Synthesis of the First Complex with a Hypercoordinate Ylidic Carbon Atom. Crystal and Molecular Structure of $[\{Au(PPh_3)\}_4CS({=}O)Me_2](ClO_4)_2$

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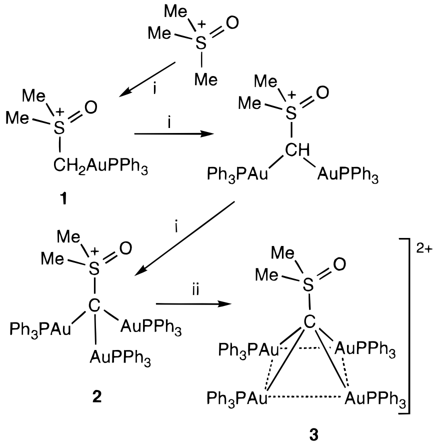
The number of complexes with a clustering of $AuPR_3$ groups around a hypercoordinate carbon atom is limited to homoleptic species containing an interstitial carbon atom, $[C(AuPR_3)_5]^+$ and $[C(AuPR_3)_6]^{2+}$,[1,2] tetraaurioethanes $[MeC(AuPR_3)_4]^+$ (R = alkyl or aryl),[3a] and bis(silyl)methanium cations $[(R_3Si)_2C(AuPPh_3)_3]^+$ (R_3 = Me_3 or Me_2Ph).[3b,c] An octanuclear complex containing two $RC(AuPPh_3)_3$ (R = oxazolinyl) units connected through two Au^+ cations also shows two hypercoordinate carbon atoms.[4] The stability of these species is attributed to the tendency of gold(I) to aggregate through weak metal−metal interactions; this so-called aurophilicity arises mainly from relativistic effects.[2cd,4,5]

It is remarkable that only three sulfur ylide complexes of gold(I) are known[6,7] in contrast to the large number of their phosphorus homologues.[8] This fact is even more surprising considering the interest in sulfur ylides or their complexes in organic and organometallic chemistry.[9,10] In this paper we report the synthesis of three new sulfur ylide complexes containing, respectively, one, three, and four $AuPPh_3$ groups, the latter being the first complex with a hypercoordinate ylidic carbon atom. Such hypercoordination in phosphorus ylide complexes has not yet been achieved, for which steric reasons have been proposed.[11]

The reaction of $[Me_3S{=}O]ClO_4$ with $[Au(acac)PPh_3]$ (acac = acetylacetonato) in acetone, at room temperature, produces different sulfur ylide gold(I) complexes depending on the reagent ratio. Thus, the 1:1 reaction gives after 6 h $[Au\{CH_2S({=}O)Me_2\}(PPh_3)]ClO_4$ (**1**) in 75% yield, whereas the 1:4 reaction gives after 36 h $[(AuPPh_3)_3\{\mu^3\text{-}CS({=}O)Me_2\}]ClO_4$ (**2**) in 87% yield (see Scheme 1). Complex **2** is similar to the phosphorus ylide complex $[(AuPPh_3)_3\{\mu^3\text{-}CPMe_3\}]Cl$[12] and represents a new type of sulfur ylide complex. In an attempt to obtain the disubstituted $[(AuPPh_3)_2\{\mu^2\text{-}CHS({=}O)Me_2\}]ClO_4$ (see Scheme 1) we used a 1:2 ratio of the reagents or reacted **1** with $[Au(acac)PPh_3]$ (1:1), but in both reactions the diaurated complex is obtained (see below) along with complexes **1** and **2** and we could not separate the mixtures. The reaction of **2** with $AgClO_4$ and $[AuCl(PPh_3)]$ (1:1:1) (acetone, room temperature, 1.5 h) produces the hypercoordinate complex $[(AuPPh_3)_4\{\mu^4\text{-}CS({=}O)Me_2\}](ClO_4)_2$ (**3**) in 86% yield (see Scheme 1). Attempts to coordinate more $AuPPh_3$ groups, by reacting **2** with various amounts of $[Au(OClO_3)(PPh_3)]$, failed.

Scheme 1[a]



[a] (i) +$[Au(acac)PPh_3]$ − Hacac; (ii) +$AgClO_4$ + $[AuCl(PPh_3)]$ − AgCl.

These reactions are new examples of the synthetic utility of acac−gold(I) complexes.[13] Two methods have been used by Schmidbaur *et al.* to prepare gold(I) complexes with a hypercoordinate carbon atom. The first involves the use of $C[B(OMe)_2]_4$, $CH_2[B(OMe)_2]_2$, or $MeC[B(OMe)_2]_3$ as the carbon precursor and mixtures of $[AuCl(PR_3)]$ and CsF as aurating agents. Under these conditions, the hypercoordinate complexes are obtained without isolation of the corresponding intermediates containing a tetracoordinate carbon atom as in our case. The second method involves the transmetalation reaction between $(R_3Si)_2CHLi$ and $[AuCl(PPh_3)]$ followed by the auration of the resulting complex $[(R_3Si)_2CH(AuPPh_3)]$ with $[O(AuPPh_3)_3]^+$. In this case, small amounts of the intermediates $[(R_3Si)_2C(AuPPh_3)_2]$ have been detected and characterized by their spectroscopic data.[1−3]

The crystal structure of the hypercoordinate complex **3** has been established by X-ray diffraction methods showing the ylide carbon atom in a square pyramidal coordination with the $S({=}O)Me_2$ group at the apex and four $AuPPh_3$ groups in the base (Au atoms coplanar to within ±0.015 Å; C(1) lies 0.86(1) Å out of the basal plane). The ranges of Au···Au [2.7999(7)−2.8186(8) Å], C−Au [2.131(8)−2.198(8)] bond distances, and Au−C−Au bond angles [80.2(3)-81.4(3)°] are similar to those found in the only comparable structure, $[MeC\{AuP(C_6H_{11})_3\}_4]^+$.[3a] The PAuC units display a maximum deviation from linearity of 12° for Au(1). It is noticeable that the bond between the S and the aurated carbon atom is significantly shorter [S−C(1), 1.699(9) Å] than the other two S−C bonds [1.745(11), 1.756(11) Å]. There is no previous report of any crystal structure of a gold(I)

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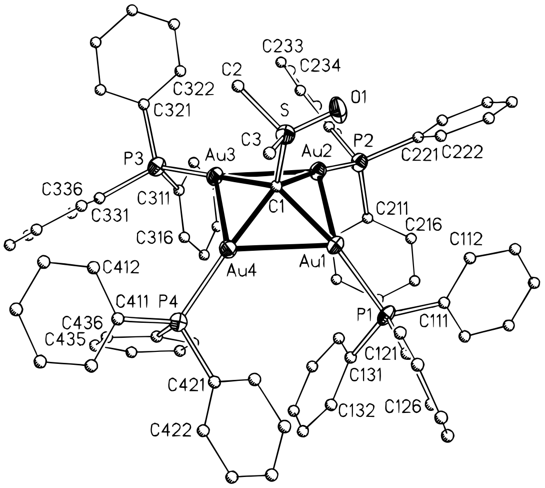

Figure 1. Structure of the cation of complex **3** in the crystal. Ellipsoids represent 50% probability levels. Selected bond lengths (Å) and angles (deg): Au(1)−C(1) 2.167(10), Au(1)−P(1) 2.269(3), Au(1)−Au(4) 2.8017(7), Au(1)−Au(2) 2.8186(8), Au(2)−C(1) 2.198(8), Au(2)−P(2) 2.270(2), Au(2)−Au(3) 2.8079(8), Au(3)−C(1) 2.162(10), Au(3)−P(3) 2.259(3), Au(3)−Au(4) 2.7999(7), Au(4)−C(1) 2.131(8), Au(4)−P(4) 2.255(3), S−O(1) 1.466(7), S−C(1) 1.699(9), S−C(3) 1.745(11), S−C(2) 1.756(11); C(1)−Au(1)−P(1) 168.0(3), Au(4)−Au(1)−Au(2) 90.25(2), C(1)−Au(2)−P(2) 175.9(3), Au(3)−Au(2)−Au(1) 89.35(2), C(1)−Au(3)−P(3) 178.0(2), Au(4)−Au(3)−Au(2) 90.51(2), C(1)−Au(4)−P(4) 170.8(2), Au(3)−Au(4)−Au(1) 89.86(2).

dimethylsulfoxylide complex to compare with complex **3**, but in [$Me_3Au\{CH_2S({=}O)Me_2\}$] the S-$C_{Au}$ [1.68(6) Å] bond is also shorter than S−Me [1.75(4), 1.82(4) Å];[14] however, the high esd's render the differences almost insignificant. The structure of **3** suggests that the lack of success in attempts to prepare similar hypercoordinate phosphorus ylides is not due to steric effects.

The equivalence of all four phosphorus atoms in **3** is observed in solution even at −60 °C (by $^{31}P\{^1H\}$ NMR). In the $^{13}C\{^1H\}$ NMR spectrum of **1** the resonance due to the CH_2 carbon appears as a doublet at 52.78 ppm ($^2J_{CP}$ = 23.2 Hz) while the quaternary ylide carbon present in **2** or **3** is not seen in their $^{13}C\{^1H\}$ NMR spectra at 300 MHz even after prolonged accumulation. The ^1H NMR spectra of the mixtures containing complexes **1**, **2**, and [$(AuPPh_3)_2\{\mu^2\text{-}CHS({=}O)Me_2\}]ClO_4$ show, apart from the resonances corresponding to **1** and **2**, a singlet at 3.58 ppm for the methyl groups and a triplet centered at 3.37 ppm for the CH proton coupled with two equivalent phosphorus nuclei ($^3J_{PH}$ = 6.2 Hz). The $^{31}P\{^1H\}$ NMR spectra show a singlet at 40.11 ppm corresponding to the dinuclear complex.

The stepwise metalation of the same methyl group is a remarkable feature of these acid−base reactions, attributable to the aurophilicity. If this tendency were not so important, one might have expected that, after the first $AuPPh_3$ group had replaced a hydrogen atom in a particular methyl group, further $AuPPh_3$ groups should be directed to a nonmetalated methyl group, because these hydrogen atoms should be somewhat more acidic according to the weak $+I$ effect of the $AuPPh_3$ moiety.[15] The same would be expected on steric grounds. In addition, without the aurophilic effect one could have expected the coordination of the fourth $AuPPh_3$ group to the oxygen atom.

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Note Added in Proof: A complex related to **3**, [$(AuPPh_3)_4(\mu^4\text{-}CH)]BF_4$, has recently been isolated. Its crystal structure is similar to that of **3**.[16]

Supporting Information Available: Text giving full experimental conditions and tables giving crystal data and details of the structure determination, atom coordinates, bond lengths and angles and anisotropic displacement coefficients (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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