Ylide-Metal Complexes. III. Preparation and Properties of Gold(I) Complexes of Alkylidenetriphenylphosphoranes and -arsoranes[1)]

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Ylide-gold complexes of the type triphenylphosphine(triphenylphosphonium alkylide)gold(I) chloride, $[\mathrm{Ph_3P\overset{R}{C}H\text{-}Au\text{-}PPh_3}]\mathrm{Cl}$, and bis(triphenylphosphonium alkylide)gold(I) chloride, $[\mathrm{Ph_3P\overset{R}{C}H\text{-}Au\text{-}\overset{R}{C}HPPh_3}]\mathrm{Cl}$, have been obtained from alkylidene triphenylphosphoranes, $\mathrm{Ph_3P{=}CH\text{-}R}$ (R: H, $\mathrm{CH_3}$, $\mathrm{CH(CH_3)_2}$), and (triphenylphosphine)gold(I) chloride, $\mathrm{Ph_3PAuCl}$. Bis(triphenylarsonium methylide)gold(I) chloride, $[\mathrm{Ph_3AsCH_2\text{-}Au\text{-}CH_2AsPh_3}]\mathrm{Cl}$, has been synthesized from methylenetriphenylarsorane and $\mathrm{Ph_3PAuCl}$. In these organogold complexes, the ylides are attached to the gold atom through the carbanionic donor atom. The ^{1}H-NMR spectra of $[\mathrm{Ph_3PCH_2\text{-}Au\text{-}PPh_3}]\mathrm{Cl}$ indicates an intermolecular exchange process in the temperature range +25— −50 °C.

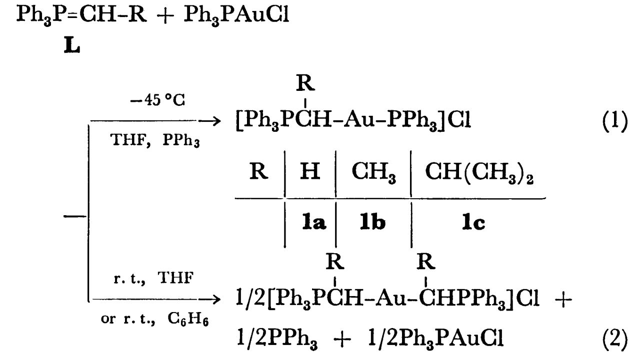
The chemistry of ylide complexes of the transition metals has been actively investigated in recent years,[2)] in particular, the complexes of methylenetrimethylphosphorane, $\mathrm{(CH_3)_3P{=}CH_2}$.[3)] The alkylidenetriphenylphosphoranes, $\mathrm{Ph_3P{=}CH\text{-}R}$ have, however, been the subject of little research. Previous papers have been concerned with the preparation and physical properties of stable 2/1 complexes[4)] of type $[\mathrm{Ph_3\,P\overset{R}{C}H\text{-}M\text{-}\overset{R}{C}HPPh_3}]\mathrm{Cl}$ and stable 1/1 complexes[5)] of type $[\mathrm{Ph_3P\overset{R}{C}H\text{-}MCl}]_n$ (M: Cu, Ag; R: H, $\mathrm{CH_3}$, $\mathrm{CH(CH_3)_2}$). 2/1 complexes[6)] of $[\mathrm{Ph_3AsCH_2\text{-}Cu\text{-}CH_2AsPh_3}]\mathrm{Cl}$ and 1/1 complexes[6)] of $[\mathrm{Ph_3AsCH_2\text{-}AgCl}]_n$ have also been reported. The present paper deals with the preparation and ^{1}H- and ^{13}C-NMR measurements of triphenylphosphine(triphenylphosphonium alkylide)gold(I) chloride $[\mathrm{Ph_3P\overset{R}{C}H\text{-}Au\text{-}PPh_3}]\mathrm{Cl}$, bis(triphenylphosphonium alkylide)gold(I) chloride $[\mathrm{Ph_3P\text{-}\overset{R}{C}H\text{-}Au\text{-}\overset{R}{C}HPPh_3}]\mathrm{Cl}$ and bis(triphenylarsonium methylide)gold(I) chloride $[\mathrm{Ph_3AsCH_2\text{-}Au\text{-}CH_2AsPh_3}]\mathrm{Cl}$.

Results and Discussion

Ylides. Alkylidenetriphenylphosphoranes, $\mathrm{Ph_3P{=}CH\text{-}R}$ (**La**, R=H[7)]; **Lb**, R=$\mathrm{CH_3}$[8)]; **Lc**, R=$\mathrm{CH(CH_3)_2}$[4)]), were prepared by the reaction of the corresponding phosphonium bromide with sodium amide in dry THF(tetrahydrofuran). Methylenetriphenylarsorane, **Ld** ($\mathrm{Ph_3As{=}CH_2}$), was obtained from methyltriphenylarsonium bromide and sodium amide as reported in the literature.[6,9)]

^{13}C-NMR data of the phosphonium ylides(**La**—**Lc**) are given in Table 1, the ^{13}C-NMR spectra of **Lb** and **Lc** being reported for the first time. The coupling constants ($^1J_{\mathrm{CP}}$) of those are larger than that of the ylide **La**. This effect should be attributed to both electronic and structural effects.[10)]

1/1 Ylide-Gold Complexes. Triphenylphosphine-(triphenylphosphonium alkylide)gold(I) chlorides, $[\mathrm{Ph_3P\overset{R}{C}H\text{-}Au\text{-}PPh_3}]\mathrm{Cl}$, have been obtained from ylide $\mathrm{Ph_3P{=}CH\text{-}R}$, (triphenylphosphine)gold(I) chloride $\mathrm{Ph_3PAuCl}$, and triphenylphosphine in a solvent at −45 °C (Eq. 1). Attempts to obtain these complexes at room temperature (r.t.) invariably resulted in the isolation of a mixture of 2/1 complexes of the type bis(triphenylphosphonium alkylide)gold(I) chloride and unreacted starting materials, $\mathrm{Ph_3PAuCl}$ and $\mathrm{PPh_3}$ as shown in Eq. 2.



All complexes except **1c** are soluble and stable in dichloromethane. The isolation of **1a** requires an excess of triphenylphosphine as a supporting ligand, and the selection of a suitable reaction temperature and solvent is very important. For example, **1a** was not obtained at room temperature or in benzene (Eq. 2). This result differs as in the case of trimethylphosphine-(trimethylphosphonium methylide)gold(I) chloride,[11)] $[\mathrm{(CH_3)_3PCH_2\text{-}Au\text{-}P(CH_3)_3}]\mathrm{Cl}$, **2**, which could be isolated from benzene at room temperature. Also, for the preparation of **2** no excess of trimethylphosphine was necessary. This result may depend on the reduced coordination capacity of triphenylphosphine as compared with that of trimethylphosphine. Steric factors[12)] seem not to be dominating for metals of coordination number 2.

The ^{1}H-NMR data of **1a** and **1b** are given in Table 1. The ^{1}H-spectrum of **1a** at −50 °C in $\mathrm{CD_2Cl_2}$ showed a double-doublet signal of the methylene protons at 2.31 ppm. This signal broadened at −30 °C, and became a sharp doublet at −10 °C (Fig. 1). The process is reversible. This temperature dependence indicates an intermolecular exchange process in solution (Eq. 3). The chemical shift of the methylene group at −10 °C corresponds to the weighted average for

Table 1. ^{1}H- and ^{13}C-NMR data of complexes and ylides

^{1}H	R-CH-P(As) δ/ppm	$^2J_{HCP}$/Hz	$^3J_{HCAuP}$/Hz	CH$_3$ δ/ppm	$^3J_{HCCP}$/Hz	$^3J_{HCCH}$/Hz	C$_6$H$_5$ δ/ppm	Solvent and standard	Temp
1a	2.31 dd	12.9	7.5	—	—	—	7.6 m	CD_2Cl_2, int-TMS	−50 °C
	2.32 d	12.9	—	—	—	—	7.6 m	CD_2Cl_2, int-TMS	−10 °C
1b	2.5 m	—	—	1.49 dd	22.5	6.8	7.6 m	CD_2Cl_2, int-TMS	−50 °C
3a	1.70 d	13.0	—	—	—	—	7.5 m	$CDCl_3$, ext-TMS	r. t.
3b	2.30 m	—	—	1.48 dd	22.2	7.4	7.6 m	$CDCl_3$, ext-TMS	r. t.
4a	1.99 s	—	—	—	—	—	7.5 m	$CDCl_3$, ext-TMS	r. t.

^{13}C	R-CH-P(As) δ/ppm	$^1J_{CP}$/Hz	CH-CH$_3$ [CH-CH] δ/ppm	$^2J_{CCP}$/Hz	CH-CH$_3$ δ/ppm	$^3J_{CCCP}$/Hz	C$_6$H$_5$ δ/ppm C-1	o	m	p	Solvent and standard
La	−4.3 d	98.6	—	—	—	—	a	a	a	a	C_6D_6, int-TMS
Lb	3.3 d	118.2	11.1 d	4.9	—	—	a	a	a	a	C_6D_6, int-TMS
Lc	21.7 d	116.2	[27.3] d	6.8	30.0 d	9.8	a	a	a	a	C_6D_6, int-TMS
3a	9.5 d	39.1	—	—	—	—	125.9	132.5	129.4	133.4	$CDCl_3$
							(85.4)	(9.8)	(12.2)	(—)	
3b	16.8 d	32.2	13.7 d	2.9	—	—	124.5	133.3	129.5	133.6	$CDCl_3$
							(84.0)	(8.8)	(11.7)	(—)	
4a	14.4 s	—	—	—	—	—	b	131.9	130.1	132.9	$CDCl_3$

Standard: Internal and external TMS (δ=0); $CDCl_3$-d_1 (77.1 ppm).
a) This signal overlapped with deuterobenzene signals. b) This signal was not observed. s: singlet, d: doublet, dd: double doublet, m: multiplet.

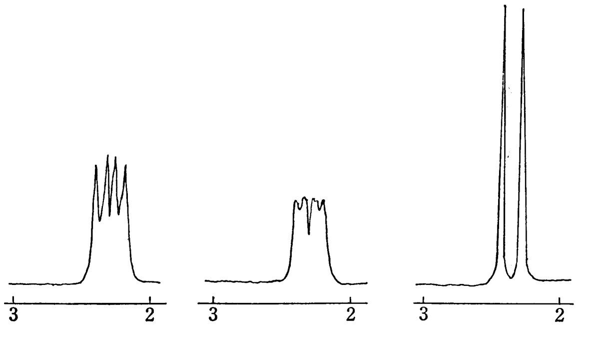


Fig. 1. ^{1}H-NMR spectra of complex **1a**, $[Ph_3PCH_2\text{-}Au\text{-}PPh_3]Cl$, at three different temperatures.

two species in Eq. 3. The small variation of chemical shifts with temperature suggest a small degree of dissociation:[13)]

$$[Ph_3PCH_2\text{-}Au\text{-}PPh_3]Cl \rightleftarrows [Ph_3PCH_2\text{-}Au]Cl + PPh_3 \qquad (3)$$

2/1 Ylide-Gold Complexes. Bis(triphenylphosphonium alkylide)gold(I) chlorides, $[Ph_3P\overset{R}{C}H\text{-}Au\text{-}\overset{R}{C}HPPh_3]Cl$, ($R=H$, **3a**; $R=CH_3$, **3b**; $R=CH(CH_3)_2$, **3c**), were prepared by the reaction of ylides $Ph_3P{=}CH\text{-}R$, with (triphenylphosphine)gold(I) chloride in dry THF at room temperature. **3a** is stable in dichloromethane at room temperature, whereas the corresponding complexes of copper and silver decompose in dichloromethane at room temperature and are stable only at −40 °C and −60 °C, respectively.

The ^{1}H- and ^{13}C-NMR data of **3a** and **3b** are summarized in Table 1. The data for **3c** is absent due to decomposition in the solvent.

Bis(triphenylarsonium methylide)gold(I) chloride, $[Ph_3AsCH_2\text{-}Au\text{-}CH_2AsPh_3]Cl$, **4a**, was obtained from methylene–triphenylarsorane $Ph_3As{=}CH_2$ and Ph_3AuCl in dry THF at room temperature.

The ^{1}H- and ^{13}C-NMR data of **4a** are shown in Table 1. The ^{1}H-NMR spectrum of **4a** showed a singlet for the methylene group at 1.99 ppm and a multiplet for the phenyl groups at 7.5 ppm in a ratio of 2 : 15.

Experimental

Measurements. The NMR spectra were measured with an FX-60 spectrometer (JEOL) for ^{13}C-NMR, a JNM-PMX-60 (JEOL) and a R-40 (Hitachi) for ^{1}H-NMR.

Starting Materials. Methylene-,[7)] ethylidene-,[8)] isobutylidene-[4)] triphenylphosphonium ylides were prepared from the corresponding phosphonium bromides by the sodium amide method. Methylenetriphenylarsorane was prepared from methyltriphenylarsonium bromide and sodium amide.[6,9)] (Triphenylphosphine)gold(I) chloride was synthesized by the method of Kowala and Swan.[14)]

Preparation of 1/1 Complexes. *Triphenylphosphine(triphenylphosphonium methylide)gold(I) Chloride (**1a**)*: (Triphenylphosphine)gold(I) chloride (0.24 g, 0.485 mmol dm^{-3}), methylenetriphenylphosphorane (0.115 g, 0.416 mmol dm^{-3}), and triphenylphosphine (0.14 g, 0.534 mmol dm^{-3}) were suspended in dry THF (15 ml) at −60 °C and stirred for approximately 1 h at −45 °C under nitrogen. The color of the ylide changed from yellow to colorless. The white complex precipitated was filtered at −70 °C, washed with dry pentane and dried under vacuum. Yield 0.28 g (87.3%), mp 139—141 °C, Found: C, 57.40; H, 4.34%. Calcd for $C_{37}H_{32}AuClP_2$; (*MW* 771.03) C, 57.64; H, 4.18%.

*Triphenylphosphine(triphenylphosphonium ethylide)gold(I) Chloride (**1b**)*: (Triphenylphosphine)gold(I) chloride (0.71 g, 1.44 mmol dm^{-3}), ethylidenetriphenylphosphorane (0.42 g, 1.45 mmol dm^{-3}), and triphenylphosphine (0.52 g, 1.98 mmol dm^{-3}) were stirred in THF (25 ml) at −60 °C for 50 min under nitrogen. The color of the ylide changed from orange to colorless. The white precipitate was filtered at −70 °C, washed with dry pentane and dried under vacuum. Yield 0.90 g (79.6%), mp 94—96 °C. Found: C, 57.24; H, 4.43%. Calcd for $C_{38}H_{34}AuClP_2$: (*MW* 785.05) C, 58.14; H, 4.37%.

*Triphenylphosphine(triphenylphosphonium isobutylide)gold(I) Chloride (**1c**)*: (Triphenylphosphine)gold(I) chloride (0.55 g, 1.11 mmol dm^{-3}), isobutylidenetriphenylphosphorane (0.36 g, 1.13 mmol dm^{-3}), and triphenylphosphine (0.39 g, 1.49 mmol dm^{-3}) were stirred in THF (20 ml) at −60 °C for 50 min under nitrogen. The color of the ylide changed from red to colorless. The white complex precipitate was filtered at −70 °C, washed with dry pentane and dried. Yield 0.85 g (94.2%), mp 92—93 °C. Found: C, 58.32; H, 4.96%. Calcd for $C_{40}H_{38}AuClP_2$: (*MW* 813.11) C, 59.09; H, 4.71%. This complex was unstable.

*Preparation of 2/1 Complexes. Bis(triphenylphosphonium methylide)gold(I) Chloride (**3a**)*: (Triphenylphosphine)gold(I) chloride (0.41 g, 0.829 mmol dm^{-3}) was added to a dry THF (20 ml) solution of methylenetriphenylphosphorane (0.54 g, 1.95 mmol dm^{-3}) at −60 °C under nitrogen. The mixture was stirred for 2 h at room temperature and the white precipitate filtered off, washed with dry pentane and dried under vacuum. Yield 0.58 g (89.1%), dec 174 °C. Found: C, 57.66; H, 4.36%. Calcd for $C_{38}H_{34}AuClP_2$: (*MW* 785.05) C, 58.14; H, 4.37%.

*Bis(triphenylphosphonium ethylide)gold(I) Chloride (**3b**) and Bis(triphenylphosphonium isobutylide)gold(I) Chloride (**3c**)*: Complex **3b** was prepared from (triphenylphosphine)gold(I) chloride (0.34 g, 0.69 mmol dm^{-3}) and ethylidenetriphenylphosphorane (0.42 g, 1.45 mmol dm^{-3}) according to the procedure for **3a**. Complex **3c** was prepared from (triphenylphosphine)gold(I) chloride (0.43 g, 0.87 mmol dm^{-3}) and isobutylidenetriphenylphosphorane (0.60 g, 1.88 mmol dm^{-3}) according to the procedure for complex **3a**. Yield 0.48 g (85.6%) for **3b** and 0.67 g (88.6%) for **3c**. Dec 154 °C **3b**, 153 °C for **3c**. Found **3b**: C, 59.33; H, 4.90%. **3c**: C, 60.95; H, 5.83%. Calcd for **3b** $C_{40}H_{38}AuClP_2$: (*MW* 813.11) C, 59.09; H, 4.71%. **3c** $C_{44}H_{46}AuClP_2$: (*MW* 869.21) C, 60.80; H, 5.33%.

*Bis(triphenylarsonium methylide)gold(I) Chloride (**4a**)*: (Triphenylphosphine)gold(I) chloride (0.11 g, 0.222 mmol dm^{-3}) was added to a THF (15 ml) solution of methylenetriphenylarsorane (0.153 g, 0.478 mmol dm^{-3}) at −70 °C under nitrogen. The mixture was stirred for several minutes at −40 °C, and then for 1 h at room temperature. The precipitated white complex was filtered, washed with pentane and dried under vacuum. Yield 0.10 g (51.6%), dec 141 °C. Found: C, 51.80; H, 4.16%. Calcd for $C_{38}H_{34}AuClAs_2$: (*MW* 872.95) C, 52.28; H, 3.93%.

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