a gift of $RuCl_3$ and Prof. H. Lehmkuhl for suggestions concerning NOE experiments.

Registry No. 1, 79681-92-8; 1′, 79732-92-6; **2a**, 85153-18-0; **2a**′, 85201-32-7; **2b**, 96151-62-1; **2b**′, 96193-47-4; 3, 88898-37-7; 3′, 88929-95-7; 4, 90502-92-4; 4′, 90581-29-6; (η-C_5H_5)RuCl(chiraphos), 79681-91-7; (η-C_5H_5)RuH(chiraphos), 96151-63-2; $CHDCl_2$, 1665-01-6.

Supplementary Material Available: CD spectra of **2a** and **2a**′ (Figure 4), 3 and 3′ (Figure 5), and 4 and 4′ (Figure 6) (3 pages). Ordering information is given on any current masthead page.

Activation of Vinylidenebis(diphenylphosphine) through Metal Complexation

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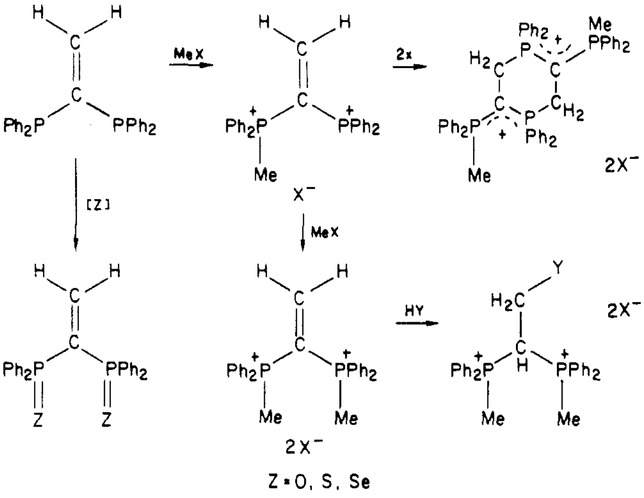
Vinylidenebis(diphenylphosphine) (vdpp) was found to give an insoluble 1:2 complex, (vdpp)·$(AuCl)_2$ (1), but a soluble 1:1 complex, $(vdpp\cdot AuCl)_2$ (2), when treated with (CO)AuCl in the appropriate molar ratio. The crystal structure determination of $(vdpp\cdot AuCl)_2\cdot CHCl_3$ revealed a dimer with a centrosymmetric eight-membered ring skeleton composed of two P,P-bridging vdpp ligands, and trigonally coordinated Au(I) centers, with the two AuP_2Cl planes parallel to each other. The vinylidene groups are not engaged in metal bonding but have become strongly activated through the vdpp–metal coordination. Methanol is added at 20 °C to give the AuCl complex of 1,1-bis(diphenylphosphino)-2-methoxyethane (6). This addition is reversible, and the CH_3OH is lost quantitatively at 150 °C, with recovery of 2. 1:1 complexes were also prepared from CuCl, AgCl, $AgOCOCH_3$, and $AgBF_4$ (3, 4a–c), but the vdpp ligands in none of these products is sufficiently activated to give similar addition reactions. Elemental analyses, osmometric molecular mass data, and ^1H, ^{13}C, and ^{31}P NMR, IR, and mass spectra were used for a preliminary characterization of the compounds. The X-ray data for 2 are as follows: $(C_{26}H_{22}AuClP_2)_2\cdot CHCl_3$, a = 9.920 (2) Å, b = 11.545 (2) Å, c = 12.272 (2) Å, α = 90.40 (1)°, β = 88.25 (2)°, γ = 109.17 (1)°, d_{calcd} = 1.723 g cm^{-3} for Z = 1, space group $P\bar{1}$; 4339 observed reflections, R = 0.033, R_w = 0.042.

Introduction

A plethora of mono- or polydentate tertiary phosphines have been designed, synthesized, and introduced as ligands to metals and metal clusters in order to meet steric and electronic specifications suitable for application to stoichiometric or catalytic reactions.[1-3] These ligand molecules may either be prepared independently and then be integrated into a coordination sphere or constructed in a template synthesis at the metal center(s). For the latter purpose, organophosphorus compounds with versatile functional groups are of prime importance. It is therefore surprising that in this context the potentially reactive phosphino olefins have received little attention. Geminally phosphine-substituted olefins in particular are still rare species and have appeared in the literature only very recently.[4-6]

In initial studies carried out in this laboratory it was found that the prototype molecule vinylidenebis(diphenylphosphine), for which convenient syntheses are available,[4,5] can be strongly activated by monoquaternization with an alkyl halide. In the absence of a suitable nucleophile, dimerization occurs to give cyclic semiylide salts in quantitative yield at room temperature.[6] Double alkylation leads to bis(phosphonium) salts whose C=C bond is sufficiently electrophilic to add even weak components like alcohols, thiols, phosphines, or amines.[6-10] A similar activation is induced by oxidation of the phosphines with oxygen or sulfur (Scheme I).

Scheme I



These results made investigations highly desirable in which the effects of (phosphine)metal complexation on the olefinic double bond is probed. A large variety of mono- or binuclear complexes are possible candidates as acceptor centers, and therefore almost any degree of activation could

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[†] X-ray structure analysis.

(1) Chatt, J.; Williams, A. A. *J. Chem. Soc.* **1951**, 3061.

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(4) Colquhoun, I. J.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1982**, 1915.

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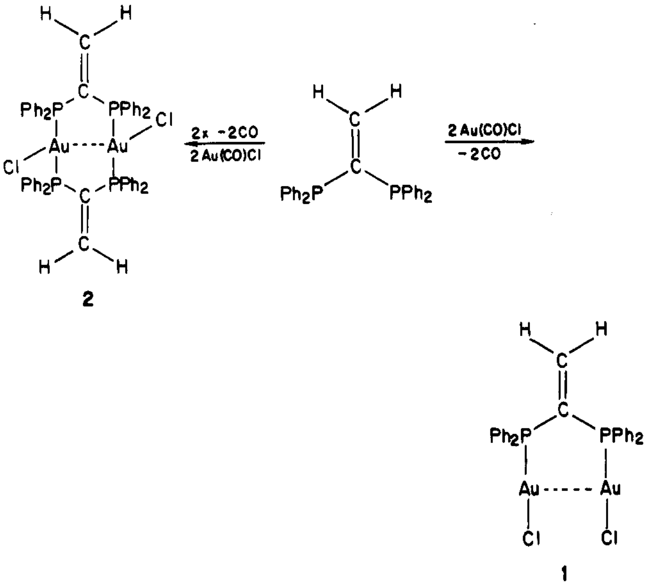
in principle be advanced. Shaw and collaborators could show in parallel and independent studies that a chelating 1,1-bis(phosphino)olefin generated at a metal–carbonyl fragment indeed undergoes addition reactions with a number of substrates.[10,11] Our own studies have also focused on binuclear complexes of a structure similar to that of the bis(diphenylphosphino)methane (dppm) complexes,[12-14] whose chemistry is one of the most rapidly developing areas.

Binuclear Vinylidenebis(diphenylphosphine) Complexes of the Coinage Metals. Vinylidenebis(diphenylphosphine) (vdpp) reacts with carbonylchlorogold(I) in the molar ratio 1:2 in tetrahydrofuran with strong effervescence to give a colorless precipitate of the expected complex **1**. This material is insoluble in all common organic solvents, including dimethyl sulfoxide, chloroform, or nitromethane. The molecular mass and structure could therefore not be determined, but a configuration similar to that of the dppm complex, which was determined by X-ray diffraction, should be valid.[13]

The same components when reacted in equimolar ratio gave again (with evolution of CO gas) a yellowish precipitate, which is soluble in a number of polar organic solvents and could be crystallized from chloroform. The yields of this 1:1 complex **2** were virtually quantitative. The composition and structure could be elucidated by analytical, diffraction, and spectroscopic methods (below). The molecular structure closely resembles that of the dppm complex.[14]



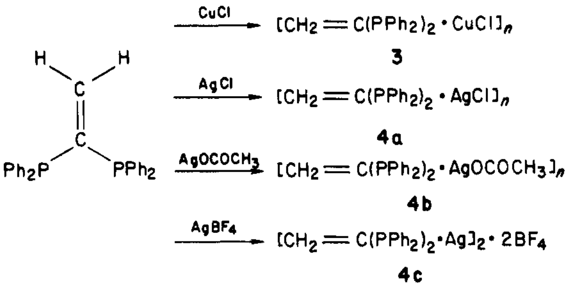
Copper(I) chloride was easily dissolved in a solution of equimolar quantities of vdpp in THF, and a colorless precipitate formed upon addition of hexane to the solution. The 1:1 complex **3** is soluble in chloroform and methylene chloride. Structures of a few related dppm complexes of copper(I) halides have been described in the literature,[15] and a similar skeletal buildup is to be anticipated for **3**.

Silver(I) chloride when treated similarly with vdpp in THF gave no well-defined products. There were no problems, however, when the reaction was carried out in methylene chloride. The off-white 1:1 complex **4a** is very soluble both in CH_2Cl_2 or $CHCl_3$. An analogous acetate **4b** was also obtained in THF, and a tetrafluoroborate **4c** was formed with $AgBF_4$ in the same solvent.

All three compounds could be obtained as colorless air- and light-stable crystalline solids in good yields. Their structures remain to be determined, but a few reference models with dppm are again already available.[16-19]

Like **3**, the silver complexes **4a–c** are soluble in chloroform. Molecular mass determinations by *osmometry* gave values slightly higher than those calculated for dimers of **4b,c** and between those for dimers and trimers in the case of **4a**, respectively (at 25 °C): calculated for dimers **4a**, 1079.5, **4b**, 1126.6, and **4c**, 1182.2; found (C = 0.01 M in chloroform) **4a**, 1483, **4b**, 1234, and **4c**, 1266. It is therefore concluded that the chloroform solutions contain largely dimeric species in the form of discrete complexes or tight ion pairs (**4c**).

The mass spectra of **4a** (field desorption, 100 °C) gave only the ion of the vdpp ligand, probably due to low volatility of the oligomer. With **4b**, a dinuclear fragment $[(vdpp)Ag_2OAc]^+$ was observed as the parent ion (m/e 670 (100%)) with correct isotopic ratios. **4c**, under similar conditions, showed the $[(vdpp\ Ag)_2]^{2+}$ double cation, however, again with the correct isotopic ratio for the two silver ions ^{107}Ag and ^{109}Ag in natural abundance. These results suggest, that in **4a** or **4b** the chloride or acetate anions, respectively, are strongly associated with the metal centers in the solid and in solutions, whereas the fluoroborate **4c** is largely ionic in character. This is also borne out by the IR absorptions of **4b** at 1560 (vs) and 1400 (vs) cm^{-1} for coordinated acetate (ν(COO)) and of **4c** at 1075 (vs) and 782 (w) cm^{-1} for uncomplexed BF_4.



Complexes **2–4** show characteristic resonances in their NMR spectra for the olefinic moiety, which clearly remains intact upon metal coordination at phosphorus. The vinylidene hydrogen atoms give rise to signals in the low-field olefin region very close to the resonances of the aryl hydrogen atoms. In fact in a few cases even overlap of signals occurs. Quite often vinylidene carbon resonances coincide similarly with phenyl carbon resonances (Table I).

The observed spin systems provide evidence for a retained C_2 or m symmetry of the ligands in the complexes in solution. Thus the vinylidene protons give AA′XX′ spectra in all cases, and the PCP carbon atoms appear as simple triplets or symmetrical signal groups if additional P–P couplings across or with the metal atoms ($^{107,109}Ag$)

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Table I. NMR Spectra[a] of Compounds 2, 3, 4a–c, and 6

	2	3	4a	4b	4c	6
solvent	$CDCl_3/CD_3OD$	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$	CD_3OD
$\delta(CH_2)$ (AA′X′)	6.4	6.3	6.25 (m)	6.26	6.7	3.53
$\delta(C_6H_5)$ (m)	7.0–7.75	7.2	6.8–7.5	7.25	7.55	6.9–8.2
$\delta(CH_3)$				1.73 (s)		2.80 (s)
$\delta(CH)$						5.73 (br)
$\delta(CH_2)$ (N)	145.5 (s)	138.9 (s)	139.4 (s)	140.1 (s)	142.6 ("t", 7)	67.8 (br)
$\delta(CP_2)$ (J)	135.4 (t, 43.9)	142.7 (m)[b]	141.8 (s)[d]	141.8 (s)	136.6 (26.4)	32.1 (br)
$\delta(CH_3)$				24.2 (s)		58.2 (s)
$\delta(CO_2)$				177.1 (s)		
δ(C-1) (N)	124.2 (60.6)	128.9 (m)[c]	128.5 (m)[c]	128.4 (m)[c]	125.1 (50.8)	125.2 (58.6)
δ(C-2) (N)	128.6	128.0	128.5[e]	128.4	129.5	129.1 (2.9)
δ(C-3) (N)	134.0	133.3	133.8[e]	133.8	134.6	134.1 (3.9)
δ(C-4)	131.9	129.8	130.2[e]	130.8	131.9	132.6
δ(P) (N)	42.3 (s)	−2.2 (s)	10.5 (425)[f]	14.7 (439.5)[f]	21.9 (534.1)[f]	46.6 (s)

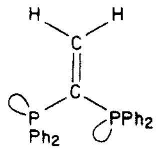
[a] δ in ppm; J/N in Hz; ^{13}C and ^{31}P spectra were ^1H decoupled. [b] Virtual septet structure. [c] Obscured by other resonances. [d] $^1J(CH) = 158$ Hz. [e] $^1J(CH) = 163 \pm 1$ Hz. [f] Unresolved ^{31}P–$^{107/109}Ag$ coupling.

occur. A detailed analysis was not carried out, as quite satisfactory treatments are already available for the dppm analogues.[20] Contrary to the situation in the methanol adduct (below), the four phenyl groups of each ligand are equivalent and only one set of carbon-13 resonances is observed, not withstanding a complex multiplet structure of the signals due to virtual coupling through the phosphorus–phosphorus spin interaction. There is ample precedence for the resulting NMR patterns.[21]

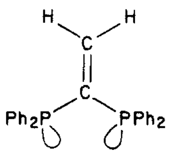
The NMR spectra of **4a** and **4b** have almost identical signals for the vdpp ligands, but the spectrum of **4c** is very different. It is therefore concluded that the first two have very similar structures, whereas the latter should be of another probably ionic type.

Crystal and Molecular Structure of 2. Like the dppm analogue $[CH_2(PPh_2)_2AuCl]_2$, the vdpp complex is found to crystallize in the form of discrete dimers with crystallographically imposed centrosymmetry as shown in Figure 1. Each chlorine atom is attached to a gold atom at a distance of 2.723 (2) Å. Together with the two not quite equidistant phosphorus atoms P1 and P2 (from two different vdpp ligands) this chlorine atom completes a distorted trigonally planar environment for each gold(I) center. (The sum of the valence angles at Au is 359.9°). The two gold atoms, which deviate only 0.03 Å from their individual Cl–P1–P2 planes, are 2.977 (1) Å apart, a distance not uncommon for gold atoms spanned by small-bite difunctional ligands.[14,22] The Au–Au* vector is approximately perpendicular (96.9°) to the coordination plane around each Au atom. The overall geometry of **2** may be described as an eight-membered $(Au–P–C–P)_2$ heterocycle with a short transannular Au–Au contact.

In crystals of the free vdpp ligand the two Ph_2P group are in a quasi E/Z conformation (A) not suitable for bridging or chelating coordination.[5] In complex **2**, however, the expected P–C bond rotation of the E-oriented PPh_2 group has occurred (B) in order to allow formation of a relatively strain-free eight-membered ring. The P1–Au–Au*–P2 torsion angle in **2** amounts to only −24.9°. All other dimensions of the free vdpp ligand are largely unchanged in complex **2** with the exception of the P1–C1–P2 valence angle which is compressed from 119.0 (3)°[5] to 115.8 (3)° upon complex formation. The latter value, however, is not much different from the corresponding P–C–P angle in the analogous dppm complex (114.2 (8)°[14]). Also, the fact that all other geometrical features of both complexes are directly comparable indicates that the observed eight-membered ring geometry best suits the different stereochemical requirements of the constituent heavy atoms, whereas the relatively flexible bridging carbon atoms have to adjust themselves to these requirements. The C=C elongation (a possible evidence for C=C activation by P→Au coordination) does not exceed the standard error of the X-ray experiments. The sum of the valence angles at the inner olefinic carbon atom C1 is 359.6°, clearly indicating a classical sp^2 state of bonding. It is this carbon atom, where the structurally diagnostic pyramidalization occurs with the addition of methanol[7] (below).



A



B

The Au–Cl distances in complex **2** (2.723 (2) Å) are rather large and exceed slightly the standard values for Au^I complexes.[22] They are still shorter, however, than in the analogous dppm complex:[14] 2.771 (4) Å. A high ionic character is therefore ascribed to these Au–Cl bonds, as in the previous example.[14] For the dppm complex it could in fact be demonstrated that a fully ionic species can be easily generated with the tetraphenylborate anion instead of the chloride counterion.[14]

Reversible Methanol Addition to the Activated C=C Bond in Complex 2. The free vdpp ligand does not add weak nucleophiles under standard conditions,[5–7] and only its quaternization or oxidation products exhibit a sufficiently activated C=C bond to allow such reactions (Scheme I). Coordination of gold atoms to both phosphorus centers has now been shown to have a similar effect.

When compound **2** was dissolved in methanol at room temperature, an addition reaction was slowly taking place which was virtually complete after a few days. Colorless needles of product **6** could be isolated after partial evaporation of the solvent. The process can be followed by NMR spectroscopy. The ^{31}P resonance is shifted by 4.3 ppm upon coordination, and the ^1H and ^{13}C signals of the vinylidene group are replaced by a set of resonances in the aliphatic region characteristic of a $P_2CH–CH_2–OCH_3$ group (see Experimental Section).

Due to the structural features, the two CH_2 hydrogen atoms in **6** are anisochronous[23] (J's are anisogamous[24]), and

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(20) Van der Ploeg, A.; Van Koten, G. *Inorg. Chim. Acta* **1981**, *51*, 225.

(21) Redfield, D. A.; Nelson, J. H.; Cary, L. W. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 727.

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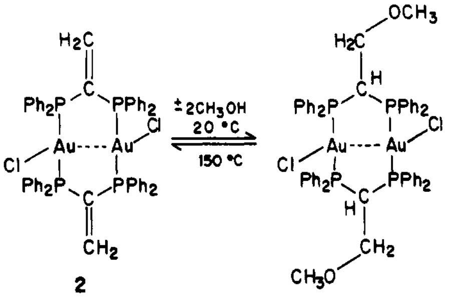
the phenyl groups at each phosphorus atom are diastereotopic, but the effect is only noticable for the C1 signals. The overall pattern is very similar to that observed in the spectra of the phosphonium salt $[(MePh_2P)_2CHCH_2OCH_3]^{2+}2I^-$ in Scheme I (Y = OCH_3). The structure of this derivative has already been confirmed by X-ray diffraction analysis.[7]

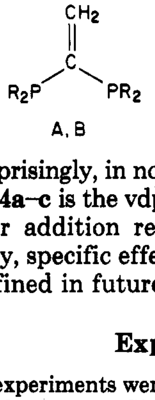


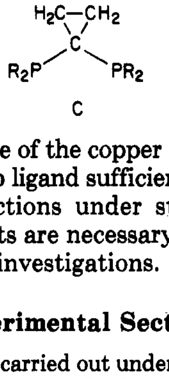
2

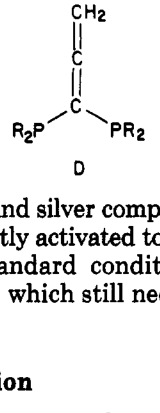
6

In a thermogravimetric analysis compound 6 was found to loose its methanol quantitatively at 150 °C. The yellow parent compound is restored at this temperature without any sign of decomposition. The identity of regenerated 2 was checked by NMR spectroscopy and analytical data.

The above reaction is thus fully reversible. This is an important observation which demonstrates that ligand activation through complex formation is possible but not necessarily irreversible. It is hoped that work in progress with other complexes and substrates will shed further light on the scope of this reaction. In parallel studies the activation of the cyclopropane ring in cyclopropylidenebis(diorganophosphines) (C) is currently investigated.[7,25] Difficulties in the preparation of suitable allene systems D have limited their study to only a few exploratory experiments.[25]


A, B


C


D

Surprisingly, in none of the copper and silver complexes 3 and 4a–c is the vdpp ligand sufficiently activated to give similar addition reactions under standard conditions. Clearly, specific effects are necessary, which still need to be defined in future investigations.

Experimental Section

All experiments were carried out under an atmosphere of dry purified nitrogen. Glassware and solvents were treated accordingly. Vinylidenebis(diphenylphosphine) (vdpp) was prepared following a published procedure.[5] CuCl, AgCl, $AgBF_4$, and $AgOCOCH_3$ either are commercially available or are easily prepared by using standard methods. Au(CO)Cl was obtained via Calderazzo's synthesis.[26]

[Vinylidenebis(diphenylphosphine)]chlorogold(I) (1). A 3.97-g sample of Au(CO)Cl (15.24 mmol) was treated with a solution of 3.02 g of vdpp (7.62 mmol) in 40 mL of tetrahydrofuran at -60 °C. CO was evolved and a white precipitate formed, which was filtered after being warmed to room temperature, washed with THF, and dried in vacuo: yield 5.72 g (87.1%); mp 265 °C (with decomposition), insoluble in $CHCl_3$, CH_3NO_2, and Me_2SO.

Anal. Calcd for $C_{26}H_{22}Au_2Cl_2P_2$ (861.25): C, 36.25; H, 2.57; Au, 45.74. Found: C, 36.22; H, 2.75; Au, 45.20.

Bis[μ-vinylidenebis(diphenylphosphine)]dichlorodigold(I) (2). A 1.96-g sample of Au(CO)Cl (7.52 mmol) was treated with a solution of 3.00 g of vdpp (7.53 mmol) in 40 mL of THF at -70 °C. CO gas was evolved and a white precipitate formed, which was filtered after warming to room temperature, washed with THF, and dried in vacuo. The product can be crystallized from $CHCl_3/CH_3OH$. Pale yellow crystals are obtained: yield 4.17 g (88.2%); mp 206 °C (with decomposition).

Anal. Calcd for $C_{52}H_{44}Au_2Cl_2P_4$ (1257.66): C, 49.66; H, 3.52; Au, 31.32; Cl, 5.63. Found: C, 49.42; H, 3.52; Au, 31.90; Cl, 5.60.

[Vinylidenebis(diphenylphosphine)]chlorocopper(I) (3) and [Vinylidenebis(diphenylphosphine)]chlorosilver(I), -(acetato)silver(I), and -(tetrafluoroborato)silver(I) (4a–c). A 1.19-g sample of CuCl (12.02 mmol) was treated with 4.77 g of vdpp (12.02 mmol) in 60 mL of THF at room temperature for 2 h. From the resulting clear solution the product could be precipitated by careful addition of 20 mL of hexane. The colorless solid 3 was filtered and dried in vacuo: yield 5.22 g (43.8%); mp 235 °C (with decomposition).

Anal. Calcd for $C_{52}H_{44}Cl_2Cu_2P_4$ (990.81): C, 63.03; H, 4.47; Cl, 7.15; Cu, 12.82. Found: C, 62.12; H, 4.51; Cl, 7.33; Cu, 13.01.

Compound 4a was prepared from 0.26 g of AgCl (18.2 mmol) and 0.72 g of vdpp (18.2 mmol) in 30 mL of CH_2Cl_2 at reflux temperature (20 min). After evaporation of the solvent, a pale yellow product remained in quantitative yield (0.98 g, 100%); mp 133 °C.

Anal. Calcd for $C_{52}H_{44}Ag_2Cl_2P_4$ (1079.46): C, 57.86; H, 4.11. Found: C, 57.65; H, 4.02.

Compound 4b was formed when 4.04 g of vdpp (10.2 mmol) and 1.63 g of $AgOCOCH_3$ (9.78 mmol) were dissolved in 40 mL of THF. After a few minutes a colorless precipitate of the product appeared, which was filtered and dried in vacuo: yield 3.45 g (52.6%), mp 172 °C (with decomposition).

Anal. Calcd for $C_{56}H_{50}Ag_2O_4P_4$ (1126.65): C, 59.69; H, 4.47; Ag, 19.14. Found: C, 59.57; H, 4.55; Ag, 19.00.

Compound 4c was prepared as described for 4b from 2.00 g of $AgBF_4$ (10.3 mmol) and 4.11 g of vdpp (10.3 mmol) in 50 mL of THF. The product can be recrystallized from $CHCl_3$: colorless plates; yield 4.43 g (73.04%); mp 245 °C (with decomposition).

Anal. Calcd for $C_{52}H_{44}Ag_2B_2F_8P_4$ (1182.17): C, 52.83; H, 3.75; Ag, 18.24; F, 12.85. Found: C, 52.54; H, 3.69; Ag, 18.13; F, 13.16.

Bis[μ-1-methoxy-2,2-bis(diphenylphosphino)ethane-*P*,*P*,*P'*,*P'*]dichlorodigold(I) (6). A 2.27-g sample of compound 2 (1.80 mmol) was dissolved in methanol. After 2 days at room temperature the solvent was allowed to evaporate slowly. After 10 days colorless needles had formed, which were collected and dried in vacuo, yield 1.59 g (67%); elimination of CH_3OH at 146–150 °C with formation of compound 2.

Anal. Calcd for $C_{54}H_{52}Au_2Cl_2O_2P_4$ (1321.75): C, 49.07; H, 3.96; Au, 29.80. Found: C, 48.33; H, 3.90; Au, 30.30.

X-ray Structure Determination of Bis[μ-vinylidenebis(diphenylphosphine)]dichlorodigold(I) (2). Crystal data: $C_{26}H_{22}AuClP_2 \cdot 0.5CHCl_3$, M_r = 688.522, triclinic, space group $P\bar{1}$, a = 9.920 (2) Å, b = 11.545 (2) Å, c = 12.272 (2) Å, α = 90.40 (1)°, β = 88.25 (2)°, γ = 109.17 (1)°, V = 1326.91 Å^3, d_{calcd} = 1.723 g/cm^3 for Z = 2, $F(000)$ = 666, T = -35 °C.

Suitable single crystals of $2 \cdot CHCl_3$ were grown from $CHCl_3$ and sealed under an atmosphere of argon in a Lindemann glass capillary. According to diffractometer measurements (Syntex $P2_1$) it crystallizes triclinicly. No higher symmetry was indicated by reduced cell calculations (TRACER). The exact cell dimensions and their esd's were obtained by a least-squares fit of the parameters of the orientation matrix to the setting angles of 15 high-order reflections from various parts of reciprocal space accurately centered on the diffractometer.

Intensity data: One form of data (h = 0 – (11), k = 0 – (±13), l = 0 – (±14); $1 \leq \theta \leq 25.0°$) was measured on a computer-controlled four-circle diffractometer equipped with a graphite monochromator and a scintillation counter. A multispeed moving crystal–stationary counter technique was employed where the peak height at the calculated peak position served to determine the final scan speed (ω scan, $\Delta\omega$ = 1°, $0.9 \leq \dot{\omega} \leq 29.3°$/min; Mo K$\alpha$ radiation, λ = 0.71069 Å). The time spent measuring the back-

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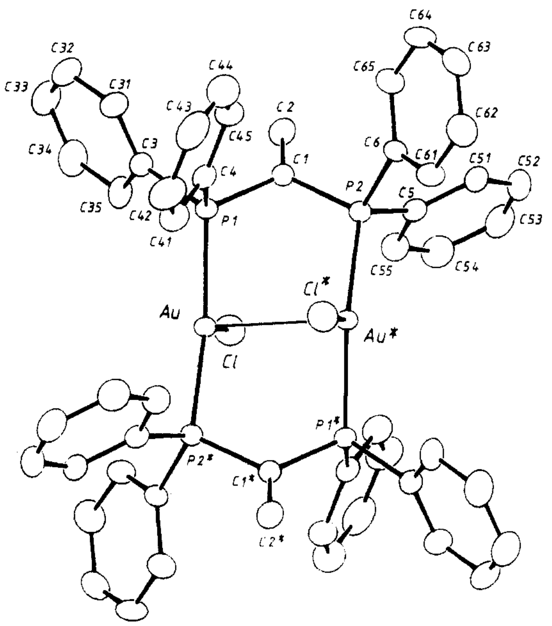

Figure 1. ORTEP representation of the molecular structure of 2 with atom numbering scheme used (thermal ellipsoids at the 50% probability level). The atoms with an asterisk are related to the ones without an asterisk by a center of inversion.

ground intensities at each end of the scan interval was half that taken to measure the peak. A monitor reflection (111), measured after every 50 reflections, served as a check on the centering and stability of the crystal and diffractometer system. There was no significant change in its intensity variation. The intensity of a reflection and its standard deviation were calculated as $I = (S - B/\beta)\dot{\omega}$ and $\sigma(I) = (S - B/\beta^2)^{1/2}\dot{\omega}$, where S is the total scan counts, B the total background counts, and β the time ratio of total background to scan. The intensity data were corrected empirically for absorption by recording scans at 10° intervals around the diffraction vectors of eight selected reflections ($\mu(\mathrm{MoK}\alpha) = 59.1$ cm^{-1}; Syntex XTL). After Lorentz and polarization corrections ($F_o = (I/Lp)^{1/2}$, $\sigma(F_o) = \sigma(I)/(2F_oLp)$) 4339 structure factors with $F_o \geq 4.0\sigma(F_o)$ out of a total of 4658 were considered statistically significant and used in all further calculations.

Structure solution and refinements: The gold atom position could be deduced from a Patterson synthesis. Subsequent Fourier syntheses revealed the remainder of the molecule. After anisotropic refinement of the non-hydrogen atoms, 13 of the 22 hydrogen atoms, including those at the ethylene part of the ligand, could be located in difference maps. The rest was calculated at idealized geometrical positions (d(C–H) = 0.975 Å). The strongest peaks, belonging to a highly disordered chloroform molecule located near an inversion center, were fitted to idealized geometry and refined as rigid body with half occupancy and individual isotropic temperature factors. A total of 281 parameters were refined by full-matrix least squares to $R = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.33$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.042$, $w = k/\sigma^2(F_o)$, and $k = 2.0$ in the last cycle (non-hydrogen atoms anisotropic and hydrogen atoms constant, SHELX 76). The function minimized was $\sum w(|F_o| - |F_c|)^2$. In the final refinement cycle the maximum shift to error ratio of parameters belonging to the complex were smaller than 0.1, whereas those of the solvent were only partially convergent. A final difference map showed peaks between 0.86 and 2.49 e/Å^3 near the solvent molecule; the highest peaks near the Au atom position had heights between 0.47 and 0.76 e/Å^3; all other peaks were equally distributed throughout the cell. Scattering factors for neutral, isolated, non-hydrogen atoms were taken from Cromer and Waber[27] and those of the hydrogen atoms, based on a bonded spherical atom model, from Stewart, Davidson, and Simpson.[28] Corrections for $\Delta f'$ and $\Delta f''$ were applied for all atoms.[29] Table II lists the final atomic coordinates and equivalent isotropic temperature factors of the non-hydrogen atoms; Table III contains important bond lengths and angles. Figure 1 gives an ORTEP representation of the molecular structure.

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 2[a]

atom	x/a	y/b	z/c	U(eq), Å^2
Au	0.3512 (0)	0.4861 (0)	0.0369 (0)	0.020
Cl	0.4198 (2)	0.6991 (1)	0.1519 (1)	0.033
P1	0.3906 (2)	0.3714 (1)	0.1809 (1)	0.020
P2	0.7169 (2)	0.4847 (1)	0.1357 (1)	0.021
C1	0.5677 (6)	0.4446 (5)	0.2357 (5)	0.021
C2	0.5869 (6)	0.4789 (6)	0.3390 (5)	0.031
C3	0.2716 (6)	0.3526 (6)	0.2998 (5)	0.025
C31	0.2294 (6)	0.2491 (6)	0.3639 (6)	0.032
C32	0.1444 (8)	0.2422 (6)	0.4564 (6)	0.038
C33	0.1006 (8)	0.3396 (9)	0.4866 (6)	0.039
C34	0.1418 (8)	0.4447 (8)	0.4225 (6)	0.040
C35	0.2264 (6)	0.4532 (6)	0.3294 (6)	0.032
C4	0.3838 (6)	0.2186 (5)	0.1423 (5)	0.023
C41	0.3014 (8)	0.1647 (6)	0.0543 (6)	0.032
C42	0.2853 (9)	0.0437 (6)	0.0243 (6)	0.041
C43	0.3567 (9)	−0.0205 (6)	0.0803 (6)	0.040
C44	0.4398 (9)	0.0329 (6)	0.1670 (8)	0.039
C45	0.4545 (8)	0.1517 (6)	0.1983 (6)	0.035
C5	0.8431 (6)	0.6242 (6)	0.1898 (5)	0.024
C51	0.9839 (6)	0.6348 (6)	0.2087 (5)	0.028
C52	1.0802 (6)	0.7472 (6)	0.2395 (6)	0.034
C53	1.0356 (8)	0.8481 (6)	0.2523 (6)	0.037
C54	0.8941 (8)	0.8366 (6)	0.2342 (6)	0.038
C55	0.7982 (6)	0.7272 (6)	0.2034 (5)	0.031
C6	0.8032 (6)	0.3688 (6)	0.1477 (5)	0.023
C61	0.8627 (6)	0.3362 (6)	0.0553 (5)	0.029
C62	0.9378 (8)	0.2525 (6)	0.0606 (6)	0.036
C63	0.9487 (6)	0.2010 (6)	0.1596 (6)	0.033
C64	0.8866 (8)	0.2316 (6)	0.2525 (6)	0.033
C65	0.8154 (6)	0.3172 (6)	0.2480 (6)	0.032
C001	0.4704 (11)	0.8592 (9)	0.3920 (8)	0.106
Cl01	0.4725 (11)	0.7264 (9)	0.4622 (8)	0.164
Cl02	0.3332 (11)	0.9122 (9)	0.4448 (8)	0.226
Cl03	0.6388 (11)	0.9760 (9)	0.3953 (8)	0.265

[a] $U_{eq} = (U_1U_2U_3)^{1/3}$, where U_1, U_2, and U_3 are eigenvalues of the U_{ij} matrix. Esd's are in parentheses.

Table III. Selected Interatomic Distances (Å) and Angles (deg) of 2 with Esd's in Units of the Last Significant Figure in Parentheses

	Bond Distances		
Au–Au*	2.977 (1)	C1–C2	1.326 (9)
Au–Cl	2.723 (2)	P1–C3	1.817 (6)
P1–Au	2.333 (1)	P1–C4	1.804 (6)
P2–Au*	2.302 (1)	P2–C5	1.820 (6)
P1–C1	1.828 (6)	P2–C6	1.818 (6)
P2–C1	1.833 (6)		
	Bond Angles		
P1–Au–Cl	94.3 (1)	P2–C1–C2	121.3 (5)
P2*–Au–Cl	110.4 (1)	Au–P1–C1	110.7 (2)
P1–Au–P2*	155.2 (2)	Au–P1–C3	116.5 (2)
Au*–Au–P1	85.8 (1)	Au–P1–C4	113.5 (2)
Au*–Au–P2	93.3 (1)	Au*–P2–C1	112.8 (2)
Au*–Au–Cl	95.7 (7)	Au*–P2–C5	111.9 (2)
P1–C1–P2	115.8 (3)	Au*–P2–C6	115.6 (2)
P1–C1–C2	122.5 (5)		

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Registry No. 1, 96452-99-2; 2, 96453-00-8; 2·0.5$CHCl_3$, 96453-01-9; 3, 96453-02-0; **4a**, 96453-03-1; **4b**, 96453-04-2; **4c**, 96453-06-4; 6, 96453-07-5; vdpp, 84494-89-3; Au(CO)Cl, 50960-82-2; CuCl, 7758-89-6; AgCl, 7783-90-6; $AgOCOCH_3$, 563-63-3; $AgBF_4$, 14104-20-2.

Supplementary Material Available: Additional crystal structure data and tables of final anisotropic thermal parameters, H atom parameters, and observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

Synthesis of Optically Active Allyltin Compounds and Their Application to Enantioselective Synthesis of Secondary Homoallyl Alcohols

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Three types of optically active allyltin compounds, $R^*_2Sn(allyl)_2$ (R^* = 2-phenylbutyl, 2-methylbutyl, and 3-phenylbutyl), $R^*R^1Sn(allyl)_2$ (R^* = 2-octyl or 2-phenylbutyl, R^1 = phenyl), and $R^*R^1R^2Sn(allyl)$ (R^* = 2-phenylbutyl, R^1 = phenyl, R^2 = methyl), have been synthesized. On the basis of ^1H NMR spectra, a π-stacking interaction between the 2-phenylbutyl and the allyl groups is suggested. Optically active allyltin compounds thus obtained were subjected to reaction with aldehydes. Among various allyltin compounds, only diallylbis(2-phenylbutyl)tin exhibits good enantioselectivity. The reaction proceeds through addition of the allyl group on the *re* face of aldehydes. The mechanism can be accounted for on the basis of a π-stacking interaction between allyl and phenyl groups.

Introduction

Enantioselective synthesis of secondary homoallyl alcohols from aldehydes and optically active allylmetal compounds has received much attention recently. As templates for chirality transfer, there have appeared three types of organometallics. One of them is based on utilization of an optically active allylic group. Hayashi et al.[1] have synthesized α-substituted allylsilanes in which silicon is directly bonded to an asymmetric α-carbon. These compounds, on treatment with aldehydes, afforded secondary homoallyl alcohols of up to 90% ee. More recently, (α-alkoxycrotyl)tin derivatives have been found to react stereoselectively with benzaldehyde.[2] Employment of a chiral metallic center is the next choice. Unfortunately, however, Paquette et al. have found the reaction of (−)-α-naphthylphenylmethylallylsilane with acetals to give rise to unsatisfactory enantiomeric excess (<6%).[3] The last type which seems to be the most general and has afforded the most successful results thus far is one containing a pure optically active ligand attached to the metal. This method has been applied to boron derivatives first by Hoffmann et al.[4] and later by Midland et al.,[5] resulting in up to ca. 90% ee. More recently, Brown et al. have succeeded in improving the enantiomeric excess up to 96% by employing *B*-allyldiisopinocampheylborane.[6] It should be noted, however, that the method is not successfully applicable to chromium derivatives which lead to less than 17% ee.[7]

Optically active organotin compounds have received considerable attention from a stereochemical standpoint in recent years despite their relatively short history.[8] It is quite surprising, however, that their synthetic application is limited[9] in contrast to the rapidly expanding synthetic utilization of organotin compounds. Among various recently developed applications, allylation of carbonyl compounds by allyltin derivatives is of particular interest.[10] Accordingly, exploitation of optically active allyltin compounds would provide a new method for an enantioselective synthesis of homoallyl alcohols.

Two types of optically active allyltin compounds may be possible. One involved a chiral tin atom which is linked to four different substituents. Although compounds of this type have been most frequently encountered thus far, satisfactory optical purity has not always been attained.[8,11]

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