],[9] [AuCl($CN^tBu$)],[37] IPr·$CS_2$,[13] IMes·$CS_2$,[13] and IDip·$CS_2$.[13] ES and fast atom bombardment (FAB) mass spectrometry data were obtained using Micromass LCT Premier and Autospec Q instruments, respectively. IR data were obtained using a Perkin-Elmer Paragon 1000 FT-IR spectrometer, KBr plates were used for solid-state IR spectroscopy, and characteristic triphenylphosphine-associated IR data are not reported. NMR spectroscopy was performed at 25 °C using Varian Mercury 300 and Bruker AV400 spectrometers in $CDCl_3$ unless otherwise indicated. All couplings are in hertz. Resonances in the $^{31}P$ NMR spectrum due to the hexafluorophosphate counteranion were observed in all cases but are not included below. Elemental analysis data were obtained from London Metropolitan University. The procedures given provide materials of sufficient purity for synthetic and spectroscopic purposes. TEM was performed at UCL using a JEOL 100 instrument operating at 100 kV.

**Preparation of [($Ph_3P$)Au($S_2C$·IPr)]$PF_6$ (1).** A dichloromethane solution (10 mL) of [AuCl($PPh_3$)] (40 mg, 0.081 mmol) was treated with a solution of IPr·$CS_2$ (19 mg, 0.083 mmol) in dichloromethane (5 mL). Upon addition of $NH_4PF_6$ (26 mg, 0.160 mmol) in methanol (5 mL), a purple coloration appeared. The reaction was stirred for 1 h and then all solvent removed. The crude product was dissolved in dichloromethane (10 mL) and filtered through Celite to remove $NH_4Cl$ and excess $NH_4PF_6$. Hexane (15 mL) was added and the crude product triturated ultrasonically to give a brown solid. This was filtered, washed with hexane (10 mL), and dried. Yield: 49 mg (73%). IR (Nujol/KBr): $\nu$(PF) 1566, 1311, 1209, 1055, 839 $cm^{-1}$. $^{31}P$ NMR: 36.0 (s, $PPh_3$) ppm. $^1H$ NMR: 1.55 (d, $CH_3$, 12H, $J_{HH}$ = 6.8 Hz), 4.87 (sept, $CHMe_2$, 2H, $J_{HH}$ = 6.8 Hz), 7.36 (s, HC=CH, 2H), 7.54−7.66 (m, $C_6H_5$, 15H) ppm. MS (ES +ve; abundance): *m*/*z* 687 (100) $[M]^+$. Elem anal. Calcd for $C_{28}H_{31}AuF_6N_2P_2S_2$: C, 40.4; H, 3.8; N, 3.4. Found: C, 40.3; H, 3.8; N, 3.4.

**Preparation of [($Ph_3P$)Au($S_2C$·IMes)]$PF_6$ (2).** A dichloromethane solution (10 mL) of [AuCl($PPh_3$)] (45 mg, 0.091 mmol) was treated with a solution of IMes·$CS_2$ (38 mg, 0.100 mmol) in dichloromethane (5 mL). Upon addition of $NH_4PF_6$ (30 mg, 0.184 mmol) in methanol (5 mL), a green coloration appeared. The reaction was stirred for 1 h and then all solvent removed. The crude product was dissolved in dichloromethane (10 mL) and filtered through Celite to remove $NH_4Cl$ and excess $NH_4PF_6$. Pentane (15 mL) was added and the solid triturated ultrasonically to give a pale-green solid. This was filtered, washed with pentane (10 mL), and dried. Yield: 75 mg (84%). IR (Nujol/KBr): $\nu$(PF) 1722, 1566, 1311, 1209, 1055, 839 $cm^{-1}$. $^{31}P$ NMR: 35.1 (s, $PPh_3$) ppm. $^1H$ NMR: 2.25 (s, *o*-$CH_3$, 12H), 2.37 (s, *p*-$CH_3$, 6H), 7.08 (s, *m*-$C_6H_2$, 4H), 7.41 (s, HC=CH, 2H), 7.45−7.60 (m, $C_6H_5$, 15H) ppm. MS (ES +ve; abundance): *m*/*z* 839 (100) $[M]^+$. Elem anal. Calcd for $C_{40}H_{39}AuF_6N_2P_2S_2$: C, 48.8; H, 4.0; N, 2.9. Found: C, 48.9; H, 4.1; N, 2.9.

**Preparation of [($Ph_3P$)Au($S_2C$·IDip)]$PF_6$ (3).** A dichloromethane solution (10 mL) of [AuCl($PPh_3$)] (50 mg, 0.101 mmol) was treated with a solution of IDip·$CS_2$ (47 mg, 0.101 mmol) in dichloromethane (5 mL). Upon addition of $NH_4PF_6$ (33 mg, 0.203 mmol) in methanol (5 mL), a green coloration appeared. The reaction was stirred for 1 h and then all solvent removed. The crude product was dissolved in dichloromethane (10 mL) and filtered through Celite to remove $NH_4Cl$ and excess $NH_4PF_6$. Pentane (15 mL) was added and the crude product triturated ultrasonically to give a green solid. This was filtered, washed with pentane (10 mL), and dried. Yield: 62 mg (58%). A purple coloration was observed in the solid state, indicating the formation of a gold colloid. IR (Nujol/KBr): $\nu$(PF) 1711, 1587, 1554, 1327, 1275, 1212, 1101, 1070, 839 $cm^{-1}$. $^{31}P$ NMR: 35.4 (s, $PPh_3$) ppm. $^1H$ NMR: 1.24 (d, $CH_3$, 12H, $J_{HH}$ = 7.1 Hz), 1.36 (d, $CH_3$, 12H, $J_{HH}$ = 6.7 Hz), 2.66 (sept, $CHMe_2$, 4H, $J_{HH}$ = 6.8 Hz), 7.38−7.63 (m, $C_6H_5$ + $C_6H_3$ + HC=CH, 15H + 6H + 2H) ppm. MS (ES +ve; abundance): *m*/*z* 923 (100) $[M]^+$. Elem anal. Calcd for $C_{46}H_{51}AuF_6N_2P_2S_2$: C, 51.7; H, 4.8; N, 2.6. Found: C, 51.7; H, 4.8; N, 2.6.

**Preparation of [($Cy_3P$)Au($S_2C$·IMes)]$PF_6$ (4).** A dichloromethane solution (10 mL) of [AuCl($PCy_3$)] (40 mg, 0.078 mmol) was treated with a solution of IMes·$CS_2$ (31 mg, 0.082 mmol) in dichloromethane (5 mL). Upon addition of $NH_4PF_6$ (25 mg, 0.153 mmol) in methanol (5 mL), a green coloration appeared. The reaction was stirred for 1 h and then all solvent removed. The crude product was dissolved in dichloromethane (10 mL) and filtered through Celite to remove $NH_4Cl$ and excess $NH_4PF_6$. Ethanol (15 mL) was added and the solvent volume reduced until precipitation of the green solid was complete. This was filtered, washed with ethanol (10 mL) and pentane (10 mL), and dried. Yield: 59 mg (75%). IR (Nujol/KBr): $\nu$(PF) 1712, 1607, 1557, 1300, 1230, 1170, 1114, 1069, 1041, 1005, 839 $cm^{-1}$. $^{31}P$ NMR: 56.7 (s, $PCy_3$) ppm. $^1H$ NMR: 1.24−1.45, 1.71−1.91, 1.96−2.08 (m × 3, Cy, 33H), 2.24 (s, *o*-$CH_3$, 12H), 2.39 (s, *p*-$CH_3$, 6H), 7.08 (s, *m*-$C_6H_2$, 4H), 7.36 (s, HC=CH, 2H) ppm. MS (ES +ve; abundance): *m*/*z* 858 (100) $[M]^+$. Elem anal. Calcd for $C_{40}H_{57}AuF_6N_2P_2S_2$: C, 47.9; H, 5.7; N, 2.8. Found: C, 48.0; H, 5.6; N, 2.8.

**Preparation of [($Me_3P$)Au($S_2C$·IMes)]$PF_6$ (5).** A dichloromethane solution (10 mL) of [AuCl($PMe_3$)] (30 mg, 0.097 mmol) was treated with a solution of IMes·$CS_2$ (41 mg, 0.108 mmol) in dichloromethane (5 mL). Upon addition of $NH_4PF_6$ (32 mg, 0.196 mmol) in methanol (5 mL), a green coloration appeared. The reaction was stirred for 30 min and then all solvent removed. The crude solid was dissolved in dichloromethane (10 mL) and filtered through diatomaceous earth (Celite) to remove $NH_4Cl$ and excess $NH_4PF_6$. All solvent was again removed and the green product triturated ultrasonically in diethyl ether (20 mL). This was filtered, washed with diethyl ether (15 mL), and dried. Yield: 65 mg (84%). IR (solid): $\nu$(PF) 1608, 1558, 1486, 1465, 1420, 1381, 1293, 1115, 1065, 1006, 958, 828 $cm^{-1}$. $^{31}P$

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NMR: −4.1 (s, PMe$_3$) ppm. $^1$H NMR: 1.58 (d, CH$_3$, 9H, $J_{HP}$ = 11.2 Hz), 2.27 (s, *o*-CH$_3$, 12H), 2.42 (s, *p*-CH$_3$, 6H), 7.11 (s, *m*-C$_6$H$_2$, 4H), 7.38 (s, HC=CH, 2H) ppm. MS (FAB +ve; abundance): *m*/*z* 653 (95) [M]$^+$. Elem anal. Calcd for $C_{25}H_{33}AuF_6N_2P_2S_2$: C, 37.6; H, 4.2; N, 3.5. Found: C, 37.5; H, 4.3; N, 3.4.

**Preparation of [($^t$BuNC)Au(S$_2$C·IMes)]PF$_6$ (6).** A dichloromethane solution (10 mL) of [AuCl(CN$^t$Bu)] (30 mg, 0.095 mmol) was treated with a solution of IMes·CS$_2$ (38 mg, 0.100 mmol) in dichloromethane (5 mL). Upon addition of NH$_4$PF$_6$ (31 mg, 0.190 mmol) in methanol (5 mL), a green coloration appeared. The reaction was stirred for 1 h and then all solvent removed. The crude product was dissolved in dichloromethane (10 mL) and filtered through Celite to remove NH$_4$Cl and excess NH$_4$PF$_6$. All solvent was again removed and the crude solid triturated ultrasonically in diethyl ether (20 mL). The green product was filtered, washed with diethyl ether (10 mL), and dried. Yield: 71 mg (93%). IR (Nujol/KBr): $\nu$(CN) 2258, 2234, $\nu$(PF) 1607, 1557, 1309, 1232, 1193, 1116, 1070, 1037, 1005, 931, 839 cm$^{-1}$. $^1$H NMR: 1.54 (s, 9H, $^t$Bu), 2.21 (s, *o*-CH$_3$, 12H), 2.38 (s, *p*-CH$_3$, 6H), 7.07 (s, *m*-C$_6$H$_2$, 4H), 7.40 (s, HC=CH, 2H) ppm. MS (ES +ve; abundance): *m*/*z* 660 (62) [M]$^+$. Elem anal. Calcd for $C_{27}H_{33}AuF_6N_3PS_2$: C, 40.4; H, 4.1; N, 5.2. Found: C, 40.3; H, 4.1; N, 5.2.

**Preparation of [(IDip)Au(S$_2$C·IPr)]PF$_6$ (7).** A dichloromethane solution (10 mL) of [AuCl(IDip)] (50 mg, 0.081 mmol) was treated with a solution of IPr·CS$_2$ (20 mg, 0.088 mmol) in dichloromethane (5 mL). Upon addition of NH$_4$PF$_6$ (27 mg, 0.166 mmol) in methanol (5 mL), a purple coloration appeared. The reaction was stirred for 30 min and then all solvent removed. The crude product was dissolved in dichloromethane (10 mL) and filtered through diatomaceous earth (Celite) to remove NH$_4$Cl and excess NH$_4$PF$_6$. All solvent was again removed and the pale-purple product triturated ultrasonically in diethyl ether (20 mL). This was filtered, washed with diethyl ether (15 mL), and dried. Yield: 55 mg (71%). IR (solid): $\nu$(PF) 1597, 1563, 1475, 1422, 185, 1365, 1354, 1330, 1256, 1207, 1181, 1137, 1092, 1062, 876, 832 cm$^{-1}$. $^1$H NMR: 1.31, 1.38 (d × 2, Me$_{IDip}$, 2 × 12H, $J_{HH}$ = 6.9 Hz), 1.46 (d, Me$_{IPr}$, 12H, $J_{HH}$ = 6.7 Hz), 2.68 (sept, CHMe$_{IDip}$, 4H, $J_{HH}$ = 6.9 Hz), 4.62 (s(br), 2H, CHMe$_{IPr}$), 7.24 (s, 2H, HC=CH$_{IDip}$), 7.38 (s, 2H, HC=CH$_{IPr}$), 7.40 (d, 4H, *m*-C$_6$H$_3$, $J_{HH}$ = 7.8 Hz), 7.62 (t, 2H, *p*-C$_6$H$_3$, $J_{HH}$ = 7.8 Hz) ppm. MS (FAB +ve; abundance): *m*/*z* 813 (100) [M]$^+$, 585 (12) [M − S$_2$C·IPr]$^+$. Elem anal. Calcd for $C_{37}H_{52}AuF_6N_4PS_2$: C, 46.3; H, 5.5; N, 5.8. Found: C, 46.2; H, 5.4; N, 5.8.

**Preparation of [(IDip)Au(S$_2$C·IMes)]PF$_6$ (8).** A dichloromethane solution (10 mL) of [AuCl(IDip)] (50 mg, 0.081 mmol) was treated with a solution of IMes·CS$_2$ (34 mg, 0.089 mmol) in dichloromethane (5 mL). Upon addition of NH$_4$PF$_6$ (26 mg, 0.160 mmol) in methanol (5 mL), a green coloration appeared. The reaction was stirred for 30 min and then all solvent removed. The crude product was dissolved in dichloromethane (10 mL) and filtered through diatomaceous earth (Celite) to remove NH$_4$Cl and excess NH$_4$PF$_6$. All solvent was again removed and the pale-green product triturated ultrasonically in diethyl ether (20 mL). This was filtered, washed with diethyl ether (15 mL), and dried. Yield: 69 mg (77%). IR (solid): $\nu$(PF) 1608, 1558, 1486, 1462, 1421, 1384, 1365, 1330, 1230, 1183, 1117, 1071, 1007, 932, 835, 760 cm$^{-1}$. $^1$H NMR: 1.15, 1.23 (d × 2, Me$_{IDip}$, 2 × 12H, $J_{HH}$ = 6.9 Hz), 2.12 (s, *o*-CH$_3$, 12H), 2.12 (s, *p*-CH$_3$, 6H), 2.47 (sept, CHMe$_{IDip}$, 4H, $J_{HH}$ = 6.9 Hz), 7.02 (s(br), HC=CH$_{IDip/IMes}$, 4H), 7.28 (d, *m*-C$_6$H$_3$, 4H, $J_{HH}$ = 7.8 Hz), 7.29 (s, *m*-C$_6$H$_2$, 4H), 7.54 (t, *p*-C$_6$H$_3$, 2H, $J_{HH}$ = 7.8 Hz) ppm. MS (FAB +ve; abundance): *m*/*z* 965 (100) [M]$^+$, 585 (9) [M − S$_2$C·IMes]$^+$. Elem anal. Calcd for $C_{49}H_{60}AuF_6N_4PS_2$: C, 53.0; H, 5.4; N, 5.0. Found: C, 52.9; H, 5.5; N, 4.9.

**Preparation of [(dppb){Au(S$_2$C·IMes)}$_2$](PF$_6$)$_2$ (9).** A dichloromethane solution (10 mL) of [(dppb)(AuCl)$_2$] (25 mg, 0.028 mmol) was treated with a solution of IMes·CS$_2$ (21 mg, 0.055 mmol) in dichloromethane (5 mL). Upon addition of NH$_4$PF$_6$ (14 mg, 0.086 mmol) in methanol (5 mL), a green coloration appeared. The reaction was stirred for 40 min and then all solvent removed. The crude product was dissolved in dichloromethane (10 mL) and filtered through Celite to remove NH$_4$Cl and excess NH$_4$PF$_6$. Diethyl ether (20 mL) was added and the solid triturated ultrasonically to give a green solid. This was filtered, washed with diethyl ether (10 mL), and dried. Yield: 46 mg (88%). IR (Nujol/KBr): $\nu$(PF) 1607, 1556, 1308, 1231, 1157, 1104, 1068, 1005, 931, 839 cm$^{-1}$. $^{31}$P NMR: 31.9 (s, dppb) ppm. $^1$H NMR: 1.62, 2.37 (m × 2, CH$_2$, 8H), 2.24 (s, *o*-CH$_3$, 24H), 2.31 (s, *p*-CH$_3$, 12H), 7.02 (s, *m*-C$_6$H$_2$, 8H), 7.39 (s, HC=CH, 4H), 7.41−7.56 (m, C$_6$H$_5$, 20H) ppm. MS (FAB +ve; abundance): *m*/*z* 1727 (5) [M + PF$_6$]$^+$. Elem anal. Calcd for $C_{72}H_{76}Au_2F_{12}N_4P_4S_4$: C, 46.2; H, 4.1; N, 3.0. Found: C, 46.2; H, 4.1; N, 3.1.

**Preparation of [(dppf){Au(S$_2$C·IMes)}$_2$](PF$_6$)$_2$ (10).** A dichloromethane solution (10 mL) of [(dppf)(AuCl)$_2$] (50 mg, 0.049 mmol) was treated with a solution of IMes·CS$_2$ (37.4 mg, 0.098 mmol) in dichloromethane (10 mL). The addition of NH$_4$PF$_6$ (24 mg, 0.147 mmol) in methanol (5 mL) resulted in a green coloration. The reaction was stirred for 1 h and then all solvent removed. The crude product was dissolved in dichloromethane (10 mL) and filtered through Celite to remove NH$_4$Cl and excess NH$_4$PF$_6$. The solvent was again removed and the crude solid triturated ultrasonically in diethyl ether (20 mL) to yield a green solid. This was filtered, washed with diethyl ether (10 mL), and dried. Yield: 88 mg (90%). IR (Nujol/KBr): $\nu$(PF) 1612, 1563, 1484, 1438, 1380, 1313, 1231, 1173, 1103, 1066, 1032, 1007, 828 cm$^{-1}$. $^{31}$P NMR: 29.9 (s, dppf) ppm. $^1$H NMR: 2.26 (s, *o*-CH$_3$, 24H), 2.28 (s, *p*-CH$_3$, 12H), 4.23, 4.38 (s × 2, C$_5$H$_4$, 2 × 4H), 6.99 (s, *m*-C$_6$H$_2$, 8H), 7.39−7.60 (m, C$_6$H$_5$ + HC=CH, 20H + 4H) ppm. MS (FAB +ve; abundance): *m*/*z* 1854 (3) [M + PF$_6$]$^+$, 1328 (42) [M − IMesCS$_2$]$^+$. Elem anal. Calcd for $C_{78}H_{76}Au_2F_{12}FeN_4P_4S_4$: C, 46.9; H, 3.8; N, 2.8. Found: C, 47.0; H, 3.9; N, 2.8.

**Preparation of [(dppm){Au$_2$(S$_2$C·IMes)}](PF$_6$)$_2$ (11).** A dichloromethane solution (10 mL) of [(dppm)(AuCl)$_2$] (34 mg, 0.040 mmol) was treated with a solution of IMes·CS$_2$ (16 mg, 0.042 mmol) in dichloromethane (5 mL). The addition of NH$_4$PF$_6$ (15 mg, 0.092 mmol) in methanol (5 mL) resulted in a green coloration. The reaction was stirred for 40 min and then all solvent removed. The crude product was dissolved in dichloromethane (10 mL) and filtered through Celite to remove NH$_4$Cl and excess NH$_4$PF$_6$. Ethanol (15 mL) was added and the solvent volume reduced to precipitate an olive-green solid. This was filtered, washed with cold ethanol (10 mL) and hexane (10 mL), and dried. A further crop could be obtained by removing all solvent and triturating the solid in diethyl ether (20 mL). Yield: 49 mg (85%). IR (Nujol/KBr): $\nu$(PF) 1606, 1555, 1308, 1230, 1156, 1101, 1068, 1000, 931, 838 cm$^{-1}$. $^{31}$P NMR: 28.4 (s, dppm) ppm. $^1$H NMR: 2.28 (s(br), *o*-CH$_3$, 12H), 2.34 (s, *p*-CH$_3$, 6H), 3.72 (t, CH$_2$, 2H, $J_{HP}$ = 12.3 Hz), 7.08 (s, *m*-C$_6$H$_2$, 4H), 7.29−7.63 (m, C$_6$H$_5$ + HC=CH, 20H + 2H) ppm. MS (ES +ve; abundance): *m*/*z* 1158 (28) [M]$^+$. Elem anal. Calcd for $C_{47}H_{46}Au_2F_{12}N_2P_4S_2$: C, 39.0; H, 3.2; N, 1.9. Found: C, 38.9; H, 3.0; N, 1.8.

**Preparation of [Au$_2$(S$_2$C·IPr)$_2$](PF$_6$)$_2$ (12).** [AuCl(tht)] (17.5 mg, 0.055 mmol) and IPr·CS$_2$ (13 mg, 0.057 mmol) were dissolved in dichloromethane (15 mL), and a methanolic solution (10 mL) of NH$_4$PF$_6$ (18 mg, 0.110 mmol) was added. The reaction was stirred for 1 h and then all solvent removed. The crude product was dissolved in dichloromethane (10 mL) and filtered through Celite to remove NH$_4$Cl and excess NH$_4$PF$_6$. Ethanol (20 mL) was added and the solvent volume reduced until precipitation of the red-brown product was complete. This was filtered, washed with ethanol (10 mL) and hexane (10 mL), and dried. Yield: 37 mg (59%). IR (Nujol/KBr): $\nu$(PF) 1566, 1317, 1260, 1210, 1180, 1138, 1060,

**Table 1.** Crystallographic Data for Compounds **2**, **3**, **7**, and **8**

| data | **2** | **3** | **7** | **8** |
|---|---|---|---|---|
| formula | $[C_{40}H_{39}AuN_2PS_2](PF_6)$ | $[C_{46}H_{51}AuN_2PS_2](PF_6)$ | $[C_{37}H_{52}AuN_4S_2](PF_6)$ | $[C_{49}H_{60}AuN_4S_2](PF_6)$ |
| solvent | $0.55CH_2Cl_2 \cdot 0.45Et_2O$ | $Et_2O$ |  | $CH_2Cl_2$ |
| fw | 1064.82 | 1143.03 | 958.88 | 1195.99 |
| *T* (°C) | −100 | −100 | −100 | −100 |
| space group | $P2_12_12_1$ (No. 19) | $P2_1$ (No. 4) | $P2_1/n$ (No. 14) | *Iba*2 (No. 45) |
| *a* (Å) | 13.11504(16) | 10.65689(11) | 13.39748(6) | 16.89890(8) |
| *b* (Å) | 13.99608(18) | 13.57473(13) | 13.32238(6) | 31.95473(15) |
| *c* (Å) | 24.7953(3) | 18.59207(17) | 23.37032(12) | 19.98864(11) |
| α (deg) |  |  |  |  |
| *β* (deg) |  | 101.3289(9) | 100.4298(5) |  |
| *γ* (deg) |  |  |  |  |
| *V* (Å$^3$) | 4551.41(10) | 2637.21(5) | 4102.36(3) | 10 793.86(9) |
| *Z* | 4 | 2 | 4 | 8 |
| $\rho_{calcd}$ (g cm$^{-3}$) | 1.554 | 1.439 | 1.553 | 1.472 |
| *λ* (Å) | 0.710 73 | 0.710 73 | 1.541 84 | 1.541 84 |
| *μ* (mm$^{-1}$) | 3.516 | 2.986 | 8.557 | 7.517 |
| R1 (obs)[a] | 0.027 | 0.021 | 0.030 | 0.028 |
| wR2 (all)[b] | 0.055 | 0.033 | 0.080 | 0.074 |

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w - 1 = \sigma^2(F_o^2) + (aP)^2 + bP$.

841 cm$^{-1}$. $^1$H NMR: 1.59 (d, $CH_3$, 24H, $J_{HH}$ = 6.8 Hz), 4.96 (sept, $CHMe_2$, 4H, $J_{HH}$ = 6.8 Hz), 7.45 (s, HC=CH, 4H) ppm. MS (FAB +ve; abundance): *m*/*z* 850 (52) [M]$^+$, 653 (78) [M − Au]$^+$. Elem anal. Calcd for $C_{20}H_{32}Au_2F_{12}N_4P_2S_4$: C, 21.1; H, 2.8; N, 4.9. Found: C, 21.2; H, 2.9; N, 4.7.

**Preparation of $[Au_2(S_2C \cdot IMes)_2](PF_6)_2$ (13).** A dichloromethane solution (10 mL) of [AuCl(tht)] (32 mg, 0.100 mmol) was treated with a solution of IMes·$CS_2$ (38 mg, 0.100 mmol) in dichloromethane (5 mL) and $NH_4PF_6$ (35 mg, 0.215 mmol) in methanol (5 mL). The reaction was stirred for 1 h and then all solvent removed. The crude product was dissolved in dichloromethane (10 mL) and filtered through Celite to remove $NH_4Cl$ and excess $NH_4PF_6$. Diethyl ether (15 mL) was added and the solid triturated ultrasonically to give a dark-brown solid. This was filtered, washed with diethyl ether (10 mL), and dried. Yield: 68 mg (47%). IR (Nujol/KBr): *ν*(PF) 1606, 1554, 1307, 1231, 1170, 1117, 1070, 931, 837 cm$^{-1}$. $^1$H NMR: 2.16 (s, *o*-$CH_3$, 24H), 2.36 (s, *p*-$CH_3$, 12H), 7.05 (s, *m*-$C_6H_2$, 8H), 7.53 (s, HC=CH, 4H) ppm. MS (FAB +ve; abundance): *m*/*z* 1155 (21) [M]$^+$. Elem anal. Calcd for $C_{44}H_{48}Au_2F_{12}N_4P_2S_4$: C, 36.6; H, 3.4; N, 3.9. Found: C, 36.7; H, 3.5; N, 4.0.

**Preparation of $[Au_2(S_2C \cdot IDip)_2](PF_6)_2$ (14).** [AuCl(tht)] (9.6 mg, 0.030 mmol) and IDip·$CS_2$ (14 mg, 0.030 mmol) were dissolved in dichloromethane (15 mL), and a methanolic solution (10 mL) of $NH_4PF_6$ (21 mg, 0.129 mmol) was added. The reaction was stirred for 1 h and then all solvent removed. The crude product was dissolved in dichloromethane (10 mL) and filtered through Celite to remove $NH_4Cl$ and excess $NH_4PF_6$. Ethanol (20 mL) was added and the solvent volume reduced until precipitation of the orange-red product was complete. This was filtered, washed with ethanol (10 mL) and hexane (10 mL), and dried. Yield: 26 mg (54%). IR (Nujol/KBr): *ν*(PF) 1555, 1212, 1154, 1072, 844 cm$^{-1}$. $^1$H NMR: 1.19, 1.29 (d × 2, $CH_3$, 48H, $J_{HH}$ = 6.7 Hz), 2.52 (s(br), $CHMe_2$, 8H), 7.35 (d, *m*-$C_6H_3$, 8H, $J_{HH}$ = 8.0 Hz), 7.46 (s(br), HC=CH, 4H), 7.59 (t, *p*-$C_6H_3$, 4H, $J_{HH}$ = 8.0 Hz) ppm. MS (FAB +ve; abundance): *m*/*z* 1322 (27) [M]$^+$, 1125 (100) [M − Au]$^+$. Elem anal. Calcd for $C_{56}H_{72}Au_2F_{12}N_4P_2S_4$: C, 41.7; H, 4.5; N, 3.5. Found: C, 42.0; H, 4.6; N, 3.7.

**Preparation of NP1.** An aqueous solution (30 mL) of $HAuCl_4$ (10.8 mg, 0.032 mmol) was heated to reflux, and sodium citrate (38 mg, 0.129 mmol) in water (5 mL) was added, causing a darkening of the color. The reaction was stirred at reflux for 10 min and then for a further 15 min at room temperature. A dichloromethane−methanol (5:10 mL) solution of IMes·$CS_2$ (30 mg, 0.079 mmol) was added dropwise and the reaction stirred for a further 2 h. The resulting suspension was left to stand and the supernatant decanted, and the solid was washed with water (30 mL) to remove excess sodium citrate and cold dichloromethane (20 mL) to remove excess ligand. The dichloromethane washings yielded 16 mg of IMes·$CS_2$, indicating that only 14 mg (0.037 mmol) had been required in the surface functionalization of the nanoparticles (1:1 Au−ligand ratio). The black solid was dried under vacuum. IR: 1607, 1563, 1486, $\nu_{NCN}$1459, 1378, 1222, 1165, 1104, 1049, $\nu_{SCS}$ 931, 865 cm$^{-1}$. $^1$H NMR (acetone-*d*$^6$): 2.30 (s, *p*-$CH_3$, 6H), 2.38 (s, *o*-$CH_3$, 12H), 7.04 (s, *m*-$C_6H_2$, 4H), 7.60 (s, HC=CH, 2H) ppm.

**Preparation of NP2.** An aqueous solution (10 mL) of $HAuCl_4$ (17 mg, 0.050 mmol) and TOAB (109.4 mg, 0.200 mmol) in chloroform (15 mL) were stirred rapidly together for 15 min until phase transfer was complete. The lower organic layer was cooled to 4 °C and treated with IMes·$CS_2$ (28.5 mg, 0.075 mmol) as a dichloromethane solution (5 mL). The reaction was stirred for 10 min, and then sodium borohydride (38 mg, 1.005 mmol) was added rapidly, leading to a darkening of the solution. After 2 h of stirring below 10 °C, the organic layer was separated and washed with water (3 × 10 mL). The volume was concentrated to ca. 5 mL and ethanol (20 mL) added to precipitate the crude black solid. Centrifugation allowed the solvent to be decanted, leaving a black product, which was dried under vacuum. Excess ligand was removed by dissolving the material in warm acetonitrile, cooling the solution overnight at −20 °C, and then removing the crystalline material. IR: 1604, 1562, 1486 $\nu_{NCN}$, 1459, 1447, 1378, 1223, 1166, 1105, 1051 $\nu_{SCS}$, 930, 868 cm$^{-1}$. $^1$H NMR (acetone-*d*$^6$): 2.31 (s, *p*-$CH_3$, 6H), 2.38 (s, *o*-$CH_3$, 12H), 7.03 (s, *m*-$C_6H_2$, 4H), 7.59 (s, HC=CH, 2H) ppm.

## Crystallography

Table 1 provides a summary of the crystallographic data for compounds **2**, **3**, **7**, and **8**. The data were collected using Oxford Diffraction Xcalibur 3 (**2** and **3**) and PX Ultra (**7** and **8**) diffractometers, and the structures were refined based on $F^2$ using the *SHELXTL* and *SHELX-97* program systems.[38] The absolute structures of **2** and **3** were determined by a combination of *R*-factor tests [for **2**, $R1^+$ = 0.027, $R1^-$ = 0.070; for **3**, $R1^+$ = 0.021, $R1^-$ = 0.066] and by use of the Flack parameter [for **2**, $x^+$ = 0.000(3); for **3**, $x^+$ = 0.0000(18)]. The absolute structure of **8** was shown to be a partial polar twin by a combination of *R*-factor tests [$R1^+$ = 0.032, $R1^-$ = 0.041] and by use of the Flack

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[38] *SHELXTL PC*, version 5.1; Bruker AXS: Madison, WI, 1997. Sheldrick, G. *SHELX-97*; Institut Anorg. Chemie: Göttingen, Germany, 1998.

parameter [$x^+ = 0.319(6)$, $x^- = 0.681(6)$]. CCDC 745830–745833.

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**Supporting Information Available:** Crystallographic data in CIF format and anisotropic displacement ellipsoid plots for the structures of **2**, **3**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.