Aurolysis of α-C-deprotonated group 6 aminocarbene and thiocarbene complexes with Ph_3PAu^+†

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Deprotonated Fischer-type aminocarbene complexes, $(CO)_5M{=}C(NR_2)CH_3$ (M = Cr or W; R = Me or propyl), react with Ph_3PAu^+ by metal group substitution – $(CO)_5M$ for Ph_3PAu^+ – and attachment of the extricated $M(CO)_5$ to the deprotonated methyl group. (The products may also be seen as aminovinylgold compounds coordinated to $M(CO)_5$ moieties.) DFT calculations at the B3LYP level of theory using model compounds indicate a clear preference of the gold unit for central C to terminal coordination in the ligand $[NMe_2CCH_2]^-$, whereas the $Cr(CO)_5$ has a 7 kcal mol^{-1} preference for C(vinyl) coordination compared to N-coordination. In related thiocarbenes, the sulfur donor atom should be the preferred point of attachment for the metal carbonyl unit. The latter prediction is borne out in practice, and in the three products isolated, including $Ph_3PAu\{C({=}CH_2)SPh\}Cr(CO)_5$ in a mixed crystal with $[Ph_3PAuSPh]Cr(CO)_5$, precisely this coordination mode is present. The latter component of the mixed crystal has also been prepared independently of the vinyl one.

Introduction

We have previously shown that anionic Fischer-type carbene complexes, $[(CO)_5M{=}C(X)R^1]^-$, in which the negative charge formally resides on X (X = O or NR^2, R^1 = Ph, R^2 = H or Me; M = Cr or W), react with the fragment Ph_3PAu^+ to furnish unusual acyl or imidoyl complexes of gold(I). Since this metal exchange is related to the hydrolysis of such Fischer-type carbene complexes through the isolobal analogy, we termed it 'aurolysis'. Furthermore, when starting with N-deprotonated aminocarbene complexes, the expelled $(CO)_5M$ unit is firmly N-coordinated.[1] On the other hand, α-deprotonated alkoxycarbene complexes, $[(CO)_5M{=}C(OR)CH_2]Li$, undergo a metal substitution (group 6 metal for gold) with the same gold phosphine cation to furnish stable vinylether gold complexes, $Ph_3PAuC(OR){=}CH_2$ (R = Me or Et,) that are unsymmetrically π-coordinated to $(CO)_5M$.[2] In an attempt to further extend the utilisation of anionic carbene complexes as useful preparative synthons towards gold(I), the following questions were addressed: (i) would similar aurolysis reactions occur with α-deprotonated aminocarbene complexes and how would the carbonyl fragment then be accommodated? (ii) Could the formation of the product be substantiated by quantum mechanical calculations? (iii) What predictions are made for thiocarbene complexes and how are these borne out in practice?

We particularly focussed on α-deprotonated, Fischer-type aminocarbene complexes, since their advantages in preference to alkoxycarbenes in organic synthesis are well documented.[3] Thiocarbene complexes, due to their greater lability, are less well studied.[4] To our knowledge, no reactions of nucleophiles derived from amino- or thiocarbene complexes with any electrophilic transition metal fragments are known. The potential wealth of unknown organometallic products that can be obtained by employing such nucleophiles as organic synthons in organometallic conversions, therefore, remains unexplored.

The results of our investigation are presented below and clearly indicate the important role played by the carbene substituents in the novel isolobal metal substitution at the carbene carbon atom and subsequent coordination of the group 6 metal carbonyl moiety.

Results and discussion

A. Reactions with aminocarbene complexes

The expected bimetallic, group 6-coordinated aminovinyl gold complexes, $\{Ph_3PAuC(NR_2)CH_2\}M(CO)_5$ (**1–4**, Scheme 1), were prepared in a similar fashion to the previously reported π-bonded vinyl ether compounds of gold, *i.e.* by deprotonation and transmetallation of Fischer-type carbene complexes.[2]

Product separation of oily, dark-yellow reaction mixtures (52–68% yields after separation) was carried out by low temperature (−15 °C) silica gel column chromatography with pentane–diethyl ether (10 : 1) as eluent, followed by crystallisation from a diethyl ether solution layered with pentane at −20 °C. The same 'hydrolysis mechanism' of Casey[5] and Bernasconi[6] now translating as aurolysis, could again be invoked here to understand the metal exchange occurring at the carbene carbon. However, further investigation into the structures of **1–4** indicated a product in which the $(CO)_5M$ moiety is bonded exclusively to the carbon α to

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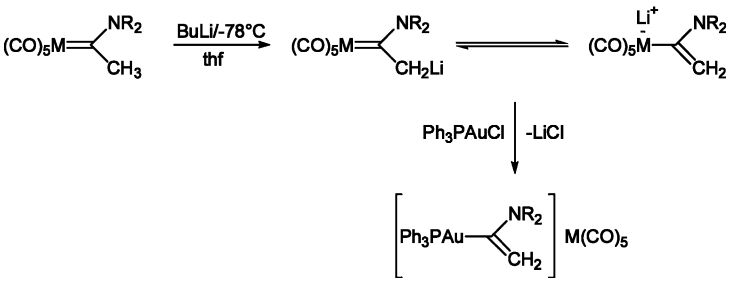
† Electronic supplementary information (ESI) available: Figure showing disorder in **7**/**7′** and preparation, physical data and crystallographic results for pure **7′**. See DOI: 10.1039/b607613k



Scheme 1

the original C(carbene) and not to a formed vinyl double bond as in the alkoxyvinyl compounds of gold. This essentially alkyl-type coordination to both pentacarbonyls affords remarkably stable products that could withstand column chromatography on SiO_2.

Spectroscopic characterisation

Infrared spectroscopy. Pentane solutions of compounds **1**–**4** exhibit the typical four absorption band ν(CO) spectra of $M(CO)_5L$ compounds. Compared to the corresponding IR absorptions for the already mentioned alkoxyvinyl complexes, the bands are now in general shifted approximately 15 cm^{-1} to lower frequencies. Such a shift is symptomatic of more back-donation from the metal atom to the π*-orbitals of its CO ligands indicating a greater partial negative charge on the $M(CO)_5$ fragments, greater polarisation of the vinyl-group 6 metal coordination in these complexes and less η^2-π-bond interaction by the metal. The broad degenerate E-vibration in the new complexes, compared to a lifted degeneracy in the alkoxycarbene complexes, could indicate a decreased steric influence by the remainder of the gold complex as $M(CO)_5$ settles in a more terminal position.

Mass spectrometry. Molecular ion peaks with intensities approximately 50% relative to base peaks were seen for each of the complexes **1**–**4** (m/z 721, 750, 852 and 881). The homoleptic rearrangement product, $(Ph_3P)_2Au^+$, the cation Ph_3PAu^+, and the uncoordinated (dialkylaminovinyl) triphenylphosphinegold moieties (m/z 529 for **1** and **3**, and 558 for **2** and **4**) were clearly identified for each complex and the latter formed the base peaks for **1** and **4**.

NMR spectroscopy. The ^{1}H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopic data for complexes **1**–**4** are reported in the Experimental section. As with previously characterised alkoxyvinyl complexes of this class,[2] the ^{1}H NMR spectra are characterised, in particular, by two distinctive signals, each integrating for a single proton and representing the two diastereotopic terminal CH_2 protons. The exact origin of the chirality around the CH_2 moiety is unknown. It could be as a result of steric hindrance or even by a weak Cr–C(7) (compare Fig. 1) interaction. Resonances for one of these appear, due to weak long range *cis*-$^4J_{P\text{–}H}$ coupling, as broadened singlet or narrow doublet resonances at δ 1.93, 1.97, 2.51 and 2.50, whereas those for the other proton are distinct doublets, due to more efficient $^4J_{P\text{–}H}$ coupling, at δ-values of 2.55, 2.52, 3.00 and 2.91. Compared to the related chemical shifts of comparable protons in previously characterised alkoxyvinyl complexes (in which the vinyl double bond is more apparent[2]), these signals are shifted approximately 0.2 and 1.2 ppm upfield. Similarly, the ^{13}C chemical shifts for the terminal carbons in **1**–**4** appear in fact quite close to the aliphatic region of the ^{13}C spectrum (δ 36.5, 40.1, 36.0 and 42.1). These upfield shifts both in the ^{1}H and ^{13}C spectra suggest that the terminal 'vinyl' CH_2-carbon atoms display less s-character in the new compounds. The ^{1}H and ^{13}C NMR resonances are, however, still situated somewhat downfield compared to literature values for methylene groups directly bonded to negatively charged $W(CO)_5$ fragments.[7] The $^{13}C\{^1H\}$ resonances for the gold-coordinated carbon atoms in **1**–**4** could be easily assigned due to their characteristically large $^2J_{C\text{–}P}$ coupling constants (117.6–134.2 Hz). They appear between δ 207.9 and 218.3, indicating carbene-like character.

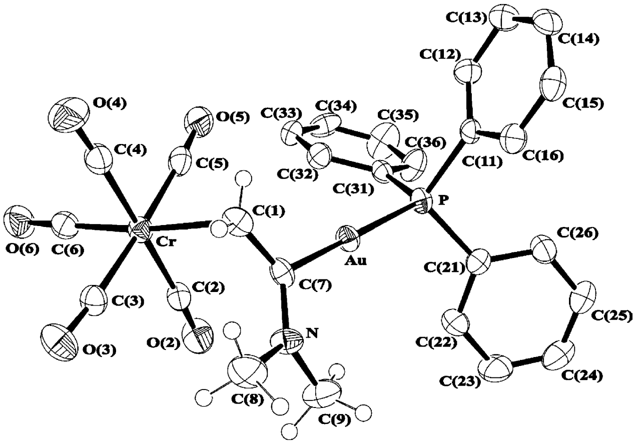


Fig. 1 ORTEP view of **1** (hydrogen atoms on phenyl rings omitted for clarity) showing the numbering scheme. Ellipsoids are shown at the 50% probability level.

Owing to restricted rotation about the C(coordinated)–N bond (*vide infra*) the proton resonances for the NCH_3 groups in each of **1** and **3** appear as two clearly separated signals at δ 2.79 and 3.45, and δ 2.79 and 3.42, respectively. In the ^{13}C NMR spectra a single broadened resonance (δ 29.2 and 29.4) represents both carbon atoms in each component. In **2** and **4** every methylene proton of the ethyl groups is separately represented as a quartet of doublets in the ^{1}H NMR spectrum. The attached CH_3 groups resonate as doublets of doublets (appearing as pseudo-triplets) at δ 1.12, 1.13 and δ 1.20, 1.29, respectively. In the ^{13}C spectra of **2** and **4** the signals for the *cis* and *trans* methylene carbon atoms, like those for the NCH_3 groups in **1** and **3**, appear as broad resonances (δ 25.2 and 27.5) whereas two clearly separated signals each for the terminal CH_3 groups are observed (δ 12.5 and 13.6 in **2**, δ 12.9 and 14.0 in **4**).

Table 1 Selected bond lengths (Å) and angles (°) with s.u.s in parenthesis for complex **1**

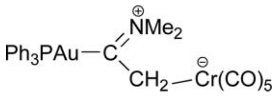
Au–C(7)	2.067(5)	Cr–C(1)–C(7)	100.9(4)
Cr–C(1)	2.337(6)	C(7)–Au–P	174.9(1)
Cr–C(7)	2.947(5)	Au–C(7)–C(1)	118.3(4)
Au–P	2.295(1)	Au–C(7)–N	118.7(4)
C(1)–C(7)	1.406(8)	C(1)–C(7)–N	122.6(5)
C(7)–N	1.348(7)	C(7)–N–C(8)	122.3(5)

The $^{31}P\{^{1}H\}$ NMR spectra of **1–4** exhibit singlet peaks, with chemical shifts between 38.0 and 41.9 ppm for the PPh_3 moiety coordinated to the gold atom.

X-Ray crystal structure determination of complex 1

The low-temperature (178(2) K) crystal and molecular structures of complex **1** (Fig. 1) were determined by X-ray diffraction techniques. The molecular structure clearly shows a formal triphenylphosphine gold(I) moiety coordinated in an unusual fashion to a square pyramidal $Cr(CO)_5$ fragment. Selected bond lengths and angles are listed in Table 1.

Of greatest interest in the structure of **1** is the coordination of the pentacarbonylchromium unit to the gold complex. In contrast to a related product, referred to above, in which an alkoxyvinylgold complex becomes π-coordinated to a $Cr(CO)_5$ fragment, a distance of 2.947(5) Å (previously[2] already relatively long at 2.629(7) Å) between Cr and C(7) now completely rules out such a bonding mode. Furthermore, a relatively short C(coordinated)–N separation of 1.348(7) Å, a relatively long C(1)–C(7) bond length (1.406(8) Å), tetrahedral coordination around C(1) (hydrogen positions determined from the difference Fourier map) and planarity around C(7) (greatest deviation from planarity 0.041(4) Å for C(7)), demonstrate the important contribution made by the zwitterionic resonance structure in Scheme 2. Such a structure also corresponds to the results of the NMR investigation discussed above.



Scheme 2

Quantum chemical calculations

In order to gain insight into the bonding situation in **1**, we carried out DFT calculations of the model compound **1M** in which the PPh_3 ligand of **1** is replaced by PH_3. Fig. 2(a) shows the optimised geometry and the most important bond lengths and angles of **1M**. The calculated values of **1M** are very similar to the experimental data of **1**. The theoretical value for the C(1)–C(7) distance is 1.408 Å, which is in excellent agreement with the experimental value of 1.406(8) Å. In accord with the experimental structure, the calculations also give rather different distances for Cr–C(1) (2.449 Å) and Cr–C(7) (3.065 Å), indicating much stronger interaction of chromium with C(1) than with C(7). We conclude that the bonding interaction between the coordinated vinyl ligand and chromium in **1M** and **1** is best described as η^1-bonding of a terminal carbanion rather than η^2-bonding of an olefin. This agrees with calculations for aminocarbenes coordinated to iron.[8]

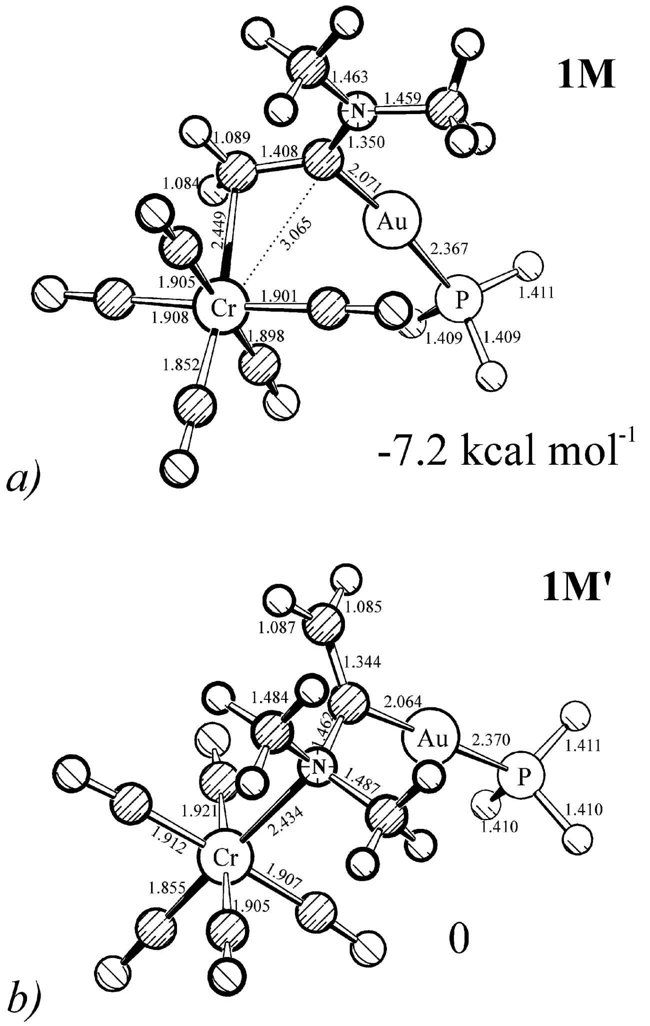
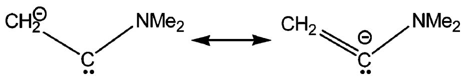


Fig. 2 Calculated geometries of **1M** and **1M′**. Distances in Å, angles in °.

The vinyl amine ligand might also bind to the $M(CO)_5$ moiety *via* the nitrogen atom of the amine group. Therefore, we also calculated the isomer of **1M** wherein the ligand is bonded to chromium through its nitrogen atom rather than the vinyl group (**1M′**, Fig. 2(b)). The calculations predict that this isomer is 7.2 kcal mol^{-1} higher in energy (electronic) than **1M**. The terminal carbon atom is softer than nitrogen and thus a better donor towards the relatively soft Cr(0) in $Cr(CO)_5$.

We performed further calculations in order to establish whether the deprotonated alkyl(amino)carbene (or aminovinyl anion, Scheme 3) ligand binds more strongly through the terminal or through the central carbon to the metal fragments $Cr(CO)_5$ and $Au(PH)_3{}^+$. The geometry optimisations of the two isomeric forms of the gold complex yielded only one minimum energy structure, $[(PH_3)Au–C(NMe_2)(CH_2)]$, with the gold atom bonded to the central carbon atom. Two isomers of the chromium complex were found as energy minima, *i.e.* for both $[(CO)_5Cr\{C(NMe_2)CH_2\}]^-$



Scheme 3

and $[(CO)_5Cr\{CH_2\ C(NMe_2)\}]^-$. The former species, where the metal atom is bonded to the central carbon, is 19.3 kcal mol^{-1} lower in energy than the latter form where the ligand is terminally bonded. It follows that the aminovinyl ligand clearly binds more strongly through the central carbon atom. The fact that the chromium unit is prepared to be terminally coordinated, combined with gold's preference for the internal carbon atom, leads to the observed products.

The results above suggest that the relative stability of the isomers **M** and **M′** could change if the amino group in **1** is replaced by a better donor, such as a thiol group. In order to test this hypothesis the related isomers of the thiocarbene model complexes **5M** and **5M′** were also calculated. The DFT calculations indeed predict that the vinyl thiocarbene ligand now binds more strongly through the sulfur atom (isomer **5M′**, Fig. 3(b)) than through the vinyl group (isomer **5M**, Fig. 3(a)). The former isomer is 6.6 kcal mol^{-1} lower in energy than the latter. This means that the relative stability of the isomers **5M** and **5M′** is opposite to that of **1M** and **1M′**.

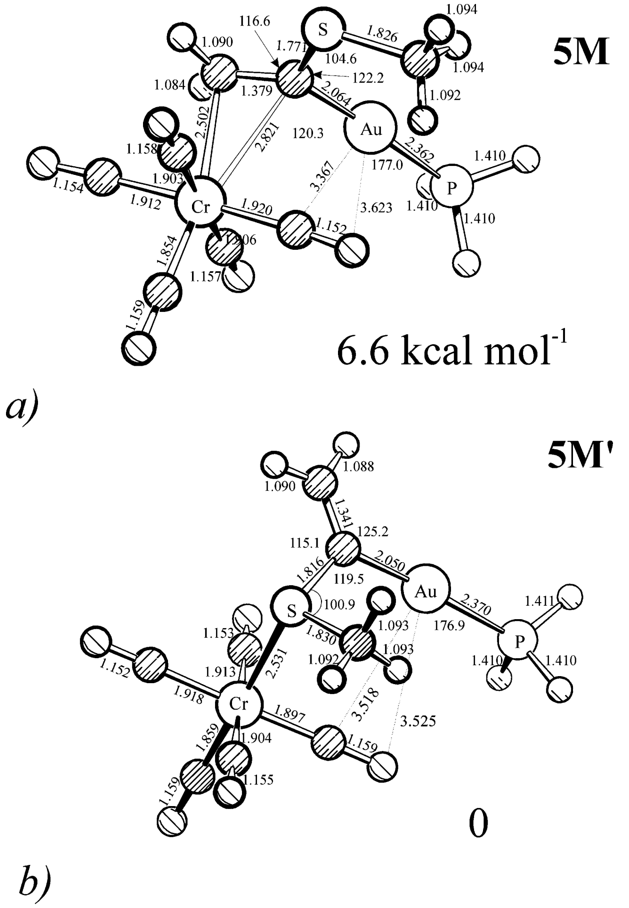


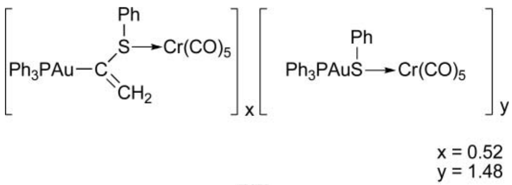
Fig. 3 Calculated geometries of **5M** and **5M′**. Distances in Å, angles in °.

B. Reactions involving thiocarbene complexes

To establish whether $Cr(CO)_5$ bonding to sulfur occurs after aurolysis as theoretically predicted, similar reactions to those above were carried out using deprotonated thiocarbene compounds (Scheme 4). Similarly to the only other structurally known alkyl-thiocarbene complex, $(CO)_5Cr{=}C(SPh)Me$,[7] the methyl and propyl groups in the thiocarbene precursor to **6**[9] also appear in the *syn* configuration. The comparable bond distances in the two compounds are almost identical.

Since only compound **6** and a modified version of **7** (*vide infra*) could be isolated in pure form, we are thus not presenting a complete synthetic protocol here. Nevertheless, physical characterisation (including a crystal and molecular structure determination involving **7**) unambiguously indicate that the theoretical predictions have been borne out in practice.

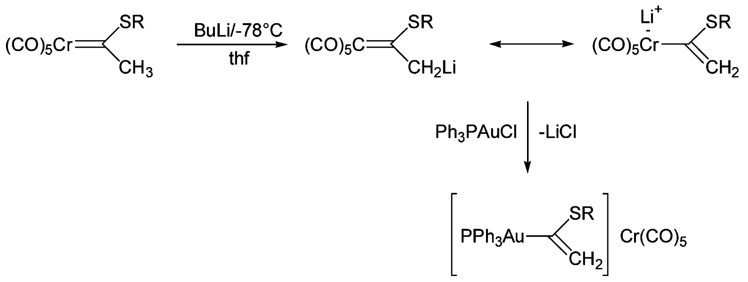
After reaction with PPh_3AuCl and work-up as described before for the aminocarbene complexes, column chromatography yielded product **5** as a yellow oil and **6** as a microcrystalline solid. Yellow–brown platelet crystals containing **7** were later obtained from a concentrated diethyl ether solution of the viscous product layered with pentane at −20 °C. As discussed later, these crystals were subjected to an X-ray investigation and shown to consist of a combination of two complexes, **7** and **7′**, crystallising together (Scheme 5).



7/7′

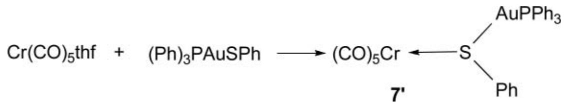
Scheme 5

Unexpectedly, in each of the attempted syntheses of **5**–**7** another product identified as Ph_3PAuBu, **8**, was formed. Its formation in significant amounts in these reactions (5–15% yield based on Au) is probably related to the fact that the thiocarbene starting materials used here are the most unstable carbene complexes employed in this study. Some measure of decomposition of the



Scheme 4

thiocarbene starting complexes before and during the synthesis of **5–7** was frequently observed. The thiocarbene starting complexes are also difficult to isolate in analytically pure form and $(CO)_5Cr{=}C(SPh)Me$, for example, was used *in situ* as prepared, thus also explaining the concomitant formation of **7′**, $Ph_3PAuS(Ph)Cr(CO)_5$. Metal-containing sulfides coordinated to group **6** metal carbonyls are rare[10,11] and we thus also prepared and characterised **7′** independently by reacting $Ph_3PAuSPh$[12] with $(CO)_5Cr(thf)$ (obtained by UV irradiation of $Cr(CO)_6$ in thf), eqn (1).



7′

(1)

In contrast to most other known neutral aryl sulfide complexes of pentacarbonylchromium,[13] **7′** is relatively stable and can even be handled in air.

During the first step of the preparation of **5–7**, a slight excess of BuLi remaining after the deprotonation of the thiocarbene complexes, is easily foreseeable. This reacts with Ph_3PAuCl, added in the second step of the synthesis, to form **8** through a simple transmetallation reaction. Since **8**, although known,[14] has not been well characterised before, its spectroscopic and physical data are reported here.

Spectroscopic characterisation of products 5–8

NMR spectroscopy. The ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopic data for the isolated products **5–8** are reported in the Experimental section. The ^1H NMR spectra exhibit two distinctive signals, each integrating for a single proton, representing two chemically non-equivalent vinyl protons. The *cis* and *trans*-vinyl proton resonances in **5–7** appear in the usual region for protons in uncoordinated vinyl groups, at δ 5.38–5.64 (*cis*-H_{vinyl}) and 5.76–6.07 (*trans*-H_{vinyl}). Similarly, the $^{13}C\{^1H\}$ resonances for the terminal CH_2-vinyl carbon atoms in **5–7** have chemical shifts at δ 121.7, 125.4 and 125.7, in the aromatic region of the ^{13}C NMR spectrum. Resonances of the carbons coordinated to gold in **5–7** could be easily identified on account of their characteristically large $^2J_{C-P}$ coupling constants (125.2–129.4 Hz) at δ 181.9, 182.4 and 180.8, respectively.

The positions of the chemical shifts reported here for the vinyl groups in **5–7** (the latter clearly visible in the spectrum of **7/7′**) strongly suggest that the vinyl thioether moieties are not coordinated to $Cr(CO)_5$ fragments through their vinyl functionality, but rather through their sulfur atoms. Further evidence for this assumption is presented in the discussion of the infrared spectra of **5–7/7′** and the X-ray crystallographic investigation of **7/7′** below. The resonances for the phenyl groups in **7′** could be assigned completely (ESI†). Of particular interest in the ^{13}C NMR spectrum of **8** is the extremely efficient two-bond J_{P-C} coupling (95.4 Hz) of the gold-coordinated CH_2 group with the ^{31}P atom across the gold atom. This coupling constant is more than double the size of the one-bond J_{P-C} coupling (44.7 Hz) observed for the C_{ipso} atoms in the PPh_3 residue.

Infrared spectroscopy. The IR spectra of **5** and **7/7′** (pentane) display only the three usual absorption bands ($A_1^{(1)}$, E, $A_1^{(2)}$) associated with complexes of the type $M(CO)_5L$, in which the degeneracy of the E vibrational mode has not been lifted in the carbonyl region. No differentiation between **7** and **7′** is possible in the spectrum of crystals of **7/7′** and the absorptions approximately match those of pure **7′**.

As discussed for the IR spectra of **1–4**, the most informative IR absorption mode for complexes of the type $Cr(CO)_5L$ is the $A_1^{(2)}$ peak assigned to the symmetric stretching of the single terminal CO ligand *trans* to the ligand (L) coordination. In the IR spectra of **5–7/7′** these peaks occurring between 1917 and 1921 cm^{-1} appear blue shifted (7–27 cm^{-1}) compared to the same CO_{trans} vibrations in complexes **1–4**, indicating that the ligands in **5–7/7′** have smaller $\sigma_{donor}/\pi_{acceptor}$ ratios than the C-coordinated aminovinylgold groups in **1–4.**

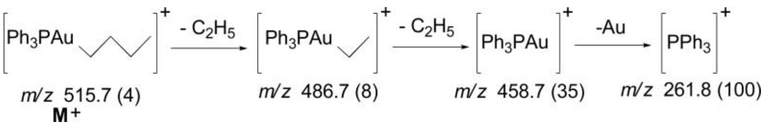
Of note is that the remaining ν(CO) absorption bands, in particular the sharp and well defined $A_1^{(1)}$ and B_1 bands measured for **5–7/7′**, are also significantly shifted to higher energy compared to their positions in the IR spectra of the CH_2-coordinated compounds **1–4**. We conclude therefore that in **5–7/7′** much less electron density is transferred to the $Cr(CO)_5$ unit than in **1–4**, indicating coordination through the sulfur rather than the terminal vinyl group.

The fact that clearly-resolved, non-degenerate vibrational modes originating from the E vibrational mode are only observed in the ν(CO) absorption bands of **6**, is a testimony to the greater steric bulk exhibited by the ^nPrS group in this molecule compared to **5**, **7** and **7′**, which contain MeS and PhS groups and hence display a single, two-fold degenerate E vibrational mode.

Mass spectrometry. The positive-ion FAB mass spectra of complexes **5–7/7′** were recorded in an *m*-nitrobenzyl alcohol matrix. The spectra mainly show the characteristic matrix peaks (*m*/*z* 154 and 307) or the Ph_3PAu^+ (*m*/*z* 459) or $(Ph_3P)_2Au^+$ (*m*/*z* 721) decomposition and fragment ions as peaks of highest intensity. No molecular ion, or other sensible fragmentation peaks were observed for **5–7/7′**. Pure **7′**, on the other hand, fragments beautifully from the molecular ion at 760, with the consecutive loss of five COs and then Cr and SPh. The conventional EI-mass spectrum of **8** is illustrated in Scheme 6 (relative intensities in parentheses).

X-Ray crystal structure determination of complex 7/7′ and 7′

The low-temperature (177 K) crystal structure of the co-crystallised complex mixture **7/7′**, was determined by X-ray diffraction techniques. The molecular structure of **7** (Fig. 4) clearly shows, as proposed by the NMR and IR spectroscopic data,



Scheme 6

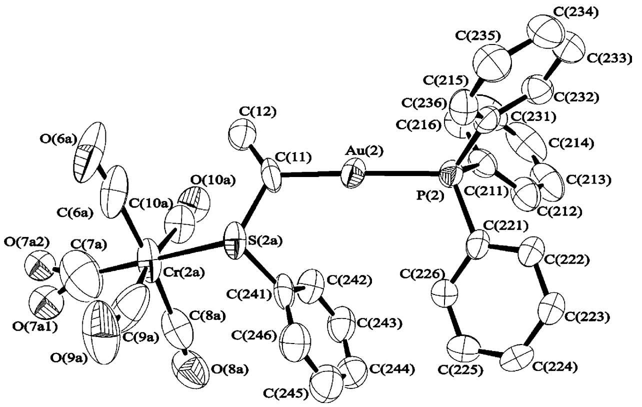


Fig. 4 ORTEP view of **7** (hydrogen atoms omitted for clarity) showing the numbering scheme. Ellipsoids are shown at the 50% probability level.

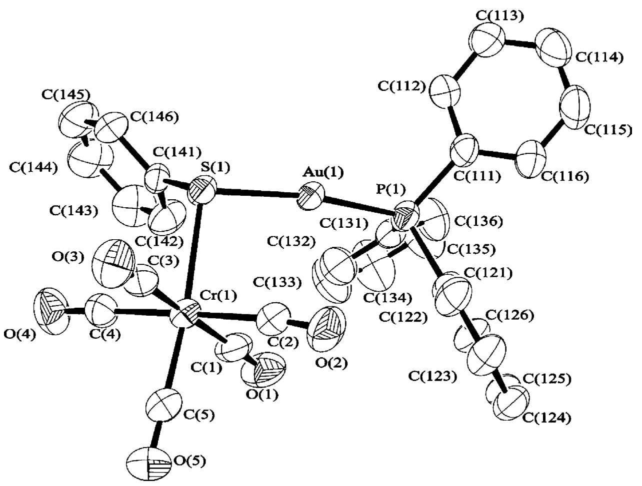


Fig. 5 ORTEP view of the full site-occupancy molecule of **7′** (hydrogen atoms omitted for clarity) showing the numbering scheme. Ellipsoids are shown at the 50% probability level.

coordination of a phenylthiolatevinyl(triphenylphospine)gold(I) moiety to a Cr(CO)$_5$ fragment through the sulfur atom of the thioether group, rather than through the carbon as found for the aminovinylgold(I) complex in **1**. Complex **7′** (Fig. 5), meanwhile, is a bimetallic complex consisting of a Ph$_3$PAuSPh complex coordinated to the Cr(CO)$_5$ fragment through the sulfur atom of the sulfide group. The final crystallographically refined ratio of **7**/**7′** is 1 : 2.87, indicating that there is in actual fact nearly three times more of **7′** present in the crystal than of **7**. The asymmetric unit of the total structure consists of one molecule of **7′** linked by a weak aurophilic Au–Au interaction [Au(1)–Au(2) 3.197(1) Å] to a molecule of **7** (at 51.7% site occupancy) which shares that site with a second molecule of **7′**, present at 48.3% site occupancy (see Fig. S1 in ESI†).

Furthermore, the molecules of **7** and **7′** occupying the same site share the atom positions in the AuPPh$_3$ moiety and only differ in the positions of their respective substituted vinyl (only for **7**) and Cr(CO)$_5$ fragments. Within the structure of **7**, disorder is observed for the oxygen atom of the CO ligand *trans* to the sulfur coordination [O(7)]. Two positions could be identified for this atom on the difference Fourier map and refined with a final refined site occupancy ratio of 0.552 : 0.448 [O(71) : O(72)]. Selected bond lengths and angles for each of the crystallographically unique fragments in the crystal structure are listed in Tables 2 and 3.

Table 2 Selected bond lengths (Å) and angles (°) with s.u.s in parenthesis for **7** in **7**/**7′**

Au(2)–C(11)	2.03(2)	C(11)–Au(2)–P(2)	168.7(7)
C(11)–C(12)	1.32(3)	Au(2)–C(11)–C(12)	128.0(18)
C(11)–S(2′)	1.81(2)	Au(2)–C(11)–S(2′)	112.7(13)
Au(2)–P(2)	2.275(2)	Cr(2′)–S(2′)–C(11)	118.0(8)
S(2′)–Cr(2′)	2.457(5)	C(11)–S(2′)–C(241)	102.1(9)
S(2′)–C(241)	1.79(2)		
Au(1)–Au(2)	3.197(1)		

Table 3 Selected bond lengths (Å) and angles (°) with s.u.s in parenthesis for **7′** in **7**/**7′**

Au–S	2.326(2), 2.373(6)	S–Au–P	171.11(1), 170.3(2)
S–C	1.787(8), 1.77(4)	Au–S–C	100.2(2), 107.6(10)
S–Cr	2.502(2), 2.490(8)	Au–S–Cr	100.9(1), 108.3(2)
Au–P	2.258(2), 2.275(2)	Cr–S–C	109.4(3), 109.1(10)

Despite the rather inaccurate bond lengths and angles obtained for **7** as a result of the partial site occupancy found for this part of the structure, the connectivity in **7** could be established beyond any doubt. The poor accuracy of the bond lengths and angles in the vinyl group of **7** does, however, not strictly allow comparison of these to other literature examples of uncoordinated vinyl ethers/amines/thioethers. The accurate bond lengths determined for the Au(2)–P(2) bond [2.275(2) Å] as well as the bond lengths and angles in the PPh$_3$ moiety of **7** (and **7′**) are normal.[15]

Although present in only small quantities in the crystal, it appears that **7** is stabilised by the formation of an intramolecular face-to-edge phenyl interaction between the PhS unit and one of the triphenylphosphine phenyl rings [H(226) · · · C(241) 3.047 Å; H(226) · · · C(242) 3.048 Å]. A further effect of this interaction could be the large Cr(2A)–S(2A)–C(11) angle [118.0(8)°], although this could also be related to steric repulsion between the Cr(CO)$_5$ fragment and the vinyl group.

A C(11)–Au(2)–P(2) angle of 168.7(7)° [bent towards Au(1)], although poorly determined, describes the distortion of the usually linear gold(I) coordination mode as a result of the relativistically enhanced[16] Au–Au interaction between Au(1) and Au(2). A similar, and more certain, description of the distortion of Au(1) toward Au(2) is given by the S–Au–P angles [171.11(1) and 170.3(2)°] in **7′** deviating significantly from the ideal 180°.

We also embarked on a crystallographic investigation of the pure **7′** prepared independently. All the bond distances and angles (compare ESI†) are identical (within the limits of error) to those in **7′** in the structure discussed above.

The structure of the uncoordinated complex Ph$_3$PAuSPh, has been reported in the literature no less than four times.[12,17] All four reported structures are isostructural and consist of dimers of the compound that are linked, in a similar fashion to the structure reported above, by weak aurophilic interactions [average Au–Au distance 3.144(8) Å]. The bond lengths and angles observed in these structures compare very well to those found for **7′** in both crystal structures. The greatest differences between the structure of the Au–Au linked dimers of **7′** and the Ph$_3$PAuSPh structures in the literature are the lengths of the Au–S bonds, due to weakening of the bond as a result of the coordination of the S to the Cr(CO)$_5$ unit. The literature Ph$_3$PAuSPh structures have an average Au–S bond distance of 2.305(3) Å, which is slightly shorter than the values found for **7′** in the pure and co-crystallised forms [2.326(2), 2.372(6), 2.328(1) and 2.318(2) Å, respectively].

Calculated structural parameters of **5M′** are in good agreement with the experimentally derived data for **7** (compare Table 2 and Fig. 3).

Conclusions

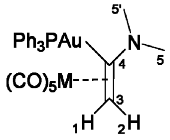
In this work we were able to show that α-deprotonated Fischer-type aminocarbene and thiocarbene complexes of group 6 metal (Cr and W) carbonyls act as synthons for α-deprotonated aminovinyl and thiovinyl ligands towards gold(I). Due to the coordination preferences of the extruded $M(CO)_5$ units, the products in the two situations differ significantly and selectively. The propensity of the N-containing functionality towards π-bond formation effects essentially alkyl coordination to the chosen metal carbonyl fragment, whereas S-coordination is preferred in the second type of conversion affording real ($M(CO)_5$-coordinated) thiolatovinyl complexes of gold.

Experimental

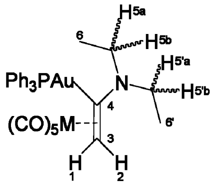
All solvents were dried and purified by conventional methods and freshly distilled under nitrogen shortly before use. Unless otherwise stated, all common reagents were used as obtained from commercial suppliers without further purification. BuLi was standardised before use according to the procedure reported by Winkle *et al.*[18] Ph_3PAuCl and the group 6 metal Fischer-type dialkylamino(methyl)carbene starting complexes as well as methyl(thiocarbene) complexes were prepared according to procedures described in the literature.[19] The preparation and characterisation of $(CO)_5CrC(SPr)Me$ (a precursor for **6**) together with its crystal and molecular structure are reported as ESI.†

All reactions and manipulations involving organometallic reagents were carried out under a dry nitrogen atmosphere using standard Schlenk and vacuum-line techniques. NMR spectra were recorded on Varian INOVA 600 (600 MHz for ^1H, 151 MHz for $^{13}C\{^1H\}$ and 243 MHz for $^{31}P\{^1H\}$) or Varian VXR 300 (300 MHz for ^1H, 75.4 MHz for $^{13}C\{^1H\}$ and 121.5 MHz for $^{31}P\{^1H\}$) NMR spectrometers. ^1H and ^{13}C chemical shifts are reported in ppm relative to the ^1H and ^{13}C residue of the deuterated solvents while ^{31}P chemical shifts are reported relative to an 85% H_3PO_4 external standard solution. IR spectra (4000–400 cm^{-1}, resolution 4 cm^{-1}) were recorded on a Perkin-Elmer 1600 series FTIR spectrometer. FAB-MS were recorded on a Micromass DG 70/70E mass spectrometer at the University of Potchefstroom, South Africa, using xenon gas for bombardment atoms and *m*-nitrobenzyl alcohol as matrix. Flash column chromatography was performed with "flash grade" silica (SDS 230–400 mesh). Melting/decomposition points were determined on a standardised Büchi 535 melting point apparatus. Crystal structure data collection and correction procedures were carried out on a Nonius Kappa CCD diffractometer by Dr J. Bacsa and Ms Hong Su of the University of Cape Town structural chemistry research group.

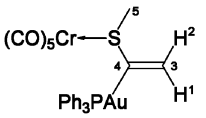
The following numbering schemes were utilised for the assignment of chemical shifts:



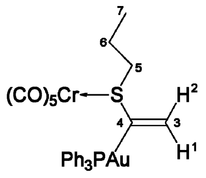
1, 3



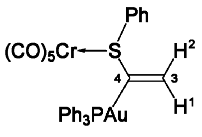
2, 4



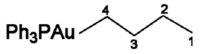
5



6



7



8

{Dimethylaminovinyl(triphenylphosphine)gold(I)-*C*}pentacarbonylchromium(0), 1

To a solution that contains 0.21 g (0.80 ml) {dimethylamino-(methyl)}carbene (pentacarbonyl)chromium(0) dissolved in 15 ml cooled (−78 °C) thf was added slowly 0.55 ml 1.6 M BuLi (0.88 mmol, 1.1 mol equiv.). The mixture was stirred at that temperature for 30 min. after which 0.40 g (0.80 mmol) Ph_3PAuCl was added and the mixture allowed to reach room temperature over a period of 3 h. Removal of the solvent *in vacuo* resulted in a dark yellow oily residue containing a mixture of products (TLC). The desired product from broad yellow bands was isolated by means of low-temperature (−15 °C) silica gel column chromatography using pentane–diethyl ether (10 : 1), as initial eluent and increasing the polarity to a pentane–diethyl ether ratio of ~2 : 1 once the non-polar impurities and unreacted starting material have been eluted from the column. The product obtained (0.31 g) was a yellow crystalline material. Yield: 54%. Mp 89 °C (decomp.) Anal. Calc. for $C_{27}H_{23}NO_5PAuCr$: C, 45.0; H, 3.2; N, 1.9. Found: C, 45.3; H, 3.3; N, 2.1%. IR (pentane solution): ν/cm^{-1} 1896, 1915, 1960, 2044. δ_H (600 MHz, CD_2Cl_2): 1.93 (1 H, br, H^1), 2.55 (1 H, d, $^4J_{trans\ P\text{–}H}$ = 8.5 Hz, H^2), 2.79 (3 H, s, $H^{5,5'}$), 3.45 (3 H, s, $H^{5,5'}$), 7.4–7.6 (15 H, m, Ph); δ_C (151 MHz, CD_2Cl_2): 29.2 (br, $C^{5,5'}$), 36.5 (br, C^3), 129.5 (d, $^2J_{P\text{–}C}$ = 10.9 Hz, C_{ortho}), 130.2 (d, $^1J_{P\text{–}C}$ = 52.1 Hz, C_{ipso}), 131.8 (C_{para}), 134.5 (d, $^3J_{P\text{–}C}$ = 13.2 Hz, C_{meta}), 216.7 (d, $^2J_{P\text{–}C}$ = 134.2 Hz, C^4), 220.9 (CO_{cis}), 226.5 (CO_{trans}); δ_P (243 MHz, CD_2Cl_2): 38.2. *m*/*z* (FAB) 721 (M^+, 20%), 529 (100), 459 (70).

{Diethylvinyl(triphenylphosphine)gold(I)-*C*}pentacarbonylchromium(0), 2

The synthesis followed the same procedure as for **1**, starting from {diethylamine(methyl)carbene}pentacarbonylchromium(0) (0.26 g, 0.80 mmol). The product was obtained as dark yellow crystals (0.60 g). Yield: 59%. Mp 82 °C (decomp.). Anal. Calc. for $C_{29}H_{27}NO_5PAuCr$: C, 46.5; H, 3.6; N, 1.9. Found: C, 46.8; H, 3.8; N, 2.0%. IR (pentane solution): ν/cm^{-1} 1893, 1915, 1958, 2043. δ_H (600 MHz, CD_2Cl_2): 1.12 (3 H, t, $^3J_{H\text{–}H}$ = 7.3 Hz, 10, $H^{6,6'}$), 1.13 (3 H, dd, $^3J_{H\text{–}H}$ = 7.3 Hz, 10, $H^{6,6'}$), 1.97 (1 H, br, H^1), 2.52 (1 H, br d, $^4J_{trans\ P\text{–}H}$ = 8.1 Hz, H^2), 2.73 (1 H, dq, $^2J_{H\text{–}H}$ = 10.2 Hz, $^3J_{H\text{–}H}$ = 7.3 Hz, $H^{5a,5'a,5b,5'b}$), 3.21 (1 H, dq, $^2J_{H\text{–}H}$ = 10.2 Hz, $^3J_{H\text{–}H}$ = 7.3 Hz, $H^{5a,5'a,5b,5'b}$), 3.46 (1 H, dq, $^2J_{H\text{–}H}$ = 10.2 Hz,

$^{3}J_{\text{H–H}} = 7.3$ Hz, $\text{H}^{5a,5'a,5b,5'b}$), 3.60 (1 H, dq, $^{2}J_{\text{H–H}} = 10.2$ Hz, $^{3}J_{\text{H–H}} = 7.3$ Hz, $\text{H}^{5a,5'a,5b,5'b}$), 7.4–7.6 (15 H, m, Ph); δ_{C} (151 MHz, CD_2Cl_2): 12.5 (C^{6}), 13.6 (C^{6}), 25.2 (br, C^{5}), 40.1 (br, C^{3}), 129.3 (d, $^{2}J_{\text{P–C}} = 10.7$ Hz, C_{ortho}), 130.2 (d, $^{1}J_{\text{P–C}} = 50.8$ Hz, C_{ipso}), 132.0 (C_{para}), 134.7 (d, $^{3}J_{\text{P–C}} = 13.7$ Hz, C_{meta}), 218.3 (d, $^{2}J_{\text{P–C}} = 131.3$ Hz, C^{4}), 220.4 (CO_{cis}), 226.2 (CO_{trans}); δ_{P} (121.5 MHz, CD_2Cl_2): 38.0. *m*/*z* (FAB) 750 (M^{+}, 35%), 721 (70), 558 (70), 459 (100).

{Dimethylaminovinyl(triphenylphosphine)gold(I)-*C*}pentacarbonyltungsten(0), 3

The synthesis followed the same procedure as for **1**, starting from the tungsten dimethylaminocarbene complex (0.32 g, 0.80 mmol). The product obtained was a yellow crystalline material (0.58 g). Yield: 68%. Mp 95 °C (decomp.). Anal. Calc. for $C_{27}H_{23}NO_5PAuW$: C, 38.0; H, 2.7; N, 1.6. Found: C, 38.2; H, 2.9; N, 1.7%. IR (pentane solution): ν/cm^{-1} 1900, 1915, 1957, 2052. δ_{H} (600 MHz, $CDCl_3$): 2.51 (1 H, br, H^{1}), 2.79 (3 H, s, $\text{H}^{5,5'}$), 3.00 (1 H, br, H^{2}), 3.42 (3 H, s, $\text{H}^{5,5'}$), 7.4–7.6 (15 H, m, Ph); δ_{C} (151 MHz, CD_2Cl_2): 29.4 (br, $\text{C}^{5,5'}$), 36.0 (d, $^{3}J_{\text{P–C}} = 3.6$ Hz, C^{3}), 129.2 (d, $^{2}J_{\text{P–C}} = 11.3$ Hz, C_{ortho}), 129.8 (d, $^{1}J_{\text{P–C}} = 54.2$ Hz, C_{ipso}), 131.5 (C_{para}), 134.2 (d, $^{3}J_{\text{P–C}} = 13.5$ Hz, C_{meta}), 201.0 (s, CO_{cis}), 203.3 (CO_{trans}), 207.9 (d, $^{2}J_{\text{P–C}} = 118.8$ Hz, C^{4}); δ_{P} (243 MHz, $CDCl_3$): 41.3. *m*/*z* (FAB) 852 (M^{+}, 50%), 721 (65), 529 (100), 459 (100).

{Diethylaminovinyl(triphenylphosphine)gold(I)-*C*}pentacarbonyltungsten(0), 4

The synthesis followed the same procedure as for **1**, starting with the diethylaminocarbene complex of tungsten pentacarbonyl (0.36 g, 0.80 mmol). The product obtained (0.46 g) was a yellow crystalline material. Yield: 52%. Mp 85 °C (decomp.). Anal. Calc. for $C_{29}H_{27}NO_5PAuW$: C, 39.5; H, 3.1; N, 1.6. Found: C, 39.7; H, 3.3; N, 1.75%. IR (pentane solution): ν/cm^{-1} 1894, 1912, 1958, 2053. δ_{H} (600 MHz, CD_2Cl_2): 1.20 (3 H, t, $^{3}J_{\text{H–H}} = 7.2$ Hz, $\text{H}^{6,6'}$), 1.29 (3 H, t, $^{3}J_{\text{H–H}} = 7.2$ Hz, $\text{H}^{6,6'}$), 2.50 (1 H, d, $^{4}J_{cis\ \text{P–H}} = 2.7$ Hz, H^{1}), 2.91 (1 H, d, $^{4}J_{trans\ \text{P–H}} = 9.0$ Hz, H^{2}), 2.96 (dq, $^{2}J_{\text{H–H}} = 10.0$ Hz, $^{3}J_{\text{H–H}} = 7.2$ Hz, $\text{H}^{5a,5'a,5b,5'b}$), 3.45 (1 H, dq, $^{2}J_{\text{H–H}} = 10.0$ Hz, $^{3}J_{\text{H–H}} = 7.2$ Hz, $\text{H}^{5a,5'a,5b,5'b}$), 3.64 (1 H, dq, $^{2}J_{\text{H–H}} = 10.0$ Hz, $^{3}J_{\text{H–H}} = 7.2$ Hz, $\text{H}^{5a,5'a,5b,5'b}$), 3.83 (1 H, dq, $^{2}J_{\text{H–H}} = 10.0$ Hz, $^{3}J_{\text{H–H}} = 7.2$ Hz, $\text{H}^{5a,5'a,5b,5'b}$), 7.4–7.6 (15 H, m, Ph); δ_{C} (151 MHz, CD_2Cl_2): 12.9 ($\text{C}^{6,6'}$), 14.0 ($\text{C}^{6,6'}$), 27.5 (br, $\text{C}^{5,5'}$), 42.1 (d, $^{3}J_{\text{P–C}} = 2.4$ Hz, C^{3}), 129.5 (d, $^{2}J_{\text{P–C}} = 12.6$ Hz, C_{ortho}), 130.2 (d, $^{1}J_{\text{P–C}} = 53.5$ Hz, C_{ipso}), 131.8 (C_{para}), 134.5 (d, $^{3}J_{\text{P–C}} = 12.7$ Hz, C_{meta}), 201.9 (CO_{cis}), 203.8 (CO_{trans}), 210.1 (d, $^{2}J_{\text{P–C}} = 117.6$ Hz, C^{4}); δ_{P} (243 MHz, CD_2Cl_2): δ 41.9. *m*/*z* (FAB) 881 (M^{+}, 65%), 721 (75), 558 (100), 459 (65).

{Methylthiolatovinyl(triphenylphospine)gold(I)-*S*}pentacarbonylchromium(0), 5

The same preparative method as for **1** was used with the methyl(methylthiolato)carbeneCr(CO)$_5$ complex (0.21 g, 0.80 mmol) as reactant. The product obtained was a dark-yellow oil. Yield: *ca.* 20%. IR (pentane solution): ν/cm^{-1} 1918, 1943, 2063. δ_{H} (600 MHz, $CDCl_3$): 2.47 (3 H, br s, H^{5}), 5.43 (1 H, br, H^{1}), 5.76 (1 H, br, H^{1}), 7.2–7.7 (15 H, m, Ph); δ_{C} (151 MHz, CD_2Cl_2): 39.7 (C^{5}), 121.7 (br, C^{3}), 129.5 (d, $^{1}J_{\text{P–C}} = 59.6$ Hz, C_{ipso}), 129.8 (d, $^{2}J_{\text{P–C}} = 9.9$ Hz, C_{ortho}), 132.1 (C_{para}), 134.9 (d, $^{3}J_{\text{P–C}} = 13.9$ Hz, C_{meta}), 181.9 (d, $^{2}J_{\text{P–C}} = 129.4$ Hz, C^{4}), 216.4 (CO_{cis}), 223.2 (CO_{trans}); δ_{P} (243 MHz, $CDCl_3$): 38.2. *m*/*z* (FAB) 721 (70%), 459 (100).

{Propylthiolatovinyl(triphenylphospine)gold(I)-*S*}pentacarbonylchromium(0), 6

The same preparative method as for **1** but using 0.24 g, 0.80 mmol of the new methyl(propylthiolato)carbeneCr(CO)$_5$ complex was employed. The product obtained was a microcrystalline solid. Yield: *ca.* 36%. IR (pentane solution): ν/cm^{-1} 1917, 1932, 1937, 2063. δ_{H} (600 MHz, $CDCl_3$): 0.92 (3 H, t, $^{3}J_{\text{H–H}} = 6.4$ Hz, H^{7}), 1.73 (2 H, m, H^{6}), 2.80 (2 H, t, $^{3}J_{\text{H–H}} = 7.1$ Hz, H^{5}), 5.38 (1 H, d, $^{4}J_{cis\ \text{P–H}} = 2.7$ Hz, H^{1}), 5.88 (1 H, d, $^{4}J_{trans\ \text{P–H}} = 12.5$ Hz, H^{2}), 7.3–7.7 (15 H, m, Ph); δ_{C} (151 MHz, $CDCl_3$): 13.2 (C^{7}), 23.0 (C^{6}), 46.3 (C^{5}), 125.4 (br, C^{3}), 129.2 (d, $^{2}J_{\text{P–C}} = 9.3$ Hz, C_{ortho}), 129.8 (d, $^{1}J_{\text{P–C}} = 50.2$ Hz, C_{ipso}), 131.5 (C_{para}), 134.2 (d, $^{3}J_{\text{P–C}} = 14.2$ Hz, C_{meta}), 182.4 (d, $^{2}J_{\text{P–C}} = 125.2$ Hz, C^{4}), 215.9 (CO_{cis}), 222.7 (CO_{trans}); δ_{P} (243 MHz, $CDCl_3$): 42.5. *m*/*z* (FAB) 721 (65%), 459 (100).

Phenylthiolatovinyl(triphenylphospine)gold(I)-*S*, 7 and {phenylthiolato(triphenyl)phosphinegold(I)-*S*}pentacarbonylchromium(0), 7′

Again, a similar synthetic procedure was used but now starting with 0.26 g (0.80 ml) methyl(phenylthiolato)carbeneCr(CO)$_5$. The product was obtained in the form of a yellow viscous oil. Yield: *ca.* 15%. IR (pentane solution): ν/cm^{-1} 1921, 1935, 1979, 2060. δ_{H} (600 MHz, $CDCl_3$): 5.64 (d, $^{4}J_{cis\ \text{P–H}} = 5.1$ Hz, H^{1}), 6.07 (d, $^{4}J_{trans\ \text{P–H}} = 12.0$ Hz, H^{2}), 7.1–7.6 (m, Ph, SPh); δ_{C} (151 MHz, $CDCl_3$): 125.7 (C^{3}), 129.9–131.8 (PPh, SPh), 180.8 (d, $^{2}J_{\text{P–C}} = 126.9$ Hz, C^{4}), 215.4 (CO_{cis}), 223.1 (CO_{trans}); δ_{P} (243 MHz, $CDCl_3$): 41.9. *m*/*z* (FAB) 721 (70%), 459 (100).

Butyl(triphenylphosphine)gold(I), 8

The by-product was obtained in all of the syntheses described above. After column chromatographic separation (first eluted product), stripping of solvent *in vacuo* furnished **8** as a colourless crystalline material in yields of 5–15% (based on Ph_3PAuCl). Mp 106 °C (decomp.), Anal. Calc. for $C_{22}H_{24}PAu$: C, 51.2; H, 4.7. Found: C, 51.0; H, 4.5%. δ_{H} (300 MHz, $CDCl_3$): 0.94 (3 H, $^{3}J_{\text{H–H}} = 7.4$ Hz, H^{1}), 1.4–1.6 (4 H, m, $\text{H}^{2,3}$), 1.86 (2 H, dt, $^{3}J_{\text{P–H}} = 4.3$ Hz, 14.7 (C^{1}), $^{3}J_{\text{H–H}} = 7.2$ Hz, H^{4}), 7.4–7.6 (15 H, m, Ph); δ_{C} (75.4 MHz, $CDCl_3$) 34.7 (C^{2}), 30.0 (d, $^{3}J_{\text{P–C}} = 4.3$ Hz, C^{3}), 31.3 (d, $^{2}J_{\text{P–C}} = 95.4$ Hz, C^{4}), 132.7 (d, $^{1}J_{\text{P–C}} = 44.7$ Hz, C_{ipso}), 129.7 (d, $^{2}J_{\text{P–C}} = 10.5$ Hz, C_{ortho}), 134.6 (d, $^{3}J_{\text{P–C}} = 13.3$ Hz, C_{meta}), 131.6 (d, $^{4}J_{\text{P–C}} = 2.4$ Hz, C_{para}); δ_{P} (121.5 MHz, $CDCl_3$): 46.4. *m*/*z* (EI) 516 (4%), 488 (8), 459 (35), 262 (100).

Crystal structure determination of complexes 1, and 7/7′

The crystallographic data collection and refinement details for complex **1** are summarised in Table 4. X-Ray quality yellow platelet single crystals of **1** were obtained by crystallisation from a concentrated diethyl ether solution layered with pentane at −20 °C. Low temperature (−95 °C) data were collected on an Enraf-Nonius KappaCCD diffractometer[20] or Bruker SMART Apex CCD diffractometer[21] using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and scaled and reduced using DENZO-SMN[22] and Bruker SAINT[23] respectively. Empirical corrections were performed using SCALEPACK[22] and SMART data were treated with SADABS.[24] The structure of **1** was solved by the heavy atom method and refined anisotropically for all the

Table 4 Crystallographic data for **1** and **7**/**7**′

	1	**7**/**7**′
Chemical formula	$C_{27}H_{23}O_5NPAuCr$	$1.48(C_{29}H_{20}O_5SPCrAu)\cdot 0.52(C_{31}H_{22}O_5SPCrAu)$
M_r/g mol^{-1}	721.4	1534.43
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	6.6251(2)	12.4049(2)
b/Å	23.8365(8)	20.7908(3)
c/Å	17.0238(5)	23.8896(3)
β/°	97.573(1)	91.437(1)
V/Å^3	2664.9(1)	6159.38(15)
Z	4	4
D_c/g cm^{-3}	1.798	1.655
T/K	178(2)	177(2)
μ(Mo-Kα)/cm^{-1}	6.003	5.265
$2\theta_{max}$/°	25.00	26.00
Crystal size/mm	0.10 × 0.22 × 0.33	0.25 × 0.30 × 0.35
Index range, hkl	−7 to 4, −28 to 28, −20 to 20	−15 to 14, −24 to 25, −25 to 29
Reflections collected	8192	33837
Independent reflections (R_{int})	4422 (0.0494)	12099 (0.0328)
Observed reflections	3729	10327
Parameters	335	868
R_1 ($F_o > 2\sigma F_o$)	0.0333	0.0476
wR_2 (all data)	0.0890	0.1087

non-hydrogen atoms by full-matrix least-squares calculations on F^2. All hydrogen atoms in **1** were placed in calculated positions, except those on the terminal CH_2-group coordinated to $Cr(CO)_5$, which were found on the difference Fourier map and refined isotropically. The structure of **7**/**7**′ was solved by direct methods. Peaks of electron density on the difference Fourier map indicated the presence of disorder, which was subsequently identified as molecules of **7** and **7**′ in the ratio 1 : 2.866. The sum of the site occupancies of the partial molecular fragments of **7** and **7**′ that share the same site in the crystal lattice was restrained to 1 after which all the non-hydrogen atoms, except O(7)′, which exhibits further disorder, were allowed anisotropic displacement parameters. Bond lengths in the C(24X) and C(25X) phenyl rings were restrained to sensible values and the carbon atoms in both rings were subjected to rigid body (DELU), flat geometry (FLAT) and similar U_{ij} (SIMU) restraints to improve their geometry. Two O(7)′ atomic positions [O(7)′1 and O(7)′2] could be found for the disorder observed in this CO ligand. The sum of the site occupancies of the two O(7) atomic sites was restrained to the refined site occupancy of the disordered fragment they belong to. All hydrogen atoms in **7** were placed in calculated positions. The isotropic displacement parameters of the calculated hydrogen atoms in both structures were fixed at 1.2 (aromatic hydrogens) and 1.5 (methyl hydrogens) times the equivalent isotropic displacement parameters of their parent atoms. All calculations were performed using SHELX-97[25] under the X-Seed[26] environment. Figures were prepared using ORTEP-3 for Windows, with the ellipsoids at the 50% probability level.[27]

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Computational methods

The geometries of the molecules were optimised at the gradient-corrected DFT level using the three-parameter fit of the exchange–ndash potential suggested by Becke[28] in conjunction with the LYP[29] exchange potential (B3LYP).[30] A quasi-relativistic small-core ECP with a (441/2111/N1) valence basis set for the metal atoms ($N = 4$ for Cr and $N = 2$ for Au)[31] and 6-31G(d) all-electron basis sets[32] for the other atoms were employed in the geometry optimisations. This is our standard basis set II.[33] The nature of the stationary points was examined by calculating the Hessian matrix at B3LYP/II. All structures are energy minima on the potential energy surface. The calculations were performed with the program package Gaussian 98.[34]

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