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Synthesis of highly stable intermediates in Michael-type additions to the double bond in $(SPPh_2)_2C{=}CH_2$

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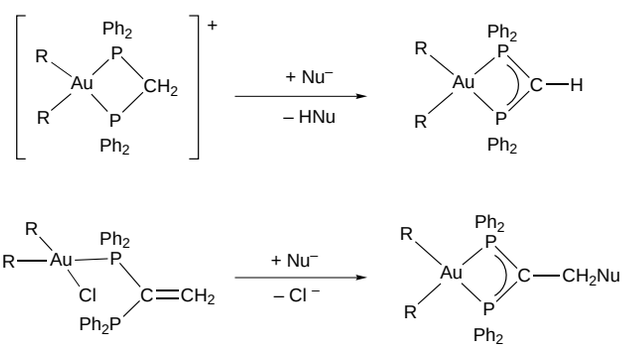
Treatment of vinylidenebis(diphenylphosphine) with elemental sulfur under reflux led to vinylidenebis(diphenylphosphine) disulfide, $(SPPh_2)_2C{=}CH_2$, in good yields. Its co-ordination to a gold(III) centre activates the carbon–carbon double bond. Thus, the chelate complex $[Au(C_6F_5)_2\{(SPPh_2)_2C{=}CH_2\}]ClO_4$ reacted rapidly with carbon- or oxygen-donor nucleophiles (Nu^-), such as $acac^-$ (acetylacetonate), CN^-, $C_5H_5^-$ or OEt^-, forming methanide-type derivatives $[Au(C_6F_5)_2\{(SPPh_2)_2CCH_2Nu\}]$. These products can be considered as intermediates in Michael-type additions of HNu to the C=C bond, which in this particular case display high stabilities, allowing their isolation as solids. The crystal structure of the cyclopentadienyl derivative has been established by X-ray crystallography and displays a square-planar gold(III) centre with a *cis* disposition of the pentafluorophenyl groups and sulfur atoms of the chelating ligand, and sp^2 hybridization of the endocyclic carbon atom with partial P–C double-bond character.

The co-ordination chemistry of vinylidenebis(diphenylphosphine)[1–4] and the reactivity of its carbon–carbon double bond in addition reactions have been studied in the last decade. In the course of these investigations it has been shown that, although the double bond in unco-ordinated vinylidenebis(diphenylphosphine) is scarcely susceptible to nucleophilic attack, except under extreme reaction conditions,[4–6] complexation to a metal centre[2a,3,4,7,8] or quaternization of the phosphorus atoms[9] activates the double bond in such a manner that various nucleophiles can be added through Michael-type reactions. In these processes the species HNu is added to complexes $[M]{-}(PPh_2)_2C{=}CH_2$ to give the products $[M]{-}(PPh_2)_2CHCH_2Nu$, where the first step is always the attack of the nucleophile Nu^- on the C_β atom of the C=C bond. However, the product formed in the first step had not been isolated.

We have recently reported that the reaction of $[Au(C_6F_5)_2Cl\{PPh_2C(=CH_2)PPh_2\}]$ with nucleophilic agents Nu^- allows the isolation of these intermediates, affording methanide-like derivatives $[Au(C_6F_5)_2\{(PPh_2)_2CCH_2Nu\}]$.[10] These complexes are structurally and electronically similar to the bis(diphenylphosphino)methanide derivative $[Au(C_6F_5)_2\{(PPh_2)_2CH\}]$, which is formed by extraction of one proton from $[Au(C_6F_5)_2\{(PPh_2)_2CH_2\}]ClO_4$ when treated with a nucleophile Nu^- (H^-); the excess electron density is delocalized over both P–C bonds[11] (Scheme 1).

In contrast, it has been reported that when the same reaction is carried out with the bis(diphenylphosphino)methane disulfide ligand the initially formed six-membered ring is rapidly transformed into a four-membered ring through the co-ordination of the methanide carbon to the gold(III) centre[12] (see Scheme 2), and this can be considered as electrophilic attack of the gold(III) centre on the unsaturated carbon.

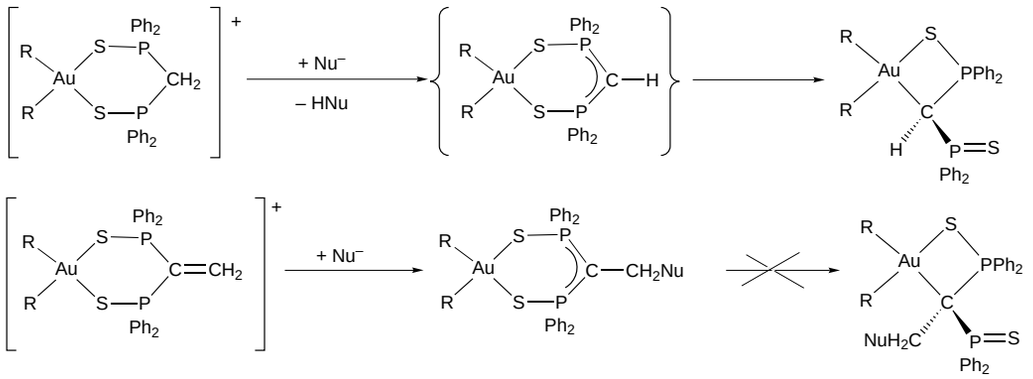
In order to investigate the stability of the intermediates in a Michael addition to vinylidenebis(diphenylphosphine) disulfide we have synthesized the chelate bis(pentafluorophenyl) complex $[Au(C_6F_5)_2\{(SPPh_2)_2C{=}CH_2\}]ClO_4$ to study its reactivity with nucleophiles Nu^-. These reactions provide optimum conditions for completion of the addition to the double bond, because the electrophile gold(III) is present in the same molecule as the carbanion; thus a similar process to that described for the $Ph_2P(S)CH_2(S)PPh_2$ derivative could be expected. Surprisingly, the products isolated in these reactions are always those formed in the first step, containing a six-membered ring and displaying both carbanion and electrophile together in the same molecule without any interaction between them (see Scheme 2). This fact reveals that these particular intermediates are not only isolable, but also even more stable than expected.



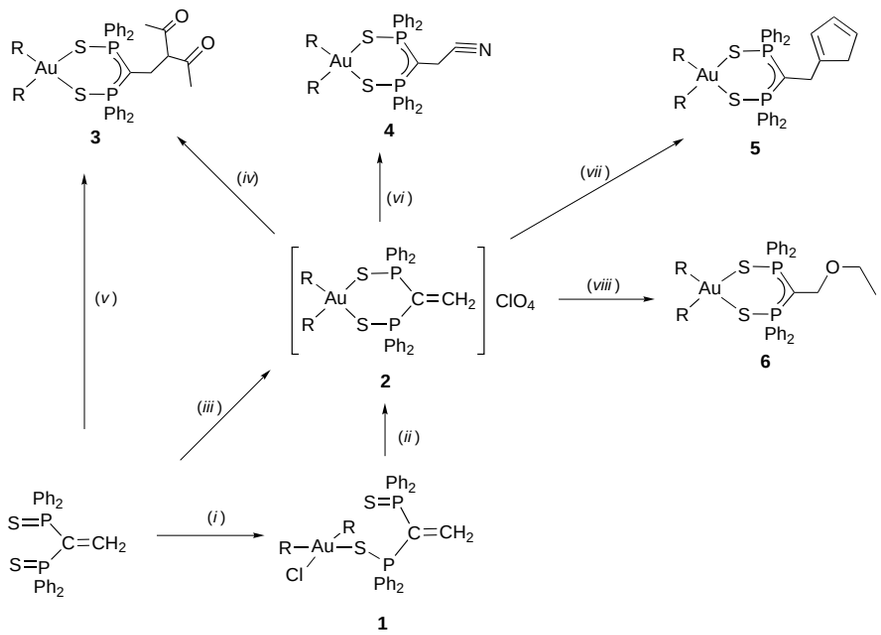
Scheme 1 $R = C_6F_5$

Results and Discussion

When vinylidenebis(diphenylphosphine) disulfide is treated with $[\{Au(C_6F_5)_2(\mu{-}Cl)\}_2]$ in a 2:1 molar ratio one of the sulfur atoms co-ordinates to the gold centre, rupturing the chlorine bridges to give the monodentate $[Au(C_6F_5)_2Cl\{SPPh_2C(=CH_2)PPh_2{=}S\}]$ **1** (Scheme 3) as a white solid soluble in common organic solvents. It presents a *cis* disposition of the pentafluorophenyl groups, as shown by its ^{19}F NMR spectrum, which shows two different types of C_6F_5 with relative intensities 1:1. Its infrared spectrum exhibits the ν(Au–Cl) stretching



Scheme 2 $R = C_6F_5$



Scheme 3 $R = C_6F_5$. (*i*) ½ [{$Au(C_6F_5)_2(\mu\text{-}Cl)$}$_2$]; (*ii*) $AgClO_4$; (*iii*) $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$; (*iv*) Tl(acac); (*v*) $[Au(C_6F_5)_2(acac)]$; (*vi*) KCN; (*vii*) TlC_5H_5; (*viii*) NaOEt

band at 334 cm^{-1} and two ν(P=S) vibrations at 594 and 613 cm^{-1}, corresponding to the single and double bond, respectively (614 cm^{-1} for the free diphosphine disulfide).

Complex **1** reacts with an equimolecular amount of $AgClO_4$ to give $[Au(C_6F_5)_2\{(SPPh_2)_2C{=}CH_2\}]ClO_4$ **2**. The same product can be prepared by a ligand-displacement reaction of $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$ with $(SPPh_2)_2C{=}CH_2$, as represented in Scheme 3. Compound **2** is obtained in good yields as a white solid, soluble in chlorinated solvents and acetone and insoluble in diethyl ether and hexane.

As mentioned above, the co-ordination of vinylidenebis(diphenylphosphine) extensively activates its double bond[2a,3,4,7,8] and the same effect is observed here for vinylidenebis(diphenylphosphine) disulfide. This activation occurs in such a manner that the nucleophilic addition in complex **2** takes place only to the C_β atom of the C=C bond, giving rise to derivatives $[Au(C_6F_5)_2\{(SPPh_2)_2CCH_2Nu\}]$, which can be considered as the products formed in the first step of a normal Michael addition, displaying their striking high stability. Thus, the reaction between equimolecular amounts of **2** and Tl(acac) (acac = acetylacetonate) gives rise to the precipitation of $TlClO_4$ and addition of acetylacetonate to the C_β atom, affording the neutral derivative $[Au(C_6F_5)_2\{(SPPh_2)_2CCH_2CH(COMe)_2\}]$ **3** (Scheme 3). This product can alternatively be prepared by treating $(SPPh_2)_2C{=}CH_2$ with $[Au(C_6F_5)_2(acac)]$, which contains the nucleophile.

Carbon- or oxygen-donor nucleophiles can be employed in these reactions. Thus, treatment of complex **2** with QNu (QNu = KCN, TlC_5H_5 or NaOEt) results in the formation of the corresponding $QClO_4$ and addition of Nu^- to the exocyclic carbon centre to give $[Au(C_6F_5)_2\{(SPPh_2)_2CCH_2Nu\}]$ ($Nu^- = CN^-$ **4**, $C_5H_5^-$ **5**, or OEt^- **6**). Complexes **3–6** are air- and moisture-stable in the solid state and soluble in common organic solvents, except hexane. Their IR spectra show a band in the region 569–579 cm^{-1} [ν(P=S)], and also bands at 1505m, 967m, 804m and 795m cm^{-1}, due to the presence of C_6F_5 groups linked to a gold(III) centre; the last two confirm the *cis* disposition.[13]

The presence of equivalent pentafluorophenyl groups is confirmed in the ^{19}F NMR spectra (see Experimental section). The addition of the nucleophile to the C_β of the double bond leads to the presence of an excess of electron density at the C_α atom, which is delocalized through both P–C bonds. This is reflected in the $^{31}P\text{-}\{^1H\}$ NMR spectra, in which the chemical shift for these phosphorus decreases from δ 41.7 in complex **2** to δ 36.0–38.0 for **3–6**. The breaking of the double bond also produces a change in both chemical shift and pattern corresponding to the protons of the CH_2 group in their NMR spectra from an AA′XX′ spin system at δ 7.15 to a triplet located between δ 2.66 and 3.47.

The structure of complex **5** has been established by X-ray diffraction studies. The molecule is shown in Fig. 1 with selected bond lengths and angles in Table 1. The gold(III) centre has a planar geometry, being bonded to the two pentafluorophenyl groups and chelated by the two sulfur atoms of the diphosphine disulfide ligand. The major deviation of the angles from the ideal 90° is positive and is observed within the chelate ligand, S–Au–S 100.81(3)°, whereas the narrowest angles are

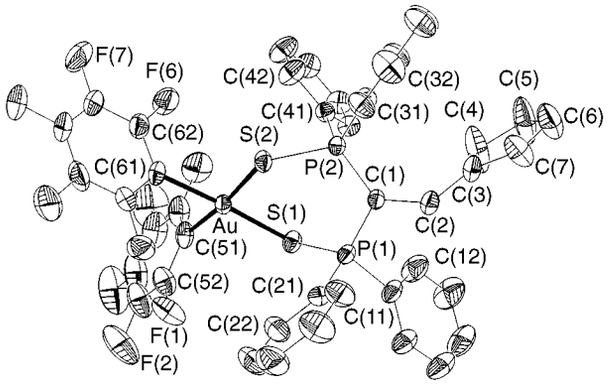


Fig. 1 Structure of complex **5** in the crystal. Displacement parameter ellipsoids represent 50% probability surfaces. Hydrogen atoms and solvent are omitted for clarity

Table 1 Selected bond lengths (Å) and angles (°) for complex **5**

Au–C(61)	2.032(3)	Au–C(51)	2.033(3)
Au–S(2)	2.3552(9)	Au–S(1)	2.3626(9)
P(1)–C(1)	1.709(3)	P(1)–C(11)	1.807(3)
P(1)–C(21)	1.813(4)	P(1)–S(1)	2.0459(11)
P(2)–C(1)	1.719(3)	P(2)–C(31)	1.802(3)
P(2)–C(41)	1.811(3)	P(2)–S(2)	2.0700(12)
C(1)–C(2)	1.538(4)	C(2)–C(3)	1.494(5)
C(3)–C(4)	1.312(6)	C(3)–C(7)	1.466(5)
C(4)–C(5)	1.460(7)	C(5)–C(6)	1.307(7)
C(6)–C(7)	1.455(6)		
C(61)–Au–C(51)	89.54(13)	C(61)–Au–S(2)	84.22(9)
C(51)–Au–S(2)	173.75(10)	C(61)–Au–S(1)	174.97(9)
C(51)–Au–S(1)	85.43(10)	S(2)–Au–S(1)	100.81(3)
C(1)–P(1)–C(11)	107.5(2)	C(1)–P(1)–C(21)	114.6(2)
C(11)–P(1)–C(21)	107.4(2)	C(1)–P(1)–S(1)	114.09(11)
C(11)–P(1)–S(1)	104.62(12)	C(21)–P(1)–S(1)	107.97(12)
C(1)–P(2)–C(31)	109.2(2)	C(1)–P(2)–C(41)	115.3(2)
C(31)–P(2)–C(41)	107.3(2)	C(1)–P(2)–S(2)	114.40(12)
C(31)–P(2)–S(2)	103.70(11)	C(41)–P(2)–S(2)	106.17(11)
P(1)–S(1)–Au	105.71(4)	P(2)–S(2)–Au	104.28(4)
C(2)–C(1)–P(1)	119.3(2)	C(2)–C(1)–P(2)	120.4(2)
P(1)–C(1)–P(2)	115.8(2)	C(3)–C(2)–C(1)	117.0(3)
C(4)–C(3)–C(7)	107.0(4)	C(4)–C(3)–C(2)	131.7(4)
C(7)–C(3)–C(2)	121.2(3)	C(3)–C(4)–C(5)	110.6(4)
C(6)–C(5)–C(4)	107.7(4)	C(5)–C(6)–C(7)	109.4(4)
C(6)–C(7)–C(3)	105.2(4)		

C–Au–S 85.43(10) and 84.22(9)°. The Au–C bond distances, 2.032(3) and 2.033(3) Å, are shorter than in other gold(III) complexes with diphosphine ligands, probably as a consequence of the higher *trans* influence of the phosphorus compared to the sulfur ligands. The Au–S distances are 2.3552(9) and 2.3626(9) Å, similar to others in gold(III) derivatives with similar ligands, *e.g.* $[Au(C_6F_5)_2(SPPh_2CHPPh_2)]$ [2.345(2) Å].[14] The P(1)–C(1) and P(2)–C(1) bond lengths are 1.709(3) and 1.719(3) Å, shorter than those found in complexes with the diphosphine, such as $[\{AuCl[PPh_2C(=CH_2)PPh_2]\}_2]$ [1.828(6) and 1.833(6) Å],[4] or in other derivatives where a Michael addition has taken place, such as $[PdI_2\{(PPh_2)_2CHCH_2OCH_2CH_2(3\text{-}SC_4H_3)\}]$ [1.84(2) and 1.90(1) Å].[3d] This indicates that the negative charge of the methanide carbon is delocalized over the P–C bonds, conferring on them a degree of multiple bonding. The C(1)–C(2) distance, 1.538(4) Å, corresponds to a single bond. The C–C distances within the cyclopentadienyl ring allow an unambiguous assignment of single- and double-bond positions, and there is no indication of disorder.

Experimental

Instrumentation and materials

The IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer, over the range 4000–200 cm^{-1}, using Nujol mulls between polyethylene sheets, ^1H, ^{19}F and ^{31}P NMR spectra on a Bruker ARX 300 in $CDCl_3$ solutions, chemical shifts being quoted relative to $SiMe_4$ (^1H, external), $CFCl_3$ (^{19}F, external) and H_3PO_4 (85%) (^{31}P, external). The elemental analyses (C, H, N, S) were performed with a Perkin-Elmer 2400 microanalyzer. Mass spectra were recorded on a VG Autospec instrument using FAB techniques and 3-nitrobenzyl alcohol as matrix. All experiments were carried out at room temperature. The starting materials $(PPh_2)_2C{=}CH_2$,[15] $(SPPh_2)_2C{=}CH_2$,[16] $[\{Au(C_6F_5)_2(\mu\text{-}Cl)\}_2]$[17] and $[Au(C_6F_5)_2(acac)]$[18] were prepared according to the literature. The complex $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$ was prepared *in situ* by reaction of $[\{Au(C_6F_5)_2(\mu\text{-}Cl)\}_2]$ with 2 equivalents of $AgClO_4$ in diethyl ether.

Syntheses

$[Au(C_6F_5)_2Cl\{SPPh_2C(=CH_2)PPh_2{=}S\}]$ 1. To a dichloromethane solution (20 cm^3) of $[\{Au(C_6F_5)_2(\mu\text{-}Cl)\}_2]$ (0.112 g, 0.1 mmol) was added $(SPPh_2)_2C{=}CH_2$ (0.092 g, 0.2 mmol). After stirring for 4 h the solution was concentrated to *ca.* 5 cm^3. Addition of hexane led to complex **1** as a white solid (0.168 g, 82%) (Found: C, 44.0; H, 1.7; S, 6.35. Calc. for $C_{38}H_{22}AuClF_{10}P_2S_2$: C, 44.45; H, 2.15; S, 6.25%). $^{31}P\text{-}\{^1H\}$ NMR: δ 41.7 (s, 1P, Au–P–S) and 45.5 (s, 1P, P=S). ^1H NMR: δ 6.89 (AA′XX′, 2 H, CH_2, $N = 65.0$ Hz). ^{19}F NMR: δ −122.4 (m, *o*-F), −153.6 (t, *p*-F, $J_{FF} = 20.0$), −159.0 (m, *m*-F), −122.6 (m, *o*-F), −157.7 (t, *p*-F, $J_{FF} = 20.2$ Hz) and −161.9 (m, *m*-F). FAB mass spectrum: $m/z = 992$ (88, $[M - Cl]^+$) and 658 (100%, $[Au\{(SPPh_2)_2C{=}CH_2\}]^+$).

$[Au(C_6F_5)_2\{(SPPh_2)_2C{=}CH_2\}]ClO_4$ 2. *Method* (*a*). To a freshly prepared solution of $[Au(C_6F_5)_2(OEt_2)]ClO_4$ (0.2 mmol) in diethyl ether (20 cm^3) was added $(SPPh_2)_2C{=}CH_2$ (0.092 g, 0.2 mmol). After stirring for 3 h a white precipitate of complex **2** was filtered off (0.205 g, 94%).

Method (*b*). A dichloromethane solution (20 cm^3) of complex **1** (0.103 g, 0.1 mmol) was treated with $AgClO_4$ (0.027 g, 0.1 mmol). After stirring for 3 h the AgCl formed was filtered off. Concentration of the solution to *ca.* 5 cm^3 and addition of diethyl ether (20 cm^3) gave complex **2** as a white solid (0.131 g, 60%) (Found: C, 41.65; H, 2.5; S, 5.95. Calc. for $C_{38}H_{22}AuClF_{10}O_4P_2S_2$: C, 41.85; H, 2.05; S, 5.9%). $^{31}P\text{-}\{^1H\}$ NMR: δ 41.7 (s). ^1H NMR: δ 7.15 (AA′XX′, 2 H, CH_2, $N = 69.2$ Hz). ^{19}F NMR: δ −122.3 (m, *o*-F), −153.7 (t, *p*-F, $J_{FF} = 20.0$ Hz) and −159.1 (m, *m*-F). FAB mass spectrum: $m/z = 992$ (65, M^+) and 658 (100%, $[Au\{(SPPh_2)_2C{=}CH_2\}]^+$).

$[Au(C_6F_5)_2\{(SPPh_2)_2CCH_2CH(COMe)_2\}]$ 3. *Method* (*a*). To a dichloromethane solution (20 cm^3) of complex **2** (0.218 g, 0.2 mmol) was added Tl(acac) (0.060 g, 0.2 mmol). The reaction mixture was stirred under nitrogen for 3 h and the $TlClO_4$ formed was then filtered off. The resulting solution was concentrated in a vacuum and the addition of hexane (15 cm^3) led to complex **3** as a yellow solid (0.120 g, 55%).

Method (*b*). To a solution of $(SPPh_2)_2C{=}CH_2$ (0.092 g, 0.2 mmol) in dichloromethane (20 cm^3) was added $[Au(C_6F_5)_2(acac)]$ (0.126 g, 0.2 mmol). After 1 h of stirring under nitrogen the solvent was evaporated and hexane was added to precipitate complex **3** as a white solid (0.153 g, 70%) (Found: C, 47.75; H, 2.7; S, 5.5. Calc. for $C_{43}H_{29}AuF_{10}O_2P_2S_2$: C, 47.35; H, 2.7; S, 5.9%). $^{31}P\text{-}\{^1H\}$ NMR: δ 36.3 (s). ^1H NMR: δ 1.26 (s, 6 H, CH_3), 2.66 (dt, 2 H, CH_2, $^3J_{HP} = 21.5$, $^3J_{HH} = 5.3$ Hz) and 2.95 (t, 1 H, CH). ^{19}F NMR: δ −121.9 (m, *o*-F), −157.1 (t, *p*-F, $J_{FF} = 20.0$ Hz) and −161.4 (m, *m*-F). FAB mass spectrum: $m/z = 1091$ (53, M^+), 758 (82, $[M - 2C_6F_5]^+$) and 658 (100% $[Au\{(SPPh_2)_2C{=}CH_2\}]^+$).

$[Au(C_6F_5)_2\{(SPPh_2)_2CCH_2CN\}]$ 4. To a suspension of complex **2** (0.218 g, 0.2 mmol) in methanol (10 cm^3) and under nitrogen was added KCN (0.012 g, 0.2 mmol) and the mixture was stirred for 2 h. Evaporation of the solvent to dryness and

Table 2 Details of data collection and structure refinement for complex **5**

Chemical formula	$C_{46}H_{34}AuF_{10}P_2S_2$
M	1099.76
Crystal habit	Irregular orange tablet
Crystal size/mm	0.70 × 0.60 × 0.30
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	11.617(2)
b/Å	12.163(2)
c/Å	16.005(2)
α/°	86.313(8)
β/°	75.125(10)
γ/°	84.972(8)
U/Å^3	2175.3(6)
Z	2
D_c/Mg m^{-3}	1.679
F(000)	1082
T/°C	−100
$2\theta_{max}$/°	55
μ(Mo-Kα)/mm^{-1}	3.627
Transmission factor range	0.625–1.0
No. reflections measured	12 427
No. unique reflections	9876
R_{int}	0.035
R^a [*F*,*F* > 4σ(*F*)]	0.028
wR^b (F^2, all reflections)	0.065
No. parameters	535
No. restraints	481
S^c	1.008
Maximum Δρ/e Å^{-3}	0.91

^{a} $R\quad (F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR\quad (F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$ and *a* and *b* are constants adjusted by the program. ^{c} $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}$, where *n* is the number of data and *p* the number of parameters.

addition of diethyl ether led to precipitation of the $KClO_4$ formed in the reaction, which was filtered off over Celite. The solution was then concentrated in a vacuum to *ca*. 5 cm^3 and hexane (15 cm^3) were added to precipitate complex **4** as a crystalline yellow solid (0.102 g, 50%) (Found: C, 46.55; H, 2.25; N, 1.2; S, 6.0. Calc. for $C_{39}H_{22}AuF_{10}NP_2S_2$: C, 46.05; H, 2.2; N, 1.4; S, 6.3%). ^{31}P-{^{1}H} NMR: δ 37.7 (s). ^{1}H NMR: δ 2.76 (t, 2 H, CH_2, $^3J_{HP}$ = 19.2 Hz). ^{19}F NMR: δ −121.9 (m, *o*-F), −156.7 (t, *p*-F, J_{FF} = 20.0 Hz) and −161.1 (m, *m*-F). FAB mass spectrum: *m*/*z* = 1019 (65, $[M + H]^+$), 684 (100, $[M - 2C_6F_5]^+$) and 658 (55%, $[Au\{(SPPh_2)_2C{=}CH_2\}]^+$).

[Au(C$_6$F$_5$)$_2${(SPPh$_2$)$_2$CCH$_2$(C$_5$H$_5$)}]·0.5C$_6$H$_{14}$ 5. To a dichloromethane solution (20 cm^3) of complex **2** (0.218 g, 0.2 mmol) under a nitrogen atmosphere was added TlC_5H_5 (0.054 g, 0.2 mmol). After stirring for 3 h the $TlClO_4$ was filtered off and the solution was concentrated to *ca*. 5 cm^3. Addition of hexane led to complex **5** as an orange solid (0.09 g, 41%) (Found: C, 50.05; H, 3.15; S, 5.75. Calc. for $C_{46}H_{34}AuF_{10}P_2S_2$: C, 50.25; H, 3.1; S, 5.85%). ^{31}P-{^{1}H} NMR: δ 36.0 (s). ^{1}H NMR: δ 1.99 (s, 2 H, CH=CC*H*$_2$CH=CH), 3.06 (t, 2 H, P$_2$CC*H*$_2$, $^3J_{HP}$ = 21.4 Hz), 5.12, 5.92, 6.01 (ABC, 3 H, C*H*=CCH$_2$C*H*=C*H*). ^{19}F NMR: δ −121.8 (m, *o*-F), −157.3 (t, *p*-F, J_{FF} = 20.1 Hz) and −161.5 (m, *m*-F). FAB mass spectrum: *m*/*z* = 1057 (100, M^+), 723 (90, $[M - 2C_6F_5]^+$) and 658 (98%, $[Au\{(SPPh_2)_2C{=}CH_2\}]^+$).

[Au(C$_6$F$_5$)$_2${(SPPh$_2$)$_2$CCH$_2$OEt}] 6. To a dichloromethane solution (20 cm^3) of complex **2** (0.218 g, 0.2 mmol) under nitrogen was added a freshly prepared solution of NaOEt (0.2 mmol). After stirring for 3 h the $NaClO_4$ was filtered off and the solution was concentrated to *ca*. 5 cm^3. Addition of hexane led to the precipitation of complex **6** as a yellow solid (0.068 g, 33%) (Found: C, 46.8; H, 2.85; S, 6.15. Calc. for $C_{40}H_{27}AuF_{10}OP_2S_2$: C, 46.35; H, 2.6; S, 6.2%). ^{31}P-{^{1}H} NMR: δ 38.0 (s). ^{1}H NMR: δ 0.82 (t, 3 H, OCH$_2$C*H*$_3$, $^3J_{HH}$ = 7.0), 2.67 (q, 2 H, OC*H*$_2$CH$_3$) and 3.47 (t, 2 H, P$_2$CC*H*$_2$, $^3J_{HP}$ = 24.7 Hz). ^{19}F NMR: δ −121.8 (m, *o*-F), −157.3 (t, *p*-F, J_{FF} = 19.9 Hz) and −161.4 (m, *m*-F). FAB mass spectrum: *m*/*z* = 991 (50, $[M - OEt]^+$) and 658 (100%, $[Au\{(SPPh_2)_2C{=}CH_2\}]^+$).

Crystallography

The crystal of complex **5** was mounted in inert oil on a glass fibre. Data were collected using monochromated Mo-Kα radiation (λ = 0.710 73 Å). Diffractometer type: Siemens P4 equipped with an LT-2 low-temperature attachment. Scan type ω. Cell constants were refined from setting angles of 65 reflections in the range 2θ = 6–25°. Absorption corrections were applied on the basis of ψ scans. The structure was solved by the heavy-atom method and refined on F^2 (program SHELXL 93).[19] The complex crystallizes with half a molecule of hexane per asymmetric unit. All non-hydrogen atoms were refined anisotropically, with the exception of the solvent carbon atoms. Hydrogen atoms were included using a riding model. Further details are given in Table 2.

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