Strong Activation of the Double Bond in $(PPh_2)_2C{=}CH_2$. Novel Synthesis of Gold(III) Methanide Complexes by Michael Addition Reactions

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Treatment of $[Au(\mu\text{-}Cl)(C_6F_5)_2]_2$ with vinylidenebis(diphenylphosphine), $(PPh_2)_2C{=}CH_2$, leads to the complex $[Au(C_6F_5)_2Cl\{PPh_2C({=}CH_2)PPh_2\}]$. The coordination of the diphosphine to a gold(III) center strongly activates the carbon−carbon double bond, and this complex, therefore, undergoes Michael-type additions with several carbon-, sulfur-, or oxygen-based nucleophiles. The complexes $[Au(C_6F_5)_2\{(PPh_2)_2CCH_2SPh\}]$, $[Au(C_6F_5)_2\{(PPh_2)_2CCH_2S_2CNEt_2\}]$, and $[\{Au(C_6F_5)_2\{(PPh_2)_2CCH_2\}\}_2O]$ have been structurally characterized by X-ray diffraction analysis. They show that the addition has taken place at the terminal carbon atom of the double bond, giving methanide-type complexes. Furthermore, the displacement of the ether molecules in $[Au(C_6F_5)_2(OR_2)_2]ClO_4$ (R = Et, ^iPr) by the diphosphine leads, in a one pot synthesis, to the complexes $[Au(C_6F_5)_2\{(PPh_2)_2CHCH_2OR\}]ClO_4$ as a consequence of ether cleavage by water.

Introduction

Although the double bond in uncoordinated vinylidenebis(diphenylphosphine) is not normally susceptible to nucleophilic attack, it has been shown that complexation to a metal center activates the double bond in such a manner that various nucleophiles can be added by Michael-type reactions.[1−9] In these processes, the nucleophile HNu is added to complexes $[M]{-}(PPh_2)_2C{=}CH_2$ to give the products $[M]{-}(PPh_2)_2CH{-}CH_2Nu$. However, reactions in which the addition takes place only at the terminal carbon atom of the double bond, thus affording species of the type $[M]{-}(PPh_2)_2C{-}CH_2Nu$ in which the central carbon atom can be regarded as a methanide carbon, are unknown. Furthermore, these species can be regarded as intermediates in the addition reactions to the double bond. This method would represent a novel synthesis of gold methanide complexes. Only one such example has been reported in the literature; the quaternization of vinylidenebis(diphenylphosphine) gave an unexpected secondary reaction of cycloaddition at the terminal carbon atom of the double bond, thus, affording a cyclic methanide derivative.[10,11]

As far as we are aware, the only previously reported gold complexes with $(PPh_2)_2C{=}CH_2$ are $[Au_2Cl_2\{\mu\text{-}(PPh_2)_2C{=}CH_2\}]$ and $[AuCl\{\mu\text{-}(PPh_2)_2C{=}CH_2\}]_2$; the latter undergoes reversible addition of methanol.[3,4] Here, we report a strong activation of the carbon−carbon double bond of the diphosphine upon coordination to a gold(III) center; stable methanide complexes are obtained after partial addition to the double bond. Furthermore, the displacement of the ether ligands in $[Au(C_6F_5)_2(OR_2)_2]ClO_4$ by the diphosphine $(PPh_2)_2C{=}CH_2$ leads, surprisingly, to the complex $[Au(C_6F_5)_2\{(PPh_2)_2CHCH_2OR\}]ClO_4$. This reaction represents an example of an extremely facile O−C bond cleavage.

Results and Discussion

The reaction of $(PPh_2)_2C{=}CH_2$ with $[Au(\mu\text{-}Cl)(C_6F_5)_2]_2$ in a molar ratio of 2:1 leads to the complex $[Au(C_6F_5)_2Cl\{PPh_2C({=}CH_2)PPh_2\}]$ (**1**, Scheme 1). Complex **1** is a yellow solid that is nonconducting in acetone (Table 1). Its IR spectrum shows bands from the diphosphine at 1100 (s), 1060 (s), 1075 (s), 791 (m), and 485−624 (s) cm^{-1}, bands characteristic of *cis*-bis(pentafluorophenyl) groups bonded to gold(III), and $\nu(Au{-}Cl)$ at 336 cm^{-1}.

The $^{31}P\{^1H\}$ NMR spectrum of **1** confirms the coordination of the diphosphine ligand through one of the phosphorus atoms (Table 2). The uncoordinated phosphorus appears as a doublet, close to the resonance of

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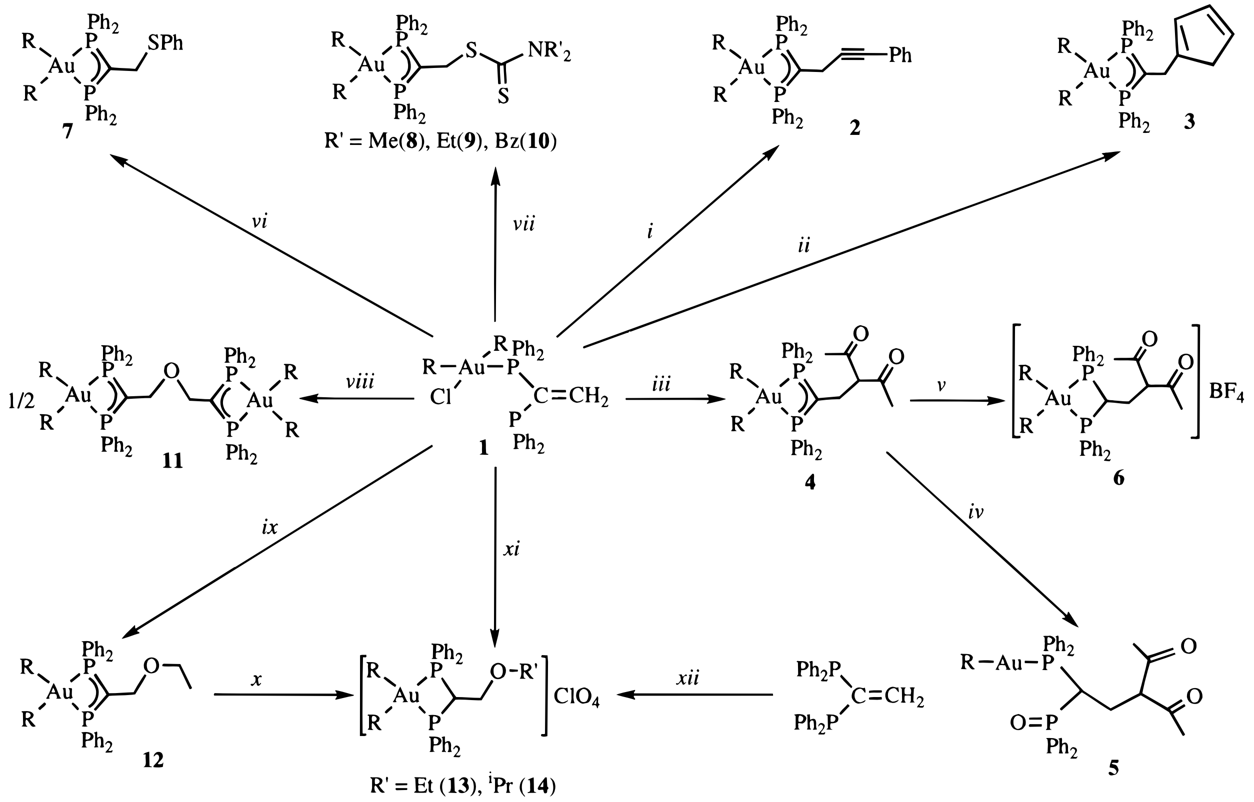
Scheme 1[a]



[a] R = C_6F_5. Legend: (i) AgCCPh; (ii) TlCp; (iii) Tl(acac); (iv) H_2O, O_2; (v) HBF_4; (vi) NaSPh; (vii) $NaS_2CNR'_2$; (viii) $^1/_2$ Ag_2O; (ix) NaOEt; (x) $HClO_4$; (xi) $AgClO_4$, OR'_2; (xii) $[AuR_2(OR'_2)_2]ClO_4$.

Table 1. Yield, Analytical Data, Melting Point, and Conductivity for the Complexes 1−14, R = C_6F_5

complex	yield (%)	analytical data[a]				melting point (°C)[b]	Λ_m[c]
		% C	% H	% N	% S		
1, $[AuR_2Cl\{PPh_2C(=CH_2)PPh_2\}]$	88	47.4 (47.9)	2.3 (2.3)			156 (dec)	3
2, $[AuR_2\{(PPh_2)_2CCH_2C{\equiv}CPh\}]$	47	52.85 (53.7)	3.1 (2.65)			110 (dec)	34
3, $[AuR_2\{(PPh_2)_2CCH_2(\eta^1\text{-}C_5H_5)\}]$	59	51.75 (52.05)	3.1 (2.75)			95	3
4, $[AuR_2\{(PPh_2)_2CCH_2(acac)\}]$	82	50.1 (50.3)	2.75 (2.85)			140 (dec)	6
5, $[AuR\{PPh_2CH(PPh_2O)CH_2(acac)\}]$	70	49.9 (50.75)	3.0 (3.35)			155 (dec)	1
6, $[AuR_2\{(PPh_2)_2CHCH_2(acac)\}]BF_4$	86	45.8 (46.35)	2.2 (2.7)			76	102
7, $[AuR_2\{(PPh_2)_2CCH_2SPh\}]$	61	51.0 (51.0)	3.1 (2.85)		3.1 (3.1)	75	23
8, $[AuR_2\{(PPh_2)_2CCH_2S_2CNMe_2\}]$	79	47.25 (47.0)	2.5 (2.7)	1.2 (1.35)	6.1 (6.1)	90 (dec)	1
9, $[AuR_2\{(PPh_2)_2CCH_2S_2CNEt_2\}]$	78	48.5 (48.0)	2.6 (3.0)	1.35 (1.3)	5.45 (5.95)	105 (dec)	30
10, $[AuR_2\{(PPh_2)_2CCH_2S_2CNBz_2\}]$	68	52.85 (53.05)	3.25 (3.0)	0.95 (1.15)	5.4 (5.35)	60	11
11, $[\{AuR_2\{(PPh_2)_2CCH_2\}\}_2O]$	52	48.9 (48.8)	2.3 (2.35)			110	
12, $[AuR_2\{(PPh_2)_2CCH_2OEt\}]$	75	49.35 (49.4)	3.25 (2.8)			130	20
13, $[AuR_2\{(PPh_2)_2CHCH_2OEt\}]ClO_4$	82	43.95 (44.8)	2.45 (2.55)			182 (dec)	159
14, $[AuR_2\{(PPh_2)_2CHCH_2O^iPr\}]ClO_4$	86	45.2 (45.25)	2.85 (2.75)			190 (dec)	149

[a] Calculated values are given in parentheses. [b] Or decomposition. [c] In acetone, Ω^{-1} cm^2 mol^{-1}.

the free diphosphine, and the phosphorus bonded to gold(III) appears as a multiplet because of the coupling with the phosphorus and the fluorine nuclei. The ^{19}F NMR spectrum shows two different pentaflurophenyl groups; two multiplets and a triplet appear for the *ortho*-, *meta*-, and *para*-fluorine nuclei, respectively, of each C_6F_5 group. In the ^1H NMR spectrum, the two vinylidene protons are inequivalent, each appearing as a multiplet that sharpens only as far as two broad doublets at −55 °C.

In the positive-ion fast atom bombardment mass spectrum (FAB^+) of **1**, the molecular ion peak appears at m/z = 959 (100). Other fragmentation peaks at m/z = 927 and 593 are assigned to $[Au(C_6F_5)_2\{(PPh_2)_2C{=}CH_2\}]^+$ and $[Au\{(PPh_2)_2C{=}CH_2\}]^+$, respectively, which will also be present in the subsequent spectra of the complexes synthesized from **1**.

Complex **1** is a suitable starting material because it can react with nucleophiles to give the methanide-type species, as a result of the partial addition to the double bond. First, we investigated reactions with several carbon-based nucleophiles, such as AgC≡CPh, TlCp, and Tl(acac) (acac = acetylacetonate); these react with **1**, with precipitation of AgCl or TlCl and addition of the nucleophile to the CH_2 group, giving the methanide derivatives $[Au(C_6F_5)_2\{(PPh_2)_2CCH_2Nu\}]$ (Nu = C≡CPh (**2**), Cp (**3**), acac (**4**)). Complexes **2**−**4** are yellow solids that are stable to air and moisture. They are nonconducting in acetone. Their $^{31}P\{^1H\}$ NMR spectra show in all of the cases a multiplet, because of the coupling of the equivalent phosphorus atoms with the fluorine nuclei; the resonances appear at very high field, as we have previously observed in this type of four-membered ring system.[12,13] The ^{19}F NMR spectra of **2**−**4** now show

Table 2. ^{1}H and ^{31}P{^{1}H} NMR Data for the Complexes 1−6, R = C_6F_5^{a}

	^{1}H NMR					
	P−C*H*−CH$_2$	C−C*H*$_2$−C	CH$_2$−C*H*	C_5H_5	2C*H*$_3$	^{31}P NMR
1, [AuR$_2$Cl{(PPh$_2$)$_2$C=CH$_2$}]		6.26 (d), 6.08 (d)^b [*J*(H−P) = 5.4 Hz]				34.6 (m), −8.4 (d) [*J*(P−P) = 50.4 Hz]
2, [AuR$_2${(PPh$_2$)$_2$CCH$_2$C≡CPh}]		3.42 (t) [*J*(H−P) = 25.7 Hz]				−32.2 (m)
3, [AuR$_2${(PPh$_2$)$_2$CCH$_2$(η^1-C$_5$H$_5$)}]		3.15 (t) [*J*(H−P) = 18.6 Hz]		6.15 (m), 5.85 (m), 5.79 (m), 1.99 (m)		−33.7 (m)
4, [AuR$_2${(PPh$_2$)$_2$CCH$_2$(acac)}]		2.55 (td) [*J*(H−P) = 20.7 Hz], [*J*(H−H) = 6.2 Hz]	3.46 (t)		1.63 (s)	−32.8(m)
5, [AuR{PPh$_2$CH(PPh$_2$O)CH$_2$(acac)}]	3.25 (m)	2.35 (m)	3.14 (m)		1.90 (s), 1.67 (s)	40.7 (m), 28.5 (d) [*J*(P−P) = 12.9 Hz]
6, [AuR$_2${(PPh$_2$)$_2$CHCH$_2$(acac)}]BF$_4$	5.95 (m)	2.26 (m)	4.61 (m)		2.11 (s)	−11.3 (m)

^{a} Recorded in CDCl$_3$, values in ppm; s = singlet, d = doublet, t = triplet, m = multiplet. ^{b} Registered at −50 °C.

only one type of pentafluorophenyl group. The ^{1}H NMR spectrum of **2** shows, apart from the resonances of the phenyl protons, a multiplet for the methylene group. The spectrum of complex **3** has five resonances, with a relative intensity of 1:1:1:2:2, at 6.15 (m), 5.85 (m), 5.79 (m), 3.15 (t), and 1.99 (m); the triplet corresponds to the methylene protons and the four remaining resonances to the cyclopentadienyl protons. The high field peak is assigned to the CH$_2$ group and the low field ones to the CH protons of the cyclopentadienyl ring (see Scheme 1). The ^{1}H−^{1}H two-dimensional (COSY) spectrum for **3** agrees with this assignment. The spectrum of complex **4** contains three resonances in a ratio of 6:2:1; the first one is a singlet (2 Me), the second is a triplet of doublets (CH$_2$), because of the coupling of the methylene protons with the equivalent phosphorus atoms and the CH proton of the acetylacetonate, and the third one appears as a triplet (CH).

In the FAB$^+$ mass spectra of complexes **2**−**4** the molecular ion peaks appear at *m*/*z* = 1028 (**2**, 45), 992 (**3**, 100) and 1027 (**4**, 100).

The methanide complex **4** is not very stable in solution and slowly changes from yellow to colorless. We have previously observed that gold(III) methanide complexes are unstable in solution because of their high reactivity toward traces of water, protic solvents, etc. On leaving a diethyl ether solution of **4** in air for 1 day, a white solid is isolated and identified as [Au(C$_6$F$_5$){PPh$_2$CH(PPh$_2$O)CH$_2$(acac)}] (**5**). A redox reaction has taken place, and the gold(III) atom has been reduced to gold(I), whereas one of the phosphorus atoms has been oxidized. Phosphine oxidation at a gold(III) center has been previously reported in other gold(III) derivatives.[14] The IR and the ^{19}F NMR spectra of **5** agree with the presence of a pentafluorophenyl group bound to gold(I); the ^{31}P{^{1}H} NMR spectrum of **5** shows two different phosphorus environments, both with a positive shift: one is a multiplet, by coupling to the phosphorus and the fluorine nuclei, and the other is a doublet. We have also carried out the protonation reaction of **4** with a solution of HBF$_4$ in diethyl ether, leading to the complex [Au(C$_6$F$_5$)$_2${(PPh$_2$)$_2$CHCH$_2$(acac)}]BF$_4$ (**6**), which has also been isolated as a white solid. It behaves as a 1:1 electrolyte in acetone. The IR spectrum shows, as the main difference from the starting material, a broad band at 1100 cm^{-1} arising from the BF$_4^-$ anion. The protonation of the methanide carbon leads to a downfield displacement for the resonance of the phosphorus atoms (Δ = 21.5 ppm). In the ^{1}H NMR spectrum, four resonances at 2.11 (s), 2.26 (m), 4.61 (m), and 5.95 (m) appear; the first corresponds to the two methyl protons of the acetylacetonate group, and the rest were assigned from the ^{1}H−^{1}H (COSY) spectrum. The multiplet at 2.26 comes from the methylene protons, the multiplet at 4.61 from the −CH− of the acac group, and, finally, the multiplet at 5.95, with the relative intensity of 1:2:3:4:3:2:1, corresponds to the methine proton coupled to the phosphorus atoms and the protons of the methylene group in such a manner that ^2J(PH) is twice ^3J(HH).

In the FAB$^+$ spectrum, the molecular ion peak does not appear, but the fragment due to the loss of the BF$_4^-$ ion, [M − BF$_4$]$^+$, is present at *m*/*z* = 1027 (100) and also the fragment [M − BF$_4$ − acac]$^+$ is present at *m*/*z* = 594 (25).

We have also studied Michel-type addition reactions with sulfur-based nucleophiles, such as thiolates and dithiocarbamates. The treatment of **1** with NaSPh or NaS$_2$CNR$_2$ in diethyl ether gives NaCl and the complexes [Au(C$_6$F$_5$)$_2${(PPh$_2$)$_2$CCH$_2$SPh}] (**7**) or [Au(C$_6$F$_5$)$_2${(PPh$_2$)$_2$CCH$_2$S$_2$CNR$_2$}] (R = Me (**8**), Et (**9**), Bz (**10**)).

Complexes **7**−**10** are deep yellow solids that are nonconducting in acetone. The ^{31}P{^{1}H} and ^{19}F NMR spectra are similar to those of the derivatives discussed above. In the ^{1}H NMR spectra, the methylene protons appear as a triplet and in compounds **8**−**10** the resonances of the inequivalent dithiocarbamate subtituents are present (Table 3).

The positive-ion fast atom bombardment mass spectra show the molecular ion peaks at *m*/*z* = 1037 (**7**, 22), 1046 (**8**, 100), 1076 (**9**, 100), and 1119 (**10**, 32).

The structures of complexes **7** and **9** have been established by X-ray diffraction studies. The molecular structure of **7** is shown in Figure 1, and selected bond lengths and angles are given in Table 4. The gold(III) center has a planar geometry, being bonded to the two pentafluorophenyl groups and chelated by the diphosphine ligand; the ligand plane is coplanar with that of the four-membered ring (mean deviation for six atoms is 0.03 Å). The bite angle is very narrow, 69.87(9)°, and is the main factor responsible for the deviation from ideal (square planar) geometry.

The Au−C, 2.087(10) and 2.099(13) Å, and Au−P distances, 2.322(3) and 2.355(2) Å, are similar to those found in bis(pentafluorophenyl)diphosphine gold(III) derivatives, such as [Au(C$_6$F$_5$)$_2${(PPh$_2$)$_2$CPPh$_2$}]^{15} or

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Table 3. ^1H **and** $^{31}P\{^1H\}$ **NMR Data for the Complexes 7−14, R =** C_6F_5[a]

	^1H NMR					
	P−C*H*−CH$_2$	C−C*H*$_2$−O/S	O/N−C*H*$_2$−R	O/N−CH$_2$−C*H*$_3$	N−C*H*$_3$	^{31}P NMR
7, $[AuR_2\{(PPh_2)_2CCH_2SPh\}]$		3.59 (t) [*J*(H−P) = 20.7 Hz]				−31.5 (m)
8, $[AuR_2\{(PPh_2)_2CCH_2S_2CNMe_2\}]$		4.01 (t) [*J*(H−P) = 22.6 Hz]			3.35 (s), 2.99 (s)	−31.2 (m)
9, $[AuR_2\{(PPh_2)_2CCH_2S_2CNEt_2\}]$		4.00 (t) [*J*(H−P) = 23.0 Hz]	3.84 (m), 3.38 (m)	1.13 (m), 0.99 (m)		−31.0 (m)
10, $[AuR_2\{(PPh_2)_2CCH_2S_2CNBz_2\}]$		4.08 (t) [*J*(H−P) = 23.0 Hz]	5.15 (s), 4.53 (s)			−30.7 (m)
11, $[\{AuR_2\{(PPh_2)_2CCH_2\}\}_2O]$		3.43 (t) [*J*(H−P) = 25.7 Hz]				−32.2 (m)
12, $[AuR_2\{(PPh_2)_2CCH_2OEt\}]$		3.75 (t) [*J*(H−P) = 24.3 Hz]	3.06 (c) [*J*(H−H) = 6.2 Hz]	0.95 (t)		−32.9 (m)
13, $[AuR_2\{(PPh_2)_2CHCH_2OEt\}]ClO_4$	7.10 (t) [*J*(H−P) = 11.1 Hz], [*J*(H−H) = 2.0 Hz]	3.97 (t) [*J*(H−P) = 23.1 Hz]	3.18 (q) [*J*(H−H) = 7.1 Hz]	1.11 (t)		−21.8 (m)
14, $[AuR_2\{(PPh_2)_2CHCH_2O^iPr\}]ClO_4$	7.12 (t) [*J*(H−P) = 11.1 Hz]	3.99 (t) [*J*(H−P) = 23.1 Hz]	3.07 (sept) [*J*(H−H) = 6.1 Hz]	0.86 (d)		−23.9 (m)

[a] Recorded in $CDCl_3$, values in ppm; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, sept = septet.

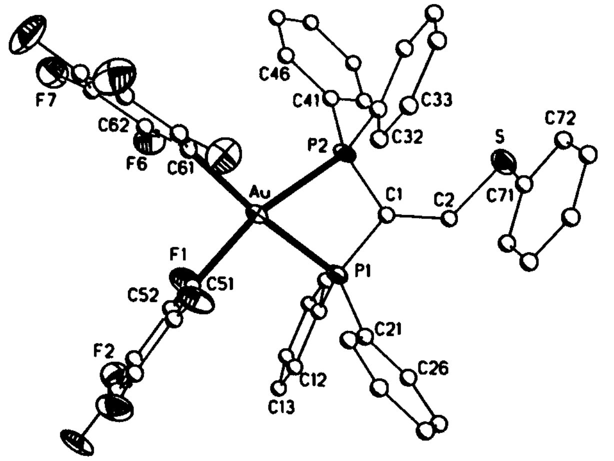

Figure 1. Molecular structure of complex **7** in the crystal showing the atom numbering scheme. Displacement parameter ellipsoids represent 50% probability surfaces. Carbon atoms are spheres of arbitrary radius. The H atoms are omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 7

Au−C(51)	2.087(10)	Au−C(61)	2.099(13)
Au−P(1)	2.322(3)	Au−P(2)	2.355(2)
P(1)−C(1)	1.716(11)	P(1)−C(11)	1.801(7)
P(1)−C(21)	1.819(7)	P(2)−C(1)	1.728(12)
P(2)−C(31)	1.819(7)	P(2)−C(41)	1.830(7)
S−C(71)	1.763(7)	S−C(2)	1.829(12)
C(1)−C(2)	1.52(2)		
C(51)−Au−C(61)	90.7(4)	C(51)−Au−P(1)	95.2(3)
C(61)−Au−P(1)	173.9(3)	C(51)−Au−P(2)	164.8(3)
C(61)−Au−P(2)	104.3(3)	P(1)−Au−P(2)	69.87(9)
C(1)−P(1)−C(11)	114.7(5)	C(1)−P(1)−C(21)	114.2(5)
C(11)−P(1)−C(21)	104.8(4)	C(1)−P(1)−Au	94.8(4)
C(11)−P(1)−Au	114.4(3)	C(21)−P(1)−Au	114.2(3)
C(1)−P(2)−C(31)	115.2(5)	C(1)−P(2)−C(41)	113.6(5)
C(31)−P(2)−C(41)	106.9(4)	C(1)−P(2)−Au	93.3(4)
C(31)−P(2)−Au	114.0(3)	C(41)−P(2)−Au	113.8(3)
C(71)−S−C(2)	104.7(5)	C(2)−C(1)−P(1)	126.9(9)
C(2)−C(1)−P(2)	131.0(9)	P(1)−C(1)−P(2)	102.1(6)
C(1)−C(2)−S	114.7(9)	C(52)−C(51)−Au	120.6(8)
C(56)−C(51)−Au	121.5(8)	C(62)−C(61)−Au	121.8(8)
C(66)−C(61)−Au	121.7(8)		

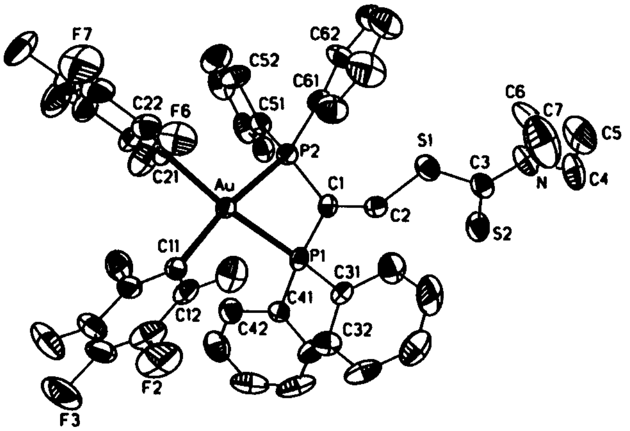

Figure 2. Molecular structure of complex **9** in the crystal (50% ellipsoids), with the atom labeling scheme. H atoms are omitted for clarity.

$[Au(C_6F_5)_2\{(PPh_2)_2CH_2\}]ClO_4$.[16] The methanide carbon atom displays a trigonal planar geometry with angles of 131.0(9)°, 126.9(9)°, and 102.1(6)°; the smallest is the P−C−P angle. The P−C distances are 1.716(11) and 1.728(12) 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), 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). 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) bond distance, 1.52(2) Å, now corresponds to a single bond, in contrast to that in the free phosphine (1.327(6) Å)[17] or in $[AuCl\{PPh_2C(=CH_2)PPh_2\}]_2$ (1.326(9) Å).

The molecular structure of **9** is shown in Figure 2, and selected bond lengths and angles are given in Table 5. Again, the gold(III) center has a square planar geometry, distorted by the ligand bite angle, P−Au−P = 69.97(6)°, and the ligand plane and four-membered ring are coplanar (mean deviation of 0.04 Å). The bond distances and angles around the methanide carbon C(1) fit well to sp^2 hybridization and are similar to those discussed for complex **7**. The C(2)−S(1) distance, 1.830(7) Å, is of the same order as that in complex **7** (1.829(12)

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Table 5. Selected Bond Lengths (Å) and Angles (deg) for 9

Au−C(11)	2.082(6)	Au−C(21)	2.086(7)
Au−P(2)	2.335(2)	Au−P(1)	2.339(2)
P(1)−C(1)	1.719(7)	P(1)−C(41)	1.825(8)
P(1)−C(31)	1.826(7)	P(2)−C(1)	1.711(7)
P(2)−C(51)	1.812(7)	P(2)−C(61)	1.817(8)
S(1)−C(3)	1.771(8)	S(1)−C(2)	1.830(7)
S(2)−C(3)	1.669(9)	N−C(3)	1.329(9)
N−C(6)	1.471(12)	N−C(4)	1.478(10)
C(1)−C(2)	1.536(9)		
C(11)−Au−C(21)	88.2(3)	C(11)−Au−P(2)	170.9(2)
C(21)−Au−P(2)	100.7(2)	C(11)−Au−P(1)	101.0(2)
C(21)−Au−P(1)	169.7(2)	P(2)−Au−P(1)	69.97(6)
C(1)−P(1)−C(41)	116.6(3)	C(1)−P(1)−C(31)	114.3(3)
C(1)−P(1)−Au	93.4(2)	C(41)−P(1)−Au	112.2(2)
C(31)−P(1)−Au	117.0(2)	C(1)−P(1)−P(2)	38.5(2)
C(41)−P(1)−P(2)	128.9(2)	C(31)−P(1)−P(2)	126.5(2)
Au−P(1)−P(2)	54.94(5)	C(1)−P(2)−C(51)	115.1(4)
C(1)−P(2)−C(61)	112.8(3)	C(1)−P(2)−Au	93.7(2)
C(51)−P(2)−Au	113.9(2)	C(61)−P(2)−Au	115.4(3)
C(1)−P(2)−P(1)	38.7(2)	C(51)−P(2)−P(1)	128.9(3)
C(61)−P(2)−P(1)	124.1(2)	Au−P(2)−P(1)	55.08(5)
C(3)−S(1)−C(2)	103.7(3)	C(3)−N−C(6)	123.7(7)
C(3)−N−C(4)	121.8(8)	C(2)−C(1)−P(2)	130.0(5)
C(2)−C(1)−P(1)	127.2(6)	P(2)−C(1)−P(1)	102.8(4)
C(1)−C(2)−S(1)	107.9(5)	N−C(3)−S(2)	123.9(6)
N−C(3)−S(1)	113.8(6)	S(2)−C(3)−S(1)	122.2(4)
C(12)−C(11)−Au	121.2(5)	C(16)−C(11)−Au	121.9(5)
C(26)−C(21)−Au	120.7(6)	C(22)−C(21)−Au	123.6(6)

Å). The C(3)−S(1) and C(3)−S(2) bond lengths are 1.771(8) and 1.669(9) Å, respectively, which indicates the presence of double bond character for S(2)−C(3).

Finally, we have carried out addition reactions of **1** with oxygen-based nucleophiles, such as Ag_2O (molar ratio of 2:1) or NaOEt, affording the complexes $[\{Au(C_6F_5)_2\{(PPh_2)_2CCH_2\}\}_2O]$ (**11**) or $[Au(C_6F_5)_2\{(PPh_2)_2CCH_2OEt\}]$ (**12**). Both are deep yellow solids that are nonconducting in acetone. Their $^{31}P\{^1H\}$ NMR spectra show one multiplet arising from the coupling of the equivalent phosphorus atoms with the fluorine nuclei. In the ^{19}F NMR spectra, both pentafluorophenyl groups are equivalent. In the ^1H NMR spectrum of **11**, the methylene protons are coupled to both phosphorus atoms and appear as a triplet; the spectrum of **12** shows, besides the triplet for the methylene group, the resonances of the CH_3-CH_2- protons that appear as a triplet and a quartet, respectively.

In the positive-ion fast atom bombardment mass spectra, the molecular ion peak is present for complex **12** at $m/z = 973$ (100) and for **11** the fragment $[M - C_6F_5]^+$ appears at $m/z = 1703$ (15).

The structure of complex **11** has been established by X-ray diffraction studies and is shown in Figure 3, and selected bond lengths and angles are given in Table 6. The molecule has crystallographic 2-fold symmetry. The precision was limited by the weak diffraction and the noncentrosymmetry. The one independent gold atom again shows a distorted square planar geometry (mean deviation of five atoms is 0.03 Å), with a diphosphine bite angle of 69.9(3)°. In contrast to **7** and **9**, the four-membered ring is slightly folded (by 9°) about the P···P axis. The distances Au−C and Au−P are of the same order as those found in other methanide complexes,[15,18] and the methanide carbon is trigonal, with angles of 132(3)°, 130(3)°, and (P−C−P) 98(2)°. The distance C(1)−C(2) of 1.42(4) Å, although imprecise, is not inconsistent with a carbon−carbon single bond. The P−C distances are 1.78(3) and 1.79(4) Å, shorter than those in $[PdI_2\{(PPh_2)_2CHCH_2OCH_2CH_2C_4H_5S\text{-}3\}]$ (1.84(2) and 1.85(2) Å) where the carbon was protonated.

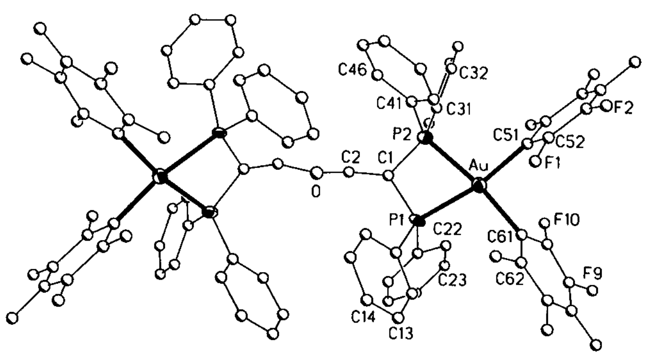

Figure 3. The structure of complex **11** in the crystal. Displacement parameter ellipsoids represent 50% probability surfaces. C, F, and O atoms are spheres of arbitrary radius. Hydrogen atoms are omitted for clarity.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for 11

Au−C(51)	2.03(3)	Au−C(61)	2.08(3)
Au−P(1)	2.346(8)	Au−P(2)	2.363(8)
P(1)−C(1)	1.79(4)	P(1)−C(11)	1.797(14)
P(1)−C(21)	1.80(2)	P(2)−C(31)	1.76(2)
P(2)−C(41)	1.77(2)	P(2)−C(1)	1.78(3)
C(1)−C(2)	1.42(4)	C(2)−O	1.49(3)
C(51)−Au−C(61)	89.9(8)	C(51)−Au−P(1)	168.9(6)
C(61)−Au−P(1)	101.2(6)	C(51)−Au−P(2)	99.0(6)
C(61)−Au−P(2)	170.5(6)	P(1)−Au−P(2)	69.9(3)
C(1)−P(1)−C(11)	115.6(13)	C(1)−P(1)−C(21)	109.1(13)
C(11)−P(1)−C(21)	103.9(9)	C(1)−P(1)−Au	95.6(12)
C(11)−P(1)−Au	115.5(7)	C(21)−P(1)−Au	117.4(7)
C(31)−P(2)−C(41)	107.0(10)	C(31)−P(2)−C(1)	110(2)
C(41)−P(2)−C(1)	116.9(13)	C(31)−P(2)−Au	111.4(7)
C(41)−P(2)−Au	115.5(8)	C(1)−P(2)−Au	95.4(12)
C(2)−C(1)−P(2)	132(3)	C(2)−C(1)−P(1)	130(3)
P(2)−C(1)−P(1)	98(2)	C(1)−C(2)−O	109(2)
C(2*)−O−C(2)[a]	106(3)		

[a] Symmetry transformations used to generate equivalent atoms (designated by *): −x + 1, −y + 1, z.

When complex **12** is treated with a solution of $HClO_4$, the color changes inmediately from yellow to colorless with the formation of the protonated species $[Au(C_6F_5)_2\{(PPh_2)_2CHCH_2OEt]ClO_4$ (**13**). In order to carry out further addition reactions, we have tried to prepare the derivative $[Au(C_6F_5)_2\{(PPh_2)_2C(=CH_2)\}]^+$, which could be used to add several nucleophiles. The treatment of **1** with $AgClO_4$ in diethyl ether led surprisingly to complex **13**, and furthermore, the reaction of $[Au(C_6F_5)_2(OR_2)_2]ClO_4$ with $(PPh_2)_2C{=}CH_2$ gave the same derivatives, $[Au(C_6F_5)_2\{(PPh_2)_2CHCH_2OR\}]ClO_4$ (R = Et (**13**), ^{i}Pr (**14**)).

We believe that in this reaction the first step could be the formation of the expected complex $[Au(C_6F_5)_2\{(PPh_2)_2C{=}CH_2\}]ClO_4$; this should be very reactive toward Michael addition reactions and react even with a weak nucleophile, such as an ether, giving the complexes $[Au(C_6F_5)_2\{(PPh_2)_2CCH_2OR_2\}]ClO_4$ (Scheme 2). The following step could be the nucleophilic attack of H_2O, affording complexes **13** and **14** and one molecule of alcohol. We have detected ethanol or 2-propanol in the ^1H NMR spectra; furthermore, we have carried out the same reaction of $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$ with $(PPh_2)_2C{=}CH_2$ under a nitrogen atmosphere and with

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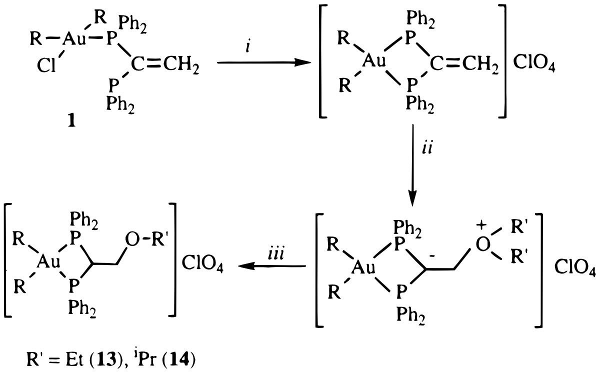
Scheme 2[a]



[a] R = C_6F_5. Legend: (i) $AgClO_4$, −AgCl; (ii) R'_2O; (iii) H_2O, −R′OH.

dry ether, leading to a new, unstable complex whose spectroscopic data correspond to the intermediate $[Au(C_6F_5)_2\{(PPh_2)_2CCH_2OEt_2\}]ClO_4$. Thus, it seems clear that traces of water are necessary to give the alcohol.

Experimental Section

Instrumentation and Materials. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer, over the range 2000−200 cm^{-1}, using Nujol mulls between polyethylene sheets. ^1H, ^{19}F, and ^{31}P NMR spectra were recorded on a Varian UNITY 300 and Bruker ARX 300 spectrometers in $CDCl_3$ solutions; chemical shifts are quoted relative to $SiMe_4$ (^1H, external), $CFCl_3$ (^{19}F, external), and H_3PO_4 (^{31}P, external). C, H, N, and S analyses were performed with a Perkin-Elmer 2400 microanalyzer. Conductivities were measured in ca. 5×10^{-4} mol dm^{-3} acetone solutions with a Jenway 4010 conductimeter, and Λ_M is given in Ω^{-1} cm^2 mol^{-1}. Mass spectra were recorded on a VG Autospec using FAB techniques and nitrobenzyl alcohol as the matrix. The starting materials $(PPh_2)_2C{=}CH_2$[19] and $[Au(\mu\text{-}Cl)(C_6F_5)_2]_2$[20] were prepared as described earlier; $[Au(C_6F_5)_2(OR_2)_2]ClO_4$ was prepared from *trans*-$[Au(C_6F_5)_2Cl_2]$ and 2 equiv of $AgClO_4$ in ether. The syntheses of the methanide complexes were carried out under a nitrogen atmosphere and with freshly distilled solvents.

Safety Note! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of the material should be prepared, and these should handled with great caution.

Synthesis of $[Au(C_6F_5)_2Cl\{PPh_2C({=}CH_2)PPh_2\}]$ (1). To a solution of $(Ph_2P)_2C{=}CH_2$ (0.079 g, 0.2 mmol) in dichloromethane (20 mL) was added $[Au(\mu\text{-}Cl)(C_6F_5)_2]_2$ (0.113 g, 0.1 mmol); the solution turned yellow. After the solution was stirred for 1 h, the solvent was concentrated to 5 mL and addition of hexane gave complex **1** as a yellow solid. ^{19}F NMR, δ: −122.1 (m, *o*-F), −123.2 (m, *o*-F), −156.7 (t, *p*-F, *J*(FF) = 19.3 Hz), −160.0 (m, *m*-F), −160.1 (m, *m*-F).

Synthesis of $[Au(C_6F_5)_2\{(PPh_2)_2CCH_2Nu\}]$ (Nu = C≡CPh (2), Cp (3), acac (4)). To a solution of **1** (0.193 g, 0.2 mmol) in diethyl ether (20 mL) was added AgC≡CPh (0.050 g, 0.24 mmol), TlCp (0.065 g, 0.24 mmol), or Tl(acac) (0.073 g, 0.24 mmol); the suspension was stirred for 1 h. The AgCl or TlCl was filtered off, and the yellow solution was evaporated to 5 mL. Addition of hexane (10 mL) gave complexes **2**−**4** as yellow solids. ^{19}F NMR, δ: **2** −121.0 (m, *o*-F), −157.5 (t, *p*-F, *J*(FF) = 19.9 Hz), −161.6 (m, *m*-F); **3** −121.1 (m, *o*-F), −158.1 (t, *p*-F, *J*(FF) = 19.9 Hz), −161.9 (m, *m*-F); **4** −121.5 (m, *o*-F), −158.1 (t, *p*-F, *J*(FF) = 20.0 Hz), −162.0 (m, *m*-F).

Synthesis of $[Au(C_6F_5)\{PPh_2CH(PPh_2O)CH_2(acac)\}]$ (5). A solution of complex **4** (0.206 g, 0.2 mmol) in diethyl ether (20 mL) was stirred at room temperature for 1 day. The solution turned colorless, and a white precipitate was formed. Concentration of the solvent in vacuo (10 mL) and addition of hexane completed the precipitation of the white solid of complex **5**. ^{19}F NMR, δ: −116.4 (m, *o*-F), −158.4 (t, *p*-F, *J*(FF) = 20.0 Hz), −162.5 (m, *m*-F).

Synthesis of $[Au(C_6F_5)_2\{(PPh_2)_2CHCH_2(acac)\}]BF_4$ (6). To a solution of complex **4** (0.206 g, 0.2 mmol) in 20 mL of diethyl ether was added HBF_4 (0.2 mmol, 54% in diethyl ether). The solution turned colorless, and a white precipitate was formed. After 15 min of stirring, the solid was filtered off to yield complex **6**. ^{19}F NMR, δ: −121.3 (m, *o*-F), −153.7 (t, *p*-F, *J*(FF) = 19.9 Hz), −159.0 (m, *m*-F).

Synthesis of $[Au(C_6F_5)_2\{(PPh_2)_2CCH_2Nu\}]$ (Nu = SPh (7), S_2CNMe_2 (8), S_2CNEt_2 (9), S_2CNBz_2 (10)). To a solution of **1** (0.193 g, 0.2 mmol) in diethyl ether (20 mL) was added NaSPh (0.027 g, 0.2 mmol), $NaS_2CNMe_2{\cdot}2H_2O$ (0.036 g, 0.2 mmol), $NaS_2CNEt_2{\cdot}3H_2O$ (0.045 g, 0.2 mmol), or NaS_2CNBz_2 (0.059 g, 0.2 mmol), and the suspension was stirred for 1 h. The solid NaCl was filtered off, and the yellow solution was evaporated to 5 mL. Addition of hexane (10 mL) gave complexes **7**−**10** as yellow solids. ^{19}F NMR δ: **7** −121.2 (m, *o*-F), −157.6 (t, *p*-F, *J*(FF) = 19.9 Hz), −161.7 (m, *m*-F); **8** −121.2 (m, *o*-F), −157.6 (t, *p*-F, *J*(FF) = 19.9 Hz), −161.7 (m, *m*-F); **9** −121.2 (m, *o*-F), −157.6 (t, *p*-F, *J*(FF) = 19.8 Hz), −161.7 (m, *m*-F); **10** −121.2 (m, *o*-F), −157.6 (t, *p*-F, *J*(FF) = 19.8 Hz), −161.6 (m, *m*-F).

Synthesis of $[\{Au(C_6F_5)_2\{(PPh_2)_2CCH_2\}\}_2O]$ (11). To a tetrahydrofuran solution (20 mL) of complex **1** (0.193 g, 0.2 mmol) was added Ag_2O (0.023 g, 0.12 mmol). The mixture was stirred for 6 h, the white precipitate of AgCl was filtered off, and the yellow solution was concentrated to 5 mL; addition of hexane gave complex **11** as a yellow solid. ^{19}F NMR, δ: −120.9 (m, *o*-F), −157.5 (t, *p*-F, *J*(FF) = 19.9 Hz), −161.6 (m, *m*-F).

Synthesis of $[Au(C_6F_5)_2\{(PPh_2)_2CCH_2OEt\}]$ (12). To a solution of complex **1** (0.193 g, 0.2 mmol) in diethyl ether (20 mL) was added an ethanol solution of NaOEt (2.06 mL, 0.097 M, 0.2 mmol). The mixture was stirred for 30 min and then filtered to remove NaCl. Concentration to ca. 2 mL and addition of hexane (15 mL) afforded complex **12** as a yellow solid. ^{19}F NMR, δ: −120.9 (m, *o*-F), −157.8 (t, *p*-F, *J*(FF) = 19.8 Hz), −161.7 (m, *m*-F).

Synthesis of $[Au(C_6F_5)_2\{(PPh_2)_2CHCH_2OR\}]ClO_4$ (R = Et (13), ^{i}Pr (14)). To a freshly prepared solution of $[Au(C_6F_5)_2(OR_2)_2]ClO_4$ (0.2 mmol) in OR_2 (20 mL) was added $(PPh_2)_2C{=}CH_2$ (0.079 g, 0.2 mmol), and the mixture was stirred for 4 h. Complexes **13** (62%) and **14** (70%) precipitated and were filtered off. ^{19}F NMR, δ: **13** −119.7 (m, *o*-F), −153.7 (t, *p*-F, *J*(FF) = 19.8 Hz), −158.8 (m, *m*-F); **14** −119.3 (m, *o*-F), −153.4 (t, *p*-F, *J*(FF) = 20.0 Hz), −158.7 (m, *m*-F).

X-ray Structure Determinations. Crystals were mounted in inert oil on glass fibers. Data were collected using monochromated Mo Kα radiation (λ = 0.710 73). Diffractometer type: Siemens P4 equipped with a Siemens or Oxford low-temperature attachment. Scan type: ω (**7, 11**) or ω/θ (**9**). Cell constants were refined from setting angles of ca. 50 reflections in the range 2θ = 10−25°. Absorption corrections were applied on the basis of Ψ-scans. Structures were solved by the heavy-atom method and refined on F^2 (program SHELXL-93).[21] Special refinement details: The structure of complex **7** has a marked pseudosymmetry; the gold atom lies on a pseudo-special position (z = 0.5), and this results in weak reflections with l odd. The structure was extended slowly by successive

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Table 7. Details of Data Collection and Structure Refinement for the Complexes 7, 9, and 11

	7	**9**·1.5$C_2H_4Cl_2$	**11**·4$C_2H_4Cl_2$
chem form	$C_{44}H_{27}AuF_{10}P_2S$	$C_{46}H_{38}AuCl_3F_{10}NP_2S_2$	$C_{84}H_{60}Au_2Cl_8F_{20}OP_4$
cryst habit	yellow prism	yellow tablet	yellow plate
cryst size/mm	0.40 × 0.30 × 0.30	0.70 × 0.40 × 0.10	0.20 × 0.20 × 0.10
cryst syst	monoclinic	monoclinic	tetragonal
space group	$P2_1/c$	$P2_1/c$	$P\bar{4}2_1c$
a/Å	10.208(2)	14.9010(10)	19.574(3)
b/Å	18.298(2)	13.7600(10)	19.574(3)
c/Å	21.198(3)	23.985(2)	22.569(6)
β/deg	102.582(12)	92.966(7)	
U/Å^3	3864.4(10)	4911.2(6)	8647(3)
Z	4	4	4
D_c/Mg m^{-3}	1.782	1.656	1.741
M	1036.62	1224.15	2266.73
F(000)	2024	2412	4424
T/°C	−100	−100	−100
$2\theta_{max}$/deg	50	50	45
μ(Mo $K\alpha$)/mm^{-1}	4.025	3.380	3.799
transmission	0.589−0.732	0.549−1.0	0.45−0.48
no. of reflns measd	7101	11920	3310
no. of unique reflns	6711	8570	3237
R_{int}	0.074	0.043	0.31
$R^a(F, F>4\sigma(F))$	0.054	0.044	0.071
wR(F^2, all reflns)^b	0.157	0.132	0.107
no. of params	243	588	226
no. of restraints	143	0	99
S^c	0.98	0.91	0.84
max $\Delta\rho$/eÅ^{-3}	1.28	1.40	0.90

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] w$R$ $(F^2) = [\Sigma\{w(F_o{}^2 - F_c{}^2)2\}/\Sigma\{w(F_o{}^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o{}^2) + (aP)^2 + bP$, where $P = [F_o{}^2 + 2F_c{}^2]/3$ and a and b are constants adjusted by the program. [c] $S = [\Sigma\{w(F_o{}^2 - F_c{}^2)^2\}/(n - p)]^{0.5}$, where n is the number of data and p the number of parameters.

difference maps, the double images being gradually resolved. An anisotropic refinement of the light atoms was not considered suitable. The crystals of complex **11** were small and diffracted weakly (the complex crystallizes with two molecules of 1,2-dichloroethane in the asymmetric unit, one of which is badly resolved). Heavy atoms (Au, P, Cl) were refined anisotropically, others isotropically. Pentafluorophenyl rings were restrained to a local 2-fold symmetry. Phenyl rings were idealized. Other H atoms were included using a riding model. The absolute structure was determined by an x refinement;[22] $x = -0.02(2)$. Further details are given in Table 7.

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Supporting Information Available: Tables of crystal data, data collection, and solution and refinement parameters, bond distances and angles, and anisotropic thermal parameters (22 pages). Ordering information is given on any current masthead page.

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