Dinuclear Gold(I) "A-Frame" Complexes from Geminal Diauration of 2,4-Diketones, Methylenedisulfones, and Cyanomethyl Sulfones

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Treatment of the disulfones $RSO_2CH_2SO_2R$ (R = Me, Ph) with 1 or 2 equiv of organolithium reagents, followed by metathesis with a (phosphine/arsine)gold(I) halide, afforded high yields of mono- or diaurated sulfones of the types $[(R'_3P)Au]CH(SO_2R)_2$ (R = R′ = Ph) and $[(R'_3P/As)Au]_2\{\mu\text{-}C(SO_2R)_2\}$ (R = Me, $R'_3P = Ph_3P$, Ph_2MeP, Ph_3As; R = Ph, $R'_3P = PPh_3$, Ph_2MeP). Using the same procedure, $PhSO_2CH_2CN$ was transformed into $[(Ph_3P)Au]_2\{\mu\text{-}C(CN)SO_2Ph\}$. The products are stable to air and moisture and decompose at temperatures well above 150 °C. The crystal structure analysis of the diaurated compounds reveals compact A-frame core units in which the central carbon atom forms a CAu_2 triangle with an exceedingly small Au−C−Au angle and, consequently, a short aurophilic Au- - -Au contact. The corresponding angles S−C−S (or SAuC(N)) are widened in an overall distorted-tetrahedral environment. Attempted triauration using $[(R'_3P)Au]^+BF_4^-$ reagents was unsuccessful with the disulfones but gave the adduct $\{[(Ph_3P)Au]_2C(SO_2Ph)CN[Au(PPh_3)]\}^+BF_4^-$, in which the third gold atom is attached to the nitrile nitrogen atom. Benzyl phenyl sulfone was monoaurated to give the chiral product $[(Ph_3P)Au]CH(Ph)SO_2Ph$. 3-[(Triphenylphosphine)gold]pentane-2,4-dione was found to undergo a redistribution reaction induced by tri-*tert*-butoxyaluminum in benzene solution to give the diaurated diketone $[(Ph_3P)Au]_2\{\mu\text{-}C\{C(O)Me\}_2]$. Its crystal structure shows a core unit with bonding characteristics similar to those of keto instead of sulfone/cyano substituents.

Introduction

Auration of hydrocarbons has been a classical synthetic target, since these reactions could give direct access to many new types of organogold compounds.[1,2] Direct auration of methane or other unstrained alkanes—avoiding the detour via Grignard, organolithium, or other organometallic reagents—has not yet been accomplished. It is known, however, that auration may become a facile process as the C−H acidity is increased by suitable substituents.[3] Thus, even the methyl groups of common solvents such as acetone ($CH_3C(O)CH_3$), acetonitrile (CH_3CN), and chloroform ($CHCl_3$) were found to be rapidly aurated even under mild conditions if strongly electrophilic gold(I) reagents of the types $[(L)Au]^+BF_4^-$, $[(L)Au]_3O^+BF_4^-$, etc. (L = tertiary phosphine) are employed. Mononuclear products such as $(L)AuCH_2C(O)Me$ and $(L)AuCH_2CN$, respectively, are obtained in acceptable yields.[3]

More strongly activated methylene groups, X_2CH_2, are easily aurated and the compounds converted into mono- and diaurated organometallic complexes. Successful experiments were reported, for example, for cyclopentadiene[4] and malonodinitrile,[5] which give the mononuclear compounds $(CH{=}CH)_2CHAu(L)$ and finally the diaurated species $(CH{=}CH)_2C[Au(L)]_2$ and $(NC)_2C[Au(L)]_2$, respectively. With acetylacetone (pentane-2,4-dione), however, only the mononuclear compound was obtained: $[CH_3C(O)]_2CHAu(L)$.[6−9] This complex serves as a useful reagent in many transformations in (organo)gold chemistry.[10]

Other examples of polyauration of C−H acidic compounds are known from the series of phosphonium and sulfonium salts and the corresponding ylides.[11−16] Suitable substrates were also selected from prototypes

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where a methylene group is in a bridging position between different activating groups, such as the (cyanoalkyl)phosphonium salts $[NCCH_2PR_3]^+X^-$ [3,17a] or N-heterocycles and the corresponding carbenes.[17b]

The geminally diaurated compounds $X_2C[Au(L)]_2$ have interesting "A-frame" structures which reflect the strong gold−gold affinity.[3,5,18] Significant aurophilic bonding leads to very acute Au−C−Au angles (generally ca. 80°) and short Au−Au contacts (approximately 2.8 Å) and to further intermolecular clustering. These metal−metal contacts can give rise to intriguing (photo)physical phenomena, which still cannot be assigned to the structural details.

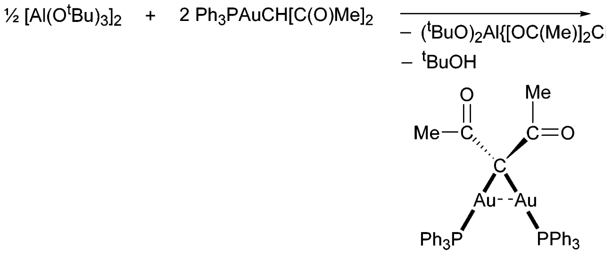
We are therefore currently investigating new classes of polyaurated functional organic compounds and in the present account report on results obtained with methylenedisulfones $RSO_2CH_2SO_2R$. The literature on aurated oxosulfonium salts and ylides is still very limited.[15,16,19] Boche et al. have described the preparation and structure of a monoaurated sulfone,[20] viz. $[(Ph_3P)Au]CH(Ph)SO_2{}^tBu$, and the groups of Fackler,[21] Vicente,[15,17] and Lin[16] have studied extensively the auration of sulfonium, oxo−sulfonium, and amino−sulfonium methylides.

We also include the preparation and structure of the first geminally diaurated 1,3-diketone, which was obtained from an unusual redistribution reaction of the classical monoaurated precursor,[6−8] induced by aluminum tri-*tert*-butoxide.

Preparations and Properties

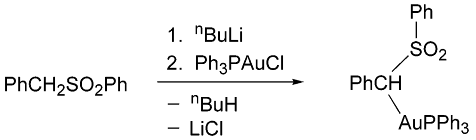
Auration of Pentane-2,4-dione. In an attempt to prepare an Au/Al mixed-metal complex of 3-[(triphenylphosphine)gold]pentane-2,4-dione, $[(Ph_3P)Au]CH[(C{=}O)Me]_2$, or its corresponding anion, this compound was treated with $^1/_3$ mole equiv of aluminum tri-*tert*-butoxide in benzene at room temperature. Workup of the reaction mixture after 2 days gave a 45% yield of an aluminum-free organogold compound, which was identified as 3,3-bis[(triphenylphosphine)gold]pentane-2,4-dione, $[(Ph_3P)Au]_2\{\mu\text{-}C[(C{=}O)Me]_2\}$. The colorless crystals (from dichloromethane/*n*-pentane) melt at 140 °C with decomposition. Elemental analysis and mass spectrometric and NMR spectroscopic data are in agreement with the proposed formula of a diketone geminally aurated at the central carbon atom. The structure was further confirmed by a single-crystal X-ray analysis (vide infra).

This composition indicates a redistribution of the $[(L)Au]^+$ units between the acetylacetonate groups, which after deprotonation of acetylacetone by *tert*-butoxide leaves the aluminum atom with unsubstituted $[acac]^-$ anions (eq 1).



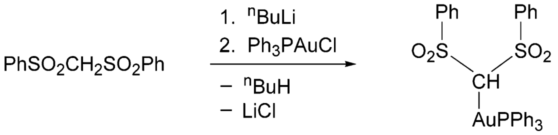
(1)

Auration of Methylenebis(methyl sulfone), Methylenebis(phenyl sulfone), and Cyanomethyl Phenyl Sulfone. The auration of sulfones and disulfones is best achieved via metalation of the substrates with a standard organometallic reagent such as *n*-butyllithium, followed by metathesis with the appropriate (phosphine/arsine)gold(I) complex. This procedure was suggested by the successful monoauration of a monosulfone by Boche et al.[20] Thus, benzyl phenyl sulfone is readily converted into the monoaurated monosulfone in 91% yield (eq 2).



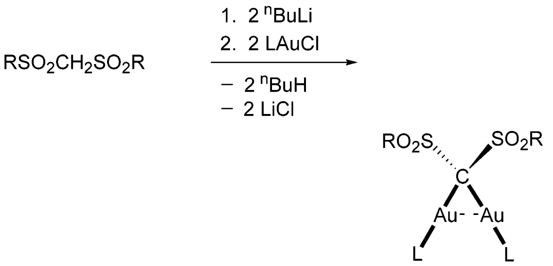
(2)

Monoauration was also carried out with $PhSO_2CH_2SO_2Ph$ as a substrate. The overall yield for the monolithiation followed by auration was 87% (eq 3).



(3)

The methylenedisulfones $RSO_2CH_2SO_2R$ (with R = Me, Ph) can be fully metalated at the bridging methylene group by employing 2 equiv of ^nBuLi followed by 2 equiv of (L)AuCl (eq 4).



(4)

R = Me; L = PPh_3, PPh_2Me, $AsPPh_3$

R = Ph; L = PPh_3, PPh_2Me

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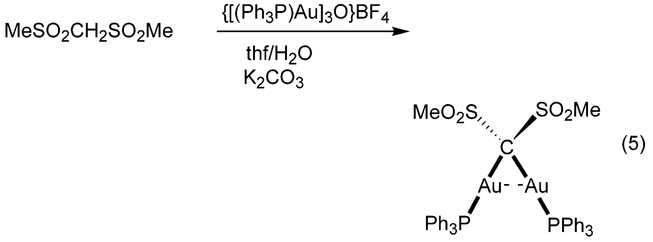
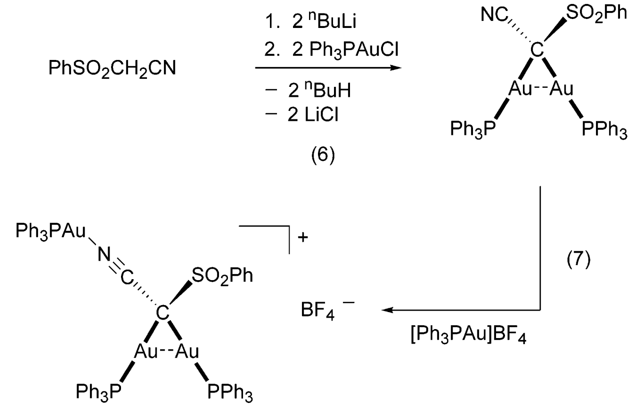
Yields were all around 90% for the combinations investigated: R = Me, L = PPh_3, $PMePh_2$, $AsPh_3$; R = Ph, L = PPh_3, $PMePh_2$.

$MeSO_2CH_2SO_2Me$ can also be diaurated directly using $\{[Ph_3P)Au]_3O\}BF_4$ in a tetrahydrofuran/water solvent mixture containing K_2CO_3.[3] The yield was 45% (eq 5).



(5)

In cyanomethyl phenyl sulfone the methylene unit is similarly activated, in this case by the sulfone and the cyano function, and its auration also affords the diaurated compound (eq 6).



(6)

(7)

While attempts to achieve triauration of the disulfone derivatives (above) with $[(Ph_3P)Au]BF_4$ or $\{[(Ph_3P)Au]_3O\}BF_4$ did not lead to well-defined products, such efforts were successful with the cyano-substituted compound (eq 7). Spectroscopic and structural investigations have shown, however, that the last of the three auration steps involved the cyano group as the donor site (below). This result is in agreement with reports by Perevalova et al.[22] and Vicente et al.[17a]

The compositions of all aurated sulfones were confirmed by elemental analyses and mass spectrometry. With FAB ionization, the complexes produced the molecular ions followed by characteristic fragment ions. It is important to note that no trinuclear ions were observed, which indicates that the addition of a $[(R_3P/As)Au]^+$ cation to the parent molecule is not a facile process. This result is in agreement with the failure of preparative attempts made in this work (except for the cyanomethyl phenyl sulfone; vide supra).

The aurated sulfones are generally colorless solids which are stable to air and moisture and melt or decompose between 150 and 200 °C. They are soluble in polar organic solvents such as di- and trichloromethane, acetone, and acetonitrile, poorly soluble in tetrahydrofuran and diethyl ether, and insoluble in pentane. The NMR spectra of solutions in CD_2Cl_2 or $CDCl_3$ show the expected sets of resonances for the alkyl or aryl substituents. Owing to free rotation about all bonds at the central carbon atom, the LAu and RSO_2 units are equivalent. Note that "frozen" conformations as present in the crystals of certain compounds (vide infra) could lead to nonequivalence of substituents.

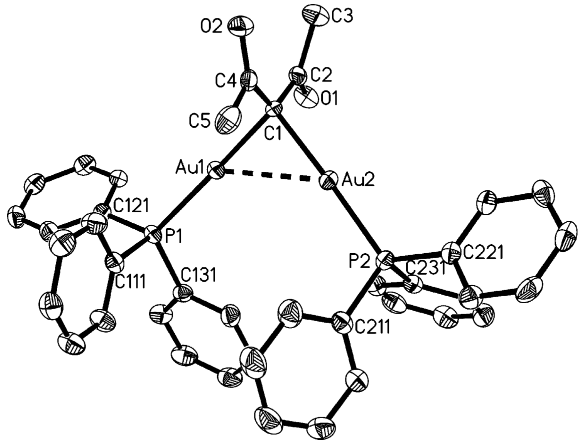


Figure 1. Molecular structure of $[(Ph_3P)Au]_2\{\mu\text{-}C\{C(O)Me\}_2\}$ (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted). Selected bond lengths (Å) and angles (deg): Au1−C1 = 2.129(4), Au2−C1 = 2.121(4), Au1- - -Au2 = 2.8569(2); Au1−C1−Au2 = 84.50(1), C2−C1−C4 = 121.7(3).

The phosphorus, carbon, and proton chemical shifts and the signal multiplicities show no anomalies. The resonance of the central carbon atom of the diaurated sulfones is generally not observed in the spectra with routine techniques. Special efforts were therefore made to detect this signal for at least one example: extended multipulse NMR experiments finally led to the discovery of the expected ^{13}C triplet resonance for $[(Ph_3P)Au]_2\{\mu\text{-}C(SO_2Ph)_2\}$ at 116.5 ppm with $^2J(PC) = 75$ Hz (in CD_2Cl_2 at 25 °C). For monoaurated sulfones this signal is easier to detect and found more upfield: the central carbon atoms of $[(Ph_3P)Au]CH(Ph)SO_2Ph$ and $[(Ph_3P)Au]CH(SO_2Ph)_2$ resonate at 80.2 and 81.1 ppm, but the coupling constants $^2J(PC)$ of 84.6 and 87.0 Hz, respectively, are similar (CD_2Cl_2, 25 °C). The corresponding C*H* resonances are doublets at 4.40 and 5.53 ppm with coupling constants $^3J(PH)$ of 8.7 and 7.9 Hz, respectively. It should be noted that these *J*(PAuC) and *J*(PAuCH) coupling constants agree with those found for standard organogold(I) complexes of the type R_3PAuR' and therefore indicate standard two-center−two-electron bonding for the connectivities involved.

The triply aurated cyanomethyl phenyl sulfone shows two ^{31}P resonances in the intensity ratio 2:1, suggesting a different bonding for the third $[(Ph_3P)Au]$ unit, as borne out by the crystal structure investigations.

Molecular Structures

3,3-Bis[(triphenylphosphine)gold]pentane-2,4-dione. Neglecting the orientation of the phenyl groups, the conformation of the core unit of the molecule approaches mirror symmetry (point group C_s), with the mirror plane containing both carbonyl groups and bisecting the Au1−C1−Au2 angle (Figure 1). The two gold atoms are equidistant from the central carbon atom (C1−Au1 = 2.129(4) Å, C1−Au2 = 2.121(4) Å), and the angle Au1−C1−Au2 is very acute at 84.5(1)°, which

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(22) Perevalova, E. G.; Struchkov, Yu. T.; Dyadchenko, V. P.; Smyslova, E. I.; Slovokhotov, Yu. L.; Grandberg, K. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1983**, 2818.

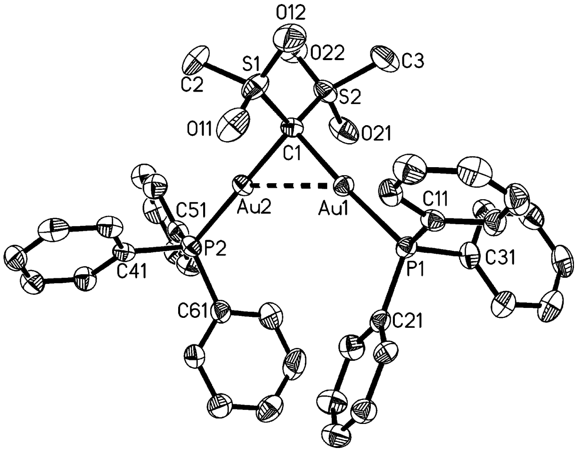

Figure 2. Molecular structure of $[(Ph_3P)Au]_2\{\mu\text{-}C(SO_2Me)_2\}$ (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted). Selected bond lengths (Å) and angles (deg): Au1−C1 = 2.087(6), Au2−C1 = 2.096(6), Au1- -Au2 = 3.1014(4); Au1−C1−Au2 = 95.7(3), S1−C1−S2 = 115.8(4).

gives rise to a short Au1- - -Au2 contact of only 2.8569(2) Å. The remaining two bonds of C1 involving the carbonyl carbon atoms are also not significantly different (C1−C2 = 1.480(6) Å, C1−C4 = 1.462(6) Å) and form the angle C2−C1−C4, which is widened to 121.7(3)°. The two carbonyl carbon atoms are in an approximately trigonal-planar configuration, with the two planes roughly bisecting the Au1−C1−Au2 angle. These details can be rationalized by resonance forms with three-center−two-electron bonds in the Au1−C1−Au2 triangle in addition to the conventional 2c−2e forms.[41]

The two carbonyl groups are in an anti conformation, with one oxygen atom (O1) oriented toward the C1−Au1−Au2 triangle and the other one (O2) away from it. The carbonyl dipoles thus point in opposite directions, but this does not lead to significant distortions of the core unit. Note that rotation of one MeCO− group around the C1−C2 or C1−C4 axis by 180° would generate a symmetry of the core unit corresponding to point group C_{2v}, but this appears not to be the ground-state conformation, as observed also in other β-diketones.[23]

Bis[(triphenylphosphine/-arsine)gold]methylenebis(methyl sulfone). The crystals of the two compounds (from CH_2Cl_2/n-C_5H_{12}) are isomorphous. The overall geometry approaches quite closely the symmetry requirements of point group C_2, the 2-fold axis passing through the central carbon atom and bisecting the Au1−C1−Au2 and S1−C1−S2 angles, as shown in Figure 2 for the Ph_3P complex.

The central carbon atom and the two sulfur atoms are in a quasi-tetrahedral configuration and show a mutually staggered conformation. The C1−Au and C1−S distances are in the ranges 2.080(5)−2.096(6) and 1.732(7)−1.770(6) Å, respectively, with Au1−C1−Au2/S1−C1−S2 angles of 94.1(1)/115.8(4)° (P) and 95.7(3)/116.2(3)° (As). The Au1−Au2 distances are 3.1014(4) Å (P) and 3.0451(3) Å (As). The data show that the influences of the Ph_3P/Ph_3As ligands on the structure of the core unit are essentially the same.

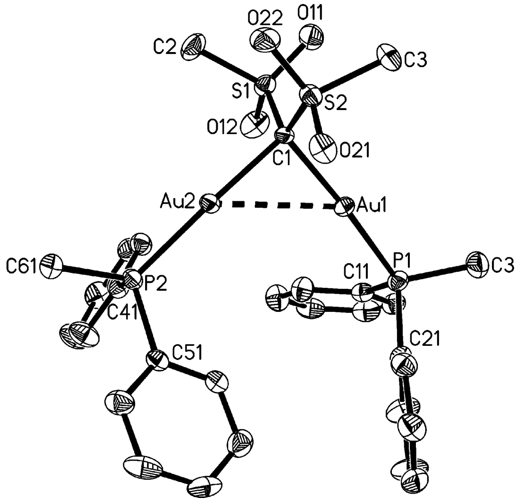

Figure 3. Molecular structure of $[(MePh_2P)Au]_2\{\mu\text{-}C(SO_2Me)_2\}$ (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted). Selected bond lengths (Å) and angles (deg): Au1−C1 = 2.109(3), Au2−C1 = 2.099(3), Au1- - -Au2 = 2.9785(2); Au1−C1−Au2 = 90.1(1), S1−C1−S2 = 115.4(2).

Bis[(diphenylmethylphosphine)gold]methylenebis(methyl sulfone) Dichloromethane Solvate. The structure is very similar to that of the triphenylphosphine analogue (vide supra), with approximate C_2 symmetry (Figure 3). Selected bond distances (Å) and angles (deg) are as follows: C1−Au1 = 2.109(3), C1−Au2 = 2.099(3), C1−S1 = 1.751(3), C1−S2 = 1.731(3), Au1- - -Au2 = 2.9785(2) Å; Au1−C1−Au2 = 90.12(2), S1−C1−S2 = 115.4(2)°. Again it appears that the ligand exchange (Ph_3P/$MePh_2P$) does not lead to significant structural changes at the S_2CAu_2 core.

Bis[(triphenylphosphine)gold]methylenebis(phenyl sulfone) Chloroform Solvate. The structure is similar to that of the methyl sulfone analogue (above) and approaches 2-fold symmetry, owing to an all-staggered conformation (Figure 4). With distances (Å) C1−Au1 = 2.104(3), C1−Au2 = 2.111(3), Au1- -Au2 = 2.9066(2), C1−S1 = 1.744(3), and C1−S2 = 1.734(3) and angles (deg) Au1−C1−Au2 = 87.2(1) and S1−C−S2 = 117.2(2)°, the core unit is virtually unchanged as compared to its methyl sulfone analogues.

It is particularly obvious from this molecular structure (Figure 4) that the central carbon atom is shielded very effectively by its substituents and that the steric crowding leaves no access for a third $[(Ph_3P)Au]^+$ nucleophile.

{Bis[(triphenylphosphine)gold]cyanomethyl}Phenyl Sulfone Dichloromethane Solvate. In the crystals of this compound the solvent molecules are heavily disordered. The asymmetric unit contains two independent molecules of the sulfone with very similar dimensions (Figure 5). These molecules do not approach the maximum attainable symmetry (point group C_s), because the oxygen atoms of the sulfone groups are not symmetrically positioned relative to this idealized mirror plane (containing the atoms N11−C11−S1 or N21−C21−S2).

The central atoms C11/C21 are in quasi-tetrahedral environments of one sulfone, one cyano, and two (phos-

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(23) (a) Grandberg, K. I.; Kuz'mina, L. G.; Smyslova, E. I.; Zinin, A. I.; Krut'ko, D. P.; Dyadchenko, V. P. *Zh. Neorg. Khim.* **1996**, *41*, 231. (b) Kuz'mina, L. G. *Koord. Khim.* **1994**, *20*, 540. (c) Fernandez, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; Lopez de Luzuriaga, J. M.; Rodriguez, M. A. *Chem. Ber.* **1995**, *128*, 121. (d) Vicente, J.; Bermudez, M. D.; Escribano, J.; Carillo, M. P.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1990**, 3083.

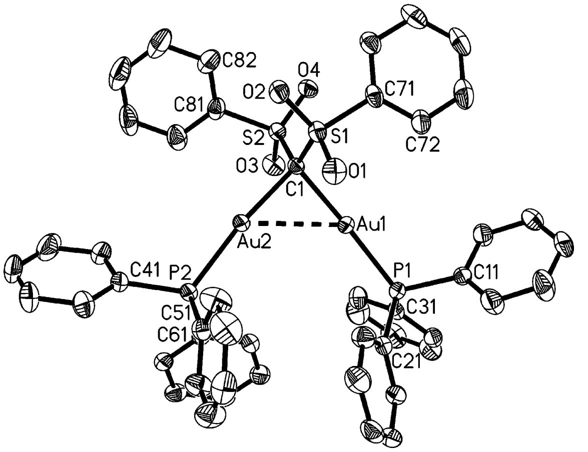

Figure 4. Molecular structure of $[(Ph_3P)Au]_2\{\mu\text{-}C(SO_2Ph)_2\}$ in crystals of the chloroform solvate (ORTEP, 50% probability ellipsoids, hydrogen atoms and chloroform molecule omitted). Selected bond lengths (Å) and angles (deg): Au1−C1 = 2.104(3), Au2−C1 = 2.111(3), Au1- - -Au2 = 2.9066(2); Au1−C1−Au2 = 87.2(1), S1−C1−S2 = 117.2(2).

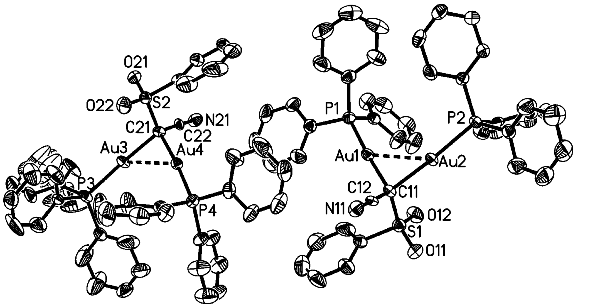

Figure 5. Molecular structure of $[(Ph_3P)Au]_2\{\mu\text{-}C(CN)SO_2Ph\}$ in crystals of the dichloromethane solvate (ORTEP, 50% probability ellipsoids, hydrogen atoms and solvent molecules omitted, one phenyl ring at P3 is disordered). The asymmetric unit contains two independent molecules with very similar geometries. Selected bond lengths (Å) and angles (deg): Au1−C11 = 2.089(7), Au2−C11 = 2.109(7), Au1- - -Au2 = 2.9689(4), Au3−C21 = 2.098(7), Au4−C21 = 2.096(6), Au3- - -Au4 = 2.9766(4); Au1−C11−Au2 = 89.8(3), S1−C11−C12 = 110.45), Au3−C21−Au4 = 90.4(2), S2−C21−C22 = 109.8(5).

phine)gold units, with angles Au1−C11−Au2 = 89.8(3)° and Au3−C21−Au4 = 90.4(2)° and distances Au1−Au2 = 2.9689(4) Å and Au3−Au4 = 2.9766(4) Å. The tetrahedral sulfone groups show no anomalies, and the C−Au−P and C−C−N axes are almost perfectly linear. The conformations at the C11−S1 and C21−S2 axes are staggered.

Bis[(triphenylphosphine)gold][*N*-((triphenylphosphine)gold)cyano]methyl Phenyl Sulfone Tetrafluoroborate Acetone Solvate. The asymmetric unit contains two cations which are associated into a hexanuclear unit, together with two anions and several acetone molecules. These solvent molecules were found to be disordered and were not considered any further.

It is obvious from the picture of the hexanuclear dication (Figure 6) that the structure contains two molecules of the diaurated cyanomethyl phenyl sulfone (above) which have both taken on an additional $[(Ph_3P)Au]BF_4$ unit with the nitrile nitrogen atoms as the donor centers. Thus, the chains C11−C12−N11 and C21−C22−N21 are extended by Au4−P4 and Au3−P3 units, respectively.

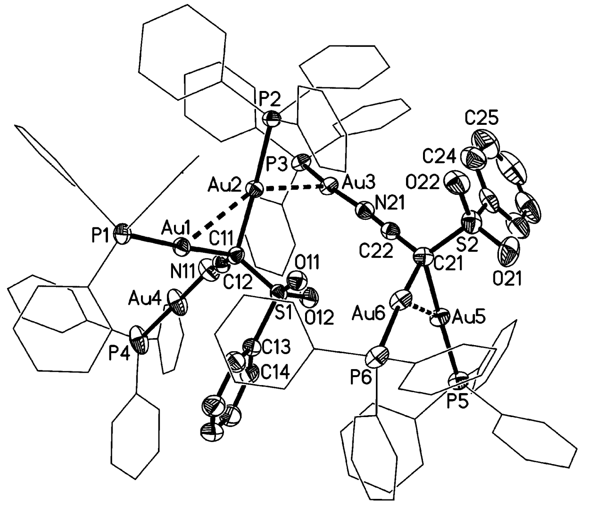

Figure 6. Molecular structure of $\{[(Ph_3P)Au]_2C(SO_2Ph)CN[Au(PPh_3)]\}^+BF_4^-$ in crystals of the acetone solvate (ORTEP with 50% probability ellipsoids for the main skeleton, hydrogen atoms, tetrafluoroborate anions, and solvent molecules omitted). The asymmetric unit contains two formula units which are aggregated via the aurophilic contact Au2- - -Au3. Selected bond lengths (Å) and angles (deg): Au1−C11 = 2.125(5), Au2−C11 = 2.110(6), Au1- - -Au2 = 2.8723(3); Au5−C21 = 2.127(6), Au6−C21 = 2.105(6), Au5- - -Au6 = 2.9018(3); Au2−Au3 = 3.0013(3); Au1−C11−Au2 = 85.5(2), S1−C11−C12 = 110.1(4); Au5−C21−Au6 = 86.6(2), S2−C21−C22 = 110.4(4).

In the association of the resulting two trinuclear cations an aurophilic contact is established between Au2 and Au3 (3.0013(3) Å). The dihedral angle P2−Au2−Au3−P3 of 95.59(6)° indicates that the two axes P2−Au2−C11 and P3−Au3−N21 are approximately at right angles ("crossed swords"). The mutual approach of Au3 and Au4 appears to be sterically hindered. Thus, the asymmetric unit features a triple Au1−Au2−Au3 grouping, a Au5−Au6 pair, and an individual Au4. The dimensions of the tetrahedral entities C11 (Au1, Au2, C12, S1) and C21 (Au5, Au6, C22, S2) are not significantly different from those of the precursor molecule: Au1- -Au2 = 2.8723(3), Au5- -Au6 = 2.9018(3) Å; Au1−C11−Au2 = 85.5(2), Au5−C21−Au6 = 86.6(2)°.

It should be noted that the angles established at the nitrile nitrogen atoms upon auration deviate very strongly from linearity: C12−N11−Au4 = 153.6(5) and C22−N21−Au3 = 162.6(5)°. We cannot offer a definitive explanation for these substantial angle compressions, other than standard packing effects. It is tempting to propose an electronic influence of the CAu_2 unit on the cyano group, but the associated dihedral angles make this unlikely (Figure 6).

The triple-bond distances C12−N11 of 1.160(8) Å and C22−N21 of 1.147(7) Å are not very different from those of the parent compound (1.144(9) and 1.134(9) Å), considering the standard deviations of the experiment. There are also no significant variations in the neighboring C−C bonds C11−C12 and C21−C22.

[(Triphenylphosphine)gold]benzyl Phenyl Sulfone. The two molecules of the unit cell are related by a center of inversion and represent the two enantiomers

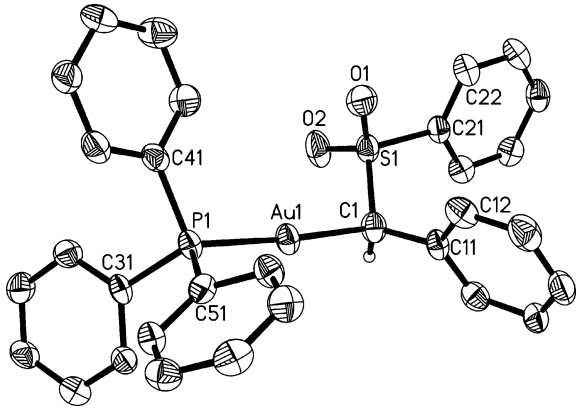

Figure 7. Molecular structure of $[(Ph_3P)Au]CH(Ph)SO_2$-Ph (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted). Selected bond lengths (Å) and angles (deg): Au1−C1 = 2.112(9), Au1−P1 = 2.281(2), S1−O1 = 1.467(7), S1−O2 = 1.443(7), S1−C1 = 1.749(9), S1−C21 = 1.775(9); P1−Au1−C1 = 175.4(3).

of this chiral compound (Figure 7). The quality of the crystals investigated was not fully satisfactory, and therefore, the geometrical parameters obtained are not very accurate and will not be discussed any further.

Conclusions

Tetragold methane complexes $C[Au(L)]_4$ have remained a synthetic challenge ever since it has been demonstrated[11,18,24−26] that auration of methane readily proceeds beyond tetracoordination to give the penta- or even hexametalated cations $\{C[Au(L)]_5\}^+$ and $\{C[Au(L)]_6\}^{2+}$. It was only with very bulky ligands L (tricyclohexylphosphine, tri-*o*-tolylphosphine) that the tetraaurated molecules could be isolated.[27] With these large ligands, the central carbon atom remains in its tetrahedral configuration, while for arrays with small ligands a square-pyramidal structure is predicted[28] and suggested[29,30] by the protonated and alkylated forms $\{HC[Au(PPh_3)]_4\}^+$ and $\{MeC[Au(PR_3)]_4\}^+$.

In this context, the chemistry and structure of methanes with a lower grade of auration and a heteroleptic substitution pattern are of great current interest. In our previous studies it has been demonstrated that phosphonium salts and their corresponding ylides may be aurated up to the P_2CAu_2, $PHCAu_2$, and $PCAu_3$ levels with tetrahedral carbon environments.[12,13] Silylmethanes were found[31] to form tetrahedral core units of the types $SiHCAu_2$ and Si_2CAu_2 and even trigonal-pyramidal Si_2CAu_3. Sulfonium salts were aurated up to the $SCAu_4$ level with a square-pyramidal structure,[10b] and mixed phosphonium/sulfonium cases are also known.[15]

The present study is extending this family of polyaurated methanes by introducing the sulfone functions: i.e. tetrahedral coordination of carbon, including two sulfur(VI) centers. It could be demonstrated that species with this set of ligands are readily accessible and are of high chemical and thermal stability. Their core units have a distorted-tetrahedral structure with strong aurophilic bonding. They qualify as “A-frame compounds” with the Au- - -Au contact representing the horizontal bar. Pentacoordination of the central carbon atom could not be achieved, probably owing to both steric and inductive effects.

Experimental Section

All experiments were carried out under an atmosphere of dry nitrogen. Solvents were dried and saturated with nitrogen. Glassware was oven-dried and filled with nitrogen. All glass apparatus was protected against incandescent light with aluminum foil. Standard equipment was used throughout. The (phosphine)- and (arsine)gold chlorides, acetylacetonate, and tris[(triphenylphosphine)gold]oxonium tetrafluoroborate were prepared as described in the literature.[32−35] All sulfones were synthesized by oxidation of the corresponding sulfides (thioethers) with hydrogen peroxide in glacial acetic acid.[36−38] The thioethers and aluminum tri-*tert*-butoxide are commercially available. The lithiation of the sulfones using alkyllithium reagents has been described previously.[20] NMR spectra were obtained on a JEOL JMN LA-400 instrument, with δ values in ppm and J values in Hz; all ^{31}P and ^{13}C spectra were ^1H-decoupled.

3,3-Bis[(triphenylphosphine)gold]pentane-2,4-dione. To a solution of $Al(O^tBu)_3$ (15 mg, 0.06 mmol) in benzene (10 mL) was added $[(Ph_3P)Au]CH(COMe)_2$ (100 mg, 0.18 mmol). After 2 days of stirring, the solvent was removed and the product was crystallized from dichloromethane on addition of *n*-pentane: yield 45 mg, 40%; mp 140 °C dec. NMR spectra were obtained in CD_2Cl_2 at 25 °C. ^{31}P NMR: 37.9 (s). ^{13}C, 205.9 (s, C=O); 134.5 (d, J = 14.0), 131.6 (s), ca. 130.8 (d, J masked), 129.4 (d, J = 11.4) (for *o*-, *p*-, *i*-, and *m*-C, Ph); 33.2 (s, Me). ^1H NMR: 7.28−7.53 (m, 30H, Ph); 2.41 (s, 6H, Me). MS (FAB): *m*/*z* 458.5 (99%) $[LAu]^+$, 720.1 (100) $[L_2Au]^+$, 1016 (34) $[M]^+$, 1472.9 (8) $[M + AuL]^+$. Anal. Calcd for $C_{41}H_{36}Au_2O_2P_2$ (1016.61): C, 48.44; H, 3.57. Found: C, 48.25; H, 3.53.

1-[(Triphenylphosphine)gold]benzyl Phenyl Sulfone. $PhCH_2SO_2Ph$ (94 mg, 0.4 mmol) was dissolved in tetrahydrofuran (10 mL) and treated with 0.25 mL of a 1.6 M solution of ^nBuLi in hexanes at −78 °C. After 2 h of stirring $(Ph_3P)AuCl$ (200 mg, 0.4 mmol) was added to the reaction mixture, which was then warmed to room temperature overnight. The solvents were removed under vacuum, and the residue was extracted with CH_2Cl_2. The solvent was again removed under vacuum, and the residue was washed with pentane and dried: 251 mg (91% yield); mp 173 °C dec. Single crystals were grown from dichloromethane/*n*-pentane on cooling to −10 °C. NMR spectra were obtained in CD_2Cl_2 at 25 °C. ^{31}P NMR: 40.6 (s). ^{13}C NMR: 80.2 (d, J = 84.6); not all aryl signals (PPh, SPh, CPh) have been assigned. ^1H NMR 4.4 (d, J = 8.7, 1H, SC*H*); 7.15−7.90 (m, 25H, Ph). MS (FAB): *m*/*z* 720 (21.47) $[L_2Au]^+$, 690 (9.23) $[M]^+$, 548 (53.73) $[M - SO_2Ph]^+$, 459 (12.61) $[LAu]^+$, 262

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(3.55) $[L]^+$. Anal. Calcd for $C_{31}H_{26}AuO_2PS\cdot 0.3C_5H_{12}$ (712.19): C, 54.8; H, 4.19. Found: C, 54.6; H, 4.11.

[(Triphenylphosphine)gold]methylenebis(phenyl sulfone). $PhSO_2CH_2SO_2Ph$ (89 mg, 0.3 mmol) was dissolved in tetrahydrofuran (10 mL) and treated with 0.19 mL of a 1.6 M solution of ^nBuLi in hexanes at −78 °C. After the mixture was stirred for 2 h, a solution of Ph_3PAuCl (150 mg, 0.3 mmol) in 20 mL of tetrahydrofuran was added. The stirred reaction mixture was warmed to room temperature overnight. The solvents were evaporated, the residue was extracted with CH_2Cl_2, and the solvent was again evaporated under vacuum. The residue was washed with pentane and diethyl ether and dried under vacuum: 196 mg (87% yield); mp 186 °C dec. Single crystals were grown from dichloromethane/*n*-pentane on cooling to −10 °C. NMR spectra were obtained in CD_2Cl_2 at 25 °C. ^{31}P NMR: 39.7 (s). ^{13}C NMR: 81.14 (d, *J* = 87, *C*HS); 134.5 (d, *J* = 14), 131.7 (s), 129.4 (d, *J* = 55), and 129.3 (d, *J* = 12) for *o*-, *p*-, *i*-, and *m*-C of PhP; 133.9, 131.5, 129.0, and 129.1, all s, for *i*-, *p*-, *m*-, and *o*-C of PhS. ^1H NMR: 5.53 (d, ^3J = 8.0, 1H, C*H*); 8.12−6.72 (m, 25H, Ph). MS (FAB): *m*/*z* 754 (7.2) $[M]^+$, 720 (21.45) $[L_2Au]^+$, 459 (100) $[LAu]^+$, 262 (3.89) $[L]^+$. Anal. Calcd for $C_{31}H_{26}AuO_4PS_2$ (754.62): C, 49.34; H, 3.47. Found: C, 48.85; H, 3.74.

Bis[(triphenylphosphine)gold]-, Bis[(triphenylarsine)gold]-, and Bis[(diphenylmethylphosphine)gold]methylenebis(methyl sulfone) and Bis[(triphenylphosphine)gold]- and Bis[(diphenylmethylphosphine)gold]methylenebis(phenyl sulfone) by Lithiation of the Sulfones. (a) General Procedure. $RSO_2CH_2SO_2R$ was lithiated with 2 equiv of ^nBuLi in tetrahydrofuran at −78 °C, and after 2 h of stirring it was treated with 2 equiv of the (L)AuCl component also dissolved in tetrahydrofuran. Evaporation of the solvent, extraction of the residue with dichloromethane, and removal of this solvent under vacuum yielded the products, which were washed with *n*-pentane or diethyl ether and dried under vacuum.

(b) R = Me, L = Ph$_3$P: 43.5 mg (0.25 mmol) of sulfone, 250 mg (0.5 mmol) of LAuCl, 2 × 20 mL of solvent. Yield: 244 mg (90%). Mp: 179 °C dec. Single crystals were grown from dichloromethane/*n*-pentane on cooling to −10 °C. NMR spectra were obtained in CD_2Cl_2 at 25 °C. ^{31}P NMR: 37.1 (s). ^{13}C NMR: 48.5 (s, Me); 134.5 (d, *J* = 13.5), 131.9 (s), 131.1 (d, *J* = 54.5), and 129.5 (d, *J* = 10.9) for *o*-, *p*-, *i*-, and *m*-C of Ph. ^1H NMR: 3.23 (s, 6H, Me); 7.15−7.90 (m, 30H, Ph). MS (FAB): *m*/*z* 1088 (3.07) $[M]^+$, 720 (88.49) $[L_2Au]^+$, 459 (100) $[LAu]^+$, 262 (4.19) $[L]^+$. Anal. Calcd for $C_{39}H_{36}Au_2O_4P_2S_2$ (1088.72): C, 43.02; H, 3.33. Found: C, 42.17; H, 3.21.

(c) R = Me, L = Ph$_3$As: 32.0 mg (0.18 mmol) of sulfone, 200 mg (0.37 mmol) of LAuCl, 2 × 20 mL of solvent. Yield: 194 mg (89%). Mp: 188 °C dec. Single crystals were grown from dichloromethane/*n*-pentane on cooling to −10 °C. NMR spectra were obtained in CD_2Cl_2 at 25 °C. ^{13}C NMR: 48.78 (s, Me); 133.79, 131.06, 130.05, and 129.75, all s, for *o*-, *p*-, *i*-, and *m*-C of Ph. ^1H NMR: 3.29 (s, 6H, Me); 7.51−7.39 (m, 30H, Ph). MS (FAB): *m*/*z* 1176 (14.01) $[M]^+$, 809 (100) $[L_2Au]^+$, 503 (62.31) $[LAu]^+$.

(d) R = Me, L = Ph$_2$MeP: 43.0 mg (0.25 mmol) of sulfone, 216 mg (0.5 mmol) of LAuCl, 2 × 20 mL of solvent. Yield: 221 mg (92%). Mp: 194 °C dec. Single crystals were grown from dichloromethane/*n*-pentane on cooling to −10 °C. NMR spectra were obtained in CD_2Cl_2 at 25 °C. ^{31}P NMR: 22.8 (s). ^{13}C NMR: 14.42 (d, ^1J(PC) = 38, PMe); 48.82 (s, SMe); 133.08 (d, *J* = 14.0), 132.18 (s), 130.82 (d, *J* = 54.5), and 129.62 (d, *J* = 12.0) for *o*-, *p*-, *i*-, and *m*-C of Ph. ^1H NMR: 2.21 (d, ^3J(PH) = 17, PMe, 6H); 3.19 (s, SMe, 6H); 7.69−7.37 (m, Ph, 20H). MS (FAB): *m*/*z* 964 (3.95) $[M]^+$, 595 (42.57) $[L_2Au]^+$, 396 (100) $[LAu]^+$. Anal. Calcd for $C_{29}H_{32}Au_2P_2O_4S_2\cdot 0.5C_5H_{12}$ (1000.65): C, 37.97; H, 3.87. Found: C, 37.62; H, 3.76.

(e) R = Ph, L = Ph$_3$P: 75 mg (0.25 mmol) of sulfone, 250 mg (0.5 mmol) of LAuCl, 2 × 20 mL of solvent. Yield: 267 mg (88%). Mp: 195 °C dec. Single crystals were grown from chloroform/*n*-pentane on cooling to −10 °C. NMR spectra were obtained in CD_2Cl_2 at 25 °C. ^{31}P NMR: 37.3 (s). ^{13}C NMR: 116.6 (t, ^2J(PC) = 75, Au$_2$*C*), 134.6 (d, *J* = 15), 131.9 (s), 130.4 (d, *J* = 55), and 129.5 (d, *J* = 12) for *o*-, *p*-, *i*-, and *m*-C of PhP; 132.8, 131.0, 128.8, and 128.1, all s, for *i*-, *p*-, *m*-, and *o*-C of PhS. ^1H NMR: 7.24−8.18 (m, 30 H, Ph). MS (FAB): *m*/*z* 1212 (14.05) $[M]^+$, 720 (47.19) $[L_2Au]^+$, 459 (100) $[LAu]^+$. Anal. Calcd for $C_{49}H_{40}Au_2O_4P_2S_2\cdot 0.15CHCl_3$ (1230.76): C, 47.96; H, 3.28. Found: C, 47.74; H, 3.59.

(f) R = Ph, L = Ph$_2$MeP: 74 mg (0.25 mmol) of sulfone, 216 mg (0.50 mmol) of LAuCl, 2 × 20 mL of solvent. Yield: 267 mg (88%). Mp 197 °C dec. Single crystals were grown from dichloromethane/*n*-pentane on cooling to −10 °C. NMR spectra were obtained in CD_2Cl_2 at 25 °C. ^{31}P NMR: 21.9 (s). ^{13}C NMR: 14.3 (d, ^1J(PC) = 36.4); 131.1 (d, *J* = 14), 131.9 (s), 130.4 (d, *J* = 55), and 128.9 (d, *J* = 12) for *o*-, *p*-, *i*-, and *m*-C of PhP; 132.8, 131.0, 128.9, and 128.8, all s, for *i*-, *p*-, *m*-, and *o*-C of PhS. ^1H NMR: 2.08 (d, ^3J(HP) = 16.5, 6H, Me); 8.18−7.23 (m, 30H, Ph). MS (FAB): *m*/*z* 1088 (9.13) $[M]^+$, 596 (45.14) $[L_2Au]^+$, 396 (100) $[LAu]^+$. Anal. Calcd for $C_{39}H_{36}Au_2O_4P_2S_2\cdot 0.5C_5H_{12}$ (1128.40): C, 44.43; H, 3.80. Found: C, 44.39; H, 3.90.

Direct Diauration of Methylenebis(methyl sulfone) with Tris[(triphenylphosphine)gold]oxonium Tetrafluoroborate. A solution of $MeSO_2CH_2SO_2Me$ (10 mg, 0.06 mmol) and potassium carbonate (17 mg, 0.12 mmol) in tetrahydrofuran (10 mL) and water (2 mL) was added to a suspension of tris[(triphenylphosphine)gold]oxonium tetrafluoroborate (86 mg, 0.06 mmol) in tetrahydrofuran (10 mL). The mixture was stirred for 1 day at room temperature. Subsequently, the solvent was removed under reduced pressure and the product extracted from the residue with dichloromethane. Following removal of the dichloromethane, the product was re-extracted with tetrahydrofuran. The solvent was evaporated, and the product was washed with *n*-pentane and dried under vacuum. Yield: 29.4 mg (45%).

Auration of Cyanomethyl Phenyl Sulfone. The procedure for the diauration was the same as that for the disulfones, using 45.7 mg (0.25 mmol) of $PhSO_2CH_2CN$ and 250 mg (0.5 mmol) of Ph_3PAuCl in 2 × 20 mL of tetrahydrofuran: yield 244 mg (89%) of bis[(triphenylphosphine)gold]cyanomethyl phenyl sulfone; mp 188 °C dec. Single crystals were grown from dichloromethane/*n*-pentane on cooling to −10 °C. NMR spectra were obtained in CD_2Cl_2 at 25 °C. ^{31}P NMR: 37.9 (s). ^{13}C NMR: 124.9 (s, *C*N); 134.6 (d, *J* = 13.5), 132.4 (s), 130.2 (d, *J* = 55.5), and 129.6 (d, *J* = 12) for *o*-, *p*-, *i*-, and *m*-C of PhP; 135.8, 133.4, 128.8, and 127.6, all s, for *i*-, *p*-, *m*-, and *o*-C of PhS. ^1H NMR: 8.15−7.33 (m, Ph). MS (FAB): *m*/*z* 1097 (8.08) $[M]^+$, 720 (47.65) $[L_2Au]^+$, 459 (100) $[LAu]^+$. IR: 2139 cm^{-1}. Anal. Calcd for $C_{44}H_{35}Au_2NO_2P_2S\cdot 0.5C_5H_{12}$ (1141.00): C, 49.26; H, 3.64. Found: C, 49.67; H, 3.82.

A 120 mg portion (0.11 mmol) of this diauration product, dissolved in 20 mL of tetrahydrofuran at −78 °C, was treated with a solution of 2 equiv (excess) of $[(Ph_3P)Au]BF_4$, prepared from 110 mg of Ph_3AuCl and 43 mg of $AgBF_4$ (0.22 mmol each) in 10 mL of tetrahydrofuran at −78 °C. The mixture was warmed to 20 °C with stirring within 2 h, and the solvent was evaporated. The residue was extracted with dichloromethane and the product precipitated from the extract by addition of diethyl ether. The yellow solid was collected and recrystallized from acetone/*n*-pentane: 84 mg (51% yield); mp 194 °C (dec). NMR spectra were obtained in CD_2Cl_2 at 25 °C. ^{31}P NMR: 37.1 (s, 2P); 29.7 (s, 1P). ^{13}C NMR: 134.64−129.35 (Ph); *C*-CN and C(*C*N) not detected. ^1H NMR: 8.3−7.15 (m, Ph). MS (FAB): *m*/*z* 1556 (11.63) $[M - BF_4]^+$, 721 (91.34) $[L_2Au]^+$, 459 (100) $[LAu]^+$. IR: 2161.5 cm^{-1}. Anal. Calcd for $C_{62}H_{50}Au_3NO_2P_3SBF_4$ (1643.71): C, 45.30; H, 3.06. Found: C, 46.25; H, 3.15.

Determination of the Crystal Structures. Specimens of suitable quality and size of $[(Ph_3P)Au]_2C(SO_2Me)_2$, $[(Ph_3As)Au]_2C(SO_2Me)_2$, $[(MePh_2P)Au]_2C(SO_2Me)_2$, $[(Ph_3P)Au]_2C(SO_2Ph)_2$, $\{[(Ph_3P)Au]_2C(SO_2Ph)CN[Au(PPh_3)]\}^+BF_4^-$, $[(Ph_3P)Au]_2C(SO_2Ph)CN$, $[(Ph_3P)Au]CHPh(SO_2Ph)$, and $[(Ph_3P)Au]_2C$-

Table 1. Crystal Data and Data Collection and Structure Refinement Details of $[(Ph_3P)Au]_2C(COMe)_2$, $[(Ph_3P)Au]_2C(SO_2Me)_2$, $[(Ph_3As)Au]_2C(SO_2Me)_2$, and $[(MePh_2P)Au]_2C(SO_2Me)_2$

	$[(Ph_3P)Au)]_2$-$C(COMe)_2$	$[(Ph_3P)Au)]_2$-$C(SO_2Me)_2$	$[(Ph_3As)Au)]_2$-$C(SO_2Me)_2$	$[(MePh_2P)Au)]_2$-$C(SO_2Me)_2$
empirical formula	$C_{41}H_{36}Au_2O_2P_2$	$C_{39}H_{36}Au_2O_4P_2S_2$	$C_{39}H_{36}Au_2As_2O_4S_2$	$C_{29}H_{32}Au_2O_4P_2S_2 \cdot CH_2Cl_2$
M_r	1016.57	1088.67	1176.57	1049.47
cryst syst	monoclinic	triclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	11.3072(2)	11.4657(2)	11.6199(2)	11.0321(1)
b/Å	14.6604(2)	11.7608(2)	11.8709(2)	12.1649(2)
c/Å	21.4490(4)	16.5754(3)	16.6124(3)	12.9915(2)
α/deg	90	103.9487(10)	103.8365(7)	95.2932(6)
β/deg	90.539(1)	99.3164(9)	99.8222(9)	92.9236(5)
γ/deg	90	115.0254(9)	114.5907(8)	93.3897(7)
V/Å^3	3555.4(1)	1874.90(6)	1926.19(6)	1730.25(4)
ρ_{calcd}/g cm^{-3}	1.899	1.928	2.029	2.014
Z	4	2	2	2
F(000)	1944	1044	1116	1000
μ(Mo Kα) (cm^{-1})	83.68	80.52	94.60	88.70
T/K	143	143	143	143
no. of rflns measd	98 575	60 997	46 589	41 195
no. of unique rflns	7008 ($R_{int} = 0.047$)	7397 ($R_{int} = 0.058$)	6577 ($R_{int} = 0.040$)	6030 ($R_{int} = 0.044$)
no. of refined params/restraints	424/0	442/0	444/0	515/0
R1 ($I \geq 2\sigma(I)$)	0.0247	0.0391	0.0282	0.0199
wR2^a	0.0525	0.0936	0.0713	0.0511
weighting scheme	$a = 0.0126$ $b = 8.6831$	$a = 0.0282$ $b = 10.2481$	$a = 0.0239$ $b = 5.6790$	$a = 0.0000$ $b = 2.1070$
σ_{fin}(max/min)/e Å^{-3}	0.905/−0.883	2.596/−1.384	2.408/−1.194	0.970/−0.663

[a] wR2= $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$.

Table 2. Crystal Data and Data Collection and Structure Refinement Details of $[(Ph_3P)Au)]_2C(SO_2Ph)_2$, $[(Ph_3P)Au)]_2C(SO_2Ph)CN$, $\{[(Ph_3P)Au]_2C(SO_2Ph)CN[Au(PPh_3)]\}^+BF_4^-$, and $[(Ph_3P)Au)]CHPh(SO_2Ph)$

	$[(Ph_3P)Au)]_2$-$C(SO_2Ph)_2$	$[(Ph_3P)Au)]_2$-$C(SO_2Ph)CN$	$\{[(Ph_3P)Au]_2C(SO_2Ph)$-$CN[Au(PPh_3)]\}^+BF_4^-$	$[(Ph_3P)Au)]CHPh$-(SO_2Ph)
empirical formula	$C_{49}H_{40}Au_2O_4P_2S_2 \cdot CHCl_3$	$C_{44}H_{35}Au_2NO_2P_2S \cdot 1.25CH_2Cl_2$	$C_{62}H_{50}Au_3NO_2P_3SBF_4$	$C_{31}H_{26}Au_2O_2PS$
M_r	1332.17	1203.82^b	1643.71	690.52
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a/Å	10.4053(1)	18.6929(1)	18.1884(2)	9.3962(2)
b/Å	17.5455(1)	26.5958(2)	20.3524(2)	11.7909(2)
c/Å	26.4409(3)	17.5871(2)	22.4324(3)	13.6671(3)
α/deg	90	90	110.9539(4)	103.2114(10)
β/deg	90.9539(3)	94.8214(4)	96.8981(5)	99.8102(9)
γ/deg	90	90	104.3732(9)	111.5949(9)
V/Å^3	4826.55(8)	8712.53(13)	7309.09(15)	1315.34(5)
ρ_{calcd}/g cm^{-3}	1.833	1.836^b	1.494^d	1.743
Z	4	4	4	2
F(000)	2576	4628^b	3136^d	676
μ(Mo Kα) (cm^{-1})	64.35	70.40^b	61.46^d	57.60
T/K	143	143	143	143
no. of rflns measd	119 907	385 009	180 683	55 211
no. of unique rflns	10 175 ($R_{int} = 0.034$)	15 244 ($R_{int} = 0.046$)	25 225 ($R_{int} = 0.059$)	4529 ($R_{int} = 0.036$)
no. of refined params/restraints	568/0	1064/0	1397/0	325/0
R1 ($I \geq 2\sigma(I)$)	0.0224	0.0463	0.0376	0.0530
wR2^a	0.0554	0.0912	0.0904	0.1181
weighting scheme	$a = 0.0212$ $b = 5.9691$	$a = 0.0085$ $b = 75.3229$	$a = 0.0383$ $b = 10.0554$	$a = 0.0124$ $b = 22.4720$
σ_{fin}(max/min)/e Å^{-3}	0.853/−0.570	1.276/−1.232	1.245/−1.748	7.432/−2.999

[a] wR2= $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$. [b] Without contributions of disordered solvent.

$(COMe)_2$ were mounted on the ends of quartz fibers in inert perfluoropolyalkyl ether and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo Kα radiation. The structures were solved by a combination of direct methods (SHELXS-97) and difference Fourier syntheses and refined by full-matrix least-squares calculations on F^2 (SHELXL-97).[39] The thermal motion was treated anisotropically for all non-hydrogen atoms. The hydrogen atoms were calculated in ideal positions and allowed to ride on their parent atoms with fixed isotropic contributions. Further information on crystal data and data collection and structure refinement details are summarized in Tables 1 and 2. The contributions of disordered solvent molecules in the structures of $[(Ph_3P)Au]_2C(SO_2Ph)CN$ and $\{[(Ph_3P)Au]_2C(SO_2Ph)CN[Au(PPh_3)]\}^+BF_4^-$ were taken into account by the SQUEEZE method.[39] The total potential solvent-accessible volume for $[(Ph_3P)Au]_2C(SO_2Ph)CN$ (solvent methylene chloride) is 209.9 Å^3, containing 19 electrons per cell; for $\{[(Ph_3P)Au]_2C(SO_2Ph)CN[Au(PPh_3)]\}^+BF_4^-$ it is 2139.6 Å^3, containing 105 electrons per cell (solvent acetone). In the structure of $[(Ph_3P)Au]_2C(SO_2Ph)CN$ one phenyl ring is disordered over two sites with occupation factors of 0.55 and 0.45. In the structure of $[(Ph_3P)Au]CHPh(SO_2Ph)$ a high residual

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[39] Sheldrick, G. M. SHELX-97, Programs for Crystal Structure Analysis; University of Göttingen, Göttingen. Germany, 1997.

electron density remained at a distance of 0.849 Å from the gold atom. As repeated measurements of other crystals consistently showed this electron density, it may be due to an unresolved disorder. Absorption corrections for all structures were carried out using DELABS, as part of the PLATON suite of programs.[40]

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Supporting Information Available: Tables giving X-ray crystallographic data for all the compounds discussed in this paper; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(40) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, 194.

(41) We agree with and are grateful to a reviewer who pointed this out.