The reaction of $(C_5Me_5)(CO)_2RuP(SiMe_3)_2$ (1)[7] with 2 equiv of pivaloyl chloride in cyclopentane (20 °C, 1 h) yields a yellow solution. Evaporation to dryness and crystallization of the residue from pentane produces a 77% yield of a yellow microcrystalline solid. Recrystallization from pentane at −30 °C yields large orange-yellow crystals suitable for X-ray diffraction (Scheme I).

The structure of **3** was assigned on the basis of spectral evidence and confirmed by a single-crystal X-ray diffraction study.[8] The asymmetric unit of the structure of complex **3** comprises a pair of enantiomeric molecules. One enantiomer is shown in Figure 1, and selected bond distances and angles are presented in Table I. The coordination of the dipivaloylphosphido ligand in **3** is of primary interest. The trigonal-pyramidal phosphorus atom is ligated by the $(C_5Me_5)(CO)_2Ru$ unit and two propeller-like oriented pivaloyl groups. The oxygen atoms of the carbonyl dipoles are directed away from the phosphorus atom, thus minimizing interactions between the π-electrons and the free electron pair on phosphorus.

The phosphorus ligand adopts a conformation in which the lone pair is orthogonal to the ruthenium HOMO. The torsion angle between the $P[C(O)(t\text{-}Bu)]_2$ lone pair and the ruthenium fragment HOMO (taken as Ru–C1O1 bond) is 112°. The position of the lone pair was assumed in the plane bisecting the C3–P–C4 angle. The torsion angle D1–P1–Ru1–C1 (D1 symbolizes the middle of the ring ligand) is 100.7°. Stereochemical activity of the phosphorus lone pair in transition-metal phosphido complexes, which has been recently pointed out by Gladysz as "gauche effect in transition-metal chemistry",[9] is also evident in the crystal structures of $(\eta^5\text{-}C_5Me_5)Fe(CO)_2PPh_2$,[10] $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(\overline{PN(Me)CH_2CH_2NMe})$,[11] and $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)PPh_2$.[9] The ruthenium to phosphorus bond (2.404 (1) Å) is only slightly shorter than the calculated value for a Ru–P single bond (2.43 Å).[12,13] The phosphorus carbon (CO) distances are close to the calculated single bond values (1.85 Å),[14] whereas the CO distances of the acylic carbonyl functions are essentially those of localized CO double bonds.

The simplicity of the ^1H NMR (C_6D_6, 200 MHz; δ 1.40 (s, 18 H, t-Bu), 1.54 (d, J = 1.2 Hz, 15 H, C_5Me_5)) and ^{13}C NMR spectra (C_6D_6, 50.309 MHz; δ_C 9.54 (d, $^3J_{PC}$ = 4.6 Hz, $C_5(CH_3)_5$), 27.92 (d, $^3J_{PC}$ = 3.7 Hz, $C(CH_3)$), 49.06 (d, $^2J_{PC}$ = 29.1 Hz, $C(CH_3)$), 100.29 (s, $C_5(CH_3)_5$), 202.50 (s, RuCO), 235.66 (d, $^1J_{PC}$ = 71.0 Hz, PC(O)) suggests that in solution both pivaloyl groups rotate freely around the P–C bonds and that this rotation is rapid on the ^1H and ^{13}C NMR time scale at room temperature. At −100 °C (in toluene-d_8) each *tert*-butyl group gives rise to a singlet in the ^1H NMR spectrum (δ_H 0.86 and 0.95). The phosphorus signal is a singlet at δ_P 56.7 (85% H_3PO_4 standard) at room temperature (in C_6D_6). At −100 °C (toluene-d_8) this signal is slightly broadened and is seen at 52.58 ppm. From the position of the ^{13}CO signals of the carbonyl ligands in **3** and **1** (δ_C 204.5) it is clear that the divaloylphosphido group is a much better acceptor ligand than the $P(SiMe_3)_2$ ligand in **1**.[15] This evidence is supported by two strong infrared absorptions of the $Ru(CO)_2$ moiety in **3** at 2038 and 1967 cm^{-1} (in hexane) (**1**: ν(CO) = 2012, 1953 cm^{-1} in hexane). In Nujol two strong bands at 1632 and 1610 cm^{-1}, which in CH_2Cl_2 solution collapse to a broad band at 1620 cm^{-1}, are attributed to the CO stretching modes of the pivaloyl groups.

A probable mechanism for the formation of **3** is depicted in Scheme I. Reaction of **1** with pivaloyl chloride is presumed to give the intermediate complex **2**, which is rapidly consumed by a second mole of pivaloyl chloride, thus preventing the isolation or spectroscopic characterization of **2**. The attempted preparation of **2** by reacting equimolar amounts of **1** and t-BuC(O)Cl yields a 1:1 mixture of **3** and unreacted **1**. Although not observed in this case rearrangement products of species such as **2** (cf. $(C_5H_5)(CO)_2FeP{=}C(OSiMe_3)(t\text{-}Bu)$[16]) may be obtained from the reaction of $(C_5H_5)(CO)_2FeP(SiMe_3)_2$ with pivaloyl chloride. Other reactions of $(R_5C_5)(CO)_2MP(SiMe_3)_2$ with acid chlorides are under investigation.

Acknowledgment. Our work was generously supported by the Deutsche Forschungsgemeinschaft, Bonn, the Fonds der Chemischen Industrie, Frankfurt, and the Degussa AG, Hanau, Germany. This assistance is grateful acknowledged.

Registry No. 1, 97889-65-1; 3, 97877-48-0; t-BuC(O)Cl, 3282-30-2.

Supplementary Material Available: Tables of observed and calculated structure factors, anisotropic and isotropic thermal parameters, bond lengths, and bond angles (43 pages). Ordering information is given on any current masthead page.

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[8] Crystal data for complex **3**: space group $P\bar{1}$, a = 9.954 (1) Å, b = 13.563 (3) Å, c = 18.072 (4) Å, α = 91.59 (2)°, β = 93.54 (2)°, γ = 96.84 (2)°, V = 2416 (1) Å^3, Z = 4, ρ_{calcd} = 1.36 g/cm^3; μ(Mo Kα, graphite-monochromator) = 7.2 cm^{-1}; 2θ/ω scan data collection at roomtemperature (3° ≤ 2θ ≤ 55°); 6377 unique reflections, 5615 unique observed ($F_o \geq 3.50(F)$); Syntex R3-four circle diffractometer; structure solving by Patterson and difference Fourier techniques and refinement by block-cascade least squares, using SHELXTL on a NOVA 3 (Data General). All non-hydrogen atoms refined anisotropical with 554 parameters and rigid groups for cyclopentadienylrings and all hydrogen atoms, given the 1.2-fold isotropic temperature factor of the $\mathbf{U}_{ij}$ tensor of the corresponding C atom; R = 0.030, R_w = 0.034, $w^{-1} = \sigma^2(F) + 0.0004F^2$, maximum rest electron density 0.38 e/Å^3.

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Isomerization of a Symmetrical Metal–Metal Bonded Gold(II) Ylide Dimer to a Mixed-Valence Gold(III)/Gold(I) Species

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Summary: The first example of the spontaneous isomerization of a metal–metal bonded gold(II) ylide dimer to its mixed-valence Au(III)/Au(I) isomer is reported. This isomerization occurs in nitromethane and other weakly protonic solvents, such as acetone. The X-ray structure of the mixed-valence species shows the presence of a 3.184 (1) Å Au(III)/Au(I) distance.

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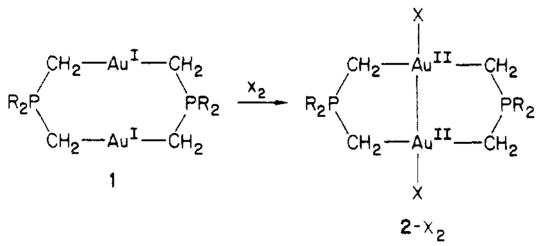
Dinuclear gold(I) complexes **1** are readily oxidized[1-3] with the halogens or pseudohalogens to form symmetric (isovalent) gold(II) species **2**-X_2.

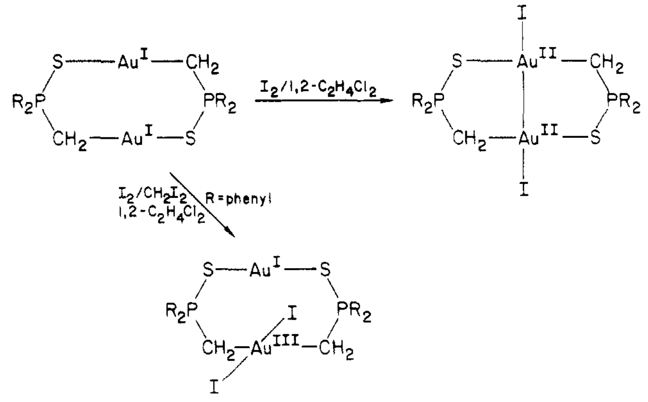


1

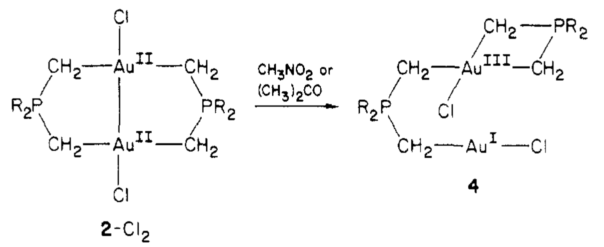
2-X_2

R=alkyl or aryl, X=halogen or pseudohalogen

Although formation of an isomeric heterovalent Au(III)/Au(I) species has been noted for the iodide complex **3** of the unsymmetrical methylenediphenylthiophophinate ligand $CH_2P(S)Ph_2^-$, isomerization of the symmetrical dinuclear gold(II) ylide complex **2**-X_2 has not been reported. The isomerization of a homovalent metal–metal bonded dimer to a heterovalent species, **4**, described here, suggests that other metal–metal bonded gold(II) dimers may behave in a similar way, under suitable conditions. Although details of the isomerization are not understood, it appears that the reaction is promoted by the solvent nitromethane and may be catalyzed by other protonic species such as acetone.



3



2-Cl_2

4

R=phenyl

When approximately 5 mg of **2**-Cl_2 is mixed with about 10 mL of CH_3NO_2, the solid slowly dissolves. In a few days at room temperature a faint yellow solution is produced. Over a period of a few weeks, this color disappears. Evaporation of the solution gives colorless crystals suitable for crystallographic investigation. A white powder residue is also formed. The crystalline product proved to be the mixed-valence Au(I)/Au(III) isomer **4**. A thermal ellipsoid drawing of this species is given in the Figure 1. This structure is a result of a refinement of 2551 reflections having $I/\sigma(I) > 3.0$. The complex refined in the space group $P2_1/n$ (no. 14) to $R = 0.0391$ and $R_W = 0.0367$ with H atoms included in fixed positions. Tables I and II and supplementary material contain the crystallographic details.

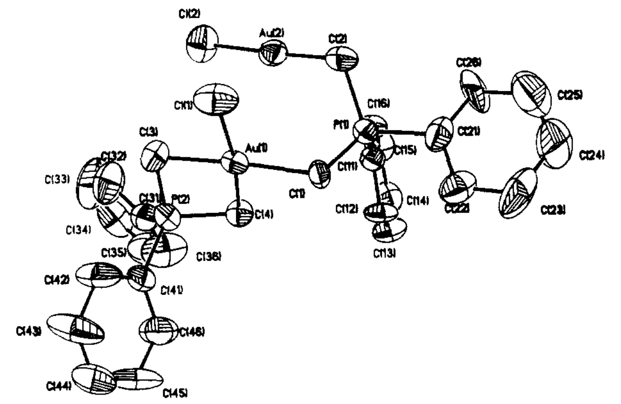


Figure 1. The molecular structure of the mixed-valent Au(III)/Au(I) dimer $ClAu^I$-μ-$[(CH_2)_2PPh_2]Au^{III}Cl[(CH_2)_2PPh_2]$.

Table I. The Crystallographic Data for $ClAu^I$-μ-$[(CH_2)_2PPh_2]Au^{III}Cl[(CH_2)_2PPh_2]$

formula	$Au_2C_{28}H_{28}Cl_2P_2$
fw	891
space group	$P2_1/n$
a,Å	14.4447 (23)
b,Å	10.1119 (20)
c,Å	19.5640 (33)
α, deg	90.0
β, deg	94.050 (14)
γ, deg	90.0
Z = 4	
vol, Å^3	2850.83 (87)
d (calcd),	2.20 g/cm^3
cryst size, mm	0.075 × 0.2 × 0.3
F(000), e	1443.58
μ(Mo Kα), cm^{-1}	105.7
orientat reflctns, number and range	25, 2θ = 20–25°
temp, °C	ambient (22 °C)
scan method	Wycoff ω scan
data collectn range, 2θ, deg	3–48
total reflctns measd	7018
no. of unique data, total with $F_0^2 > 3\sigma(R_0^2)$	2551
max and min transmissn	0.983 and 0.344
check reflctns	3
no. of parameters refined	307
R	0.0391[a]
R_w	0.0367[b]
goodness-of-fit indicator[c]	1.335
largest shift/esd in the final cycle	0.022
largest peak, e/Å^3	0.99
g	0.00016[b]

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum(w)^{1/2}(|F_o| - |F_c|)]/\sum(w)^{1/2}|F_o|$; $w^{-1} = [\sigma^2(|F_o|) + |g|F_o|^2|]$; $g = 0.00016$. [c] Goodness-of-fit = $[\sum w(|\times F_o| - |F_c|)^2/(N - N_p)]^{1/2}$.

Table II. Selected Bond Lengths (Å) and Interactions (Å) for $ClAu^I$-μ-$[(CH_2)_2PPh_2]Au^{III}Cl[(CH_2)_2PPh_2]$

Au(1)-Au(2)	3.184 (1)	Au(1)-Cl(1)	2.349 (4)
Au(1)-C(1)	2.101 (11)	Au(1)-C(3)	2.133 (13)
Au(1)-C(4)	2.067 (13)	Au(2)-Cl(2)	2.310 (4)
Au(2)-C(2)	2.028 (12)	P(1)-C(1)	1.728 (11)
P(1)-C(2)	1.801 (13)	P(2)-C(3)	1.728 (14)
P(2)-C(4)	1.728 (14)	P(2)-C(4)	1.816 (12)
	Average Values		
P-C_{phenyl}	1.810 [20]	C-C_{phenyl}	1.372 [37]

Although the reaction of **2**-Br_2 with methyllithium is thought[2] to produce a mixed-valent species containing two

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Table III. Selected Bond Angles (deg) for $ClAu^{I}$-μ-$[(CH_2)_2PPh_2]Au^{III}Cl[(CH_2)_2PPh_2]$

Au(2)-Au(1)-Cl(1)	86.1 (1)	C(1)-P(1)-C(2)	110.1 (6)
Au(2)-Au(1)-C(1)	87.5 (3)	C(11)-P(1)-C(21)	101.9 (6)
Cl(1)-Au(1)-C(1)	90.1 (4)	C(3)-P(2)-C(4)	95.2 (6)
Au(2)-Au(1)-C(3)	92.2 (3)	C(3)-P(2)-C(31)	117.3 (7)
Cl(1)-Au(1)-C(3)	96.4 (4)	C(4)-P(2)-C(31)	114.3 (7)
C(1)-Au(1)-C(3)	173.4 (5)	C(3)-P(2)-C(41)	110.9 (6)
Au(2)-Au(1)-C(4)	97.0 (3)	C(4)-P(2)-C(41)	109.5 (6)
Cl(1)-Au(1)-C(4)	172.8 (3)	C(31)-P(2)-C(41)	108.9 (6)
C(1)-Au(1)-C(4)	96.4 (5)	Au(1)-C(1)-P(1)	114.6 (6)
C(3)-Au(1)-C(4)	77.0 (5)	Au(2)-C(2)-P(1)	112.0 (6)
Au(1)-Au(2)-Cl(2)	100.0 (1)	Au(1)-C(3)-P(2)	90.5 (6)
Au(1)-Au(2)-C(2)	82.5 (3)	Au(1)-C(4)-P(2)	90.3 (5)
Cl(2)-Au(2)-C(2)	177.5 (3)		
	Average Values		
C-P(1)-C_{phenyl}	111.1 [10]	C-C-C_{phenyl}	120.0 [21]
P-C-C_{phenyl}	120.6 [17]		

bridging methylenediphenylphophoranyl ligands, no crystallographic information has been obtained about the structure. NMR results suggest two distinct methylene groups but do not conclusively rule out several possible asymmetric structures. In fact, Kaska[2] reports the structure to be symmetrical, **2**-Me_2. This confusion could arise because different isomers may occur under different conditions. This certainly appears to be the case with **2**-Cl_2. We have also recently studied the structures of two distinct isomers of the Au(III)/Au(III) tetrabromide $Au_2Br_2(ylide)_2$ and will report these novel results elsewhere.[5]

Although it is not known how **2**-Cl_2 rearranges[6] in CH_3NO_2 from the symmetrical Au(II)/Au(II) dimer to the unsymmetrical Au(III)/Au(I) species, several possibilities exist. Protonation of the Au-Au bridge with concomitant electronic rearrangement would produce two Au(II) centers with exchangeable terminal halogens. Subsequent structural rearrangment of one bridging ylide to form a chelate, followed by hydride migration and reductive loss of a proton, could produce the observed product.

Crystallography. Intensity measurments were made with the Nicolet R3m-E diffractometer. During the data collection three standard reflections were monitored every 97 reflections. The intensities were reduced by applying the Lorentz, polarization, decay, and empirical absorption corrections. The unit cell parameters and the systematic absences are consistent with the monoclinic system, space group $P2_1/n$ (no. 14).

The positions of the two independent Au atoms were derived from the SHELXTL direct methods. The positions of the remaining non-hydrogen atoms were found from successive difference Fourier syntheses and least-squares refinements. The positions of the hydrogen atoms were calculated by using an idealized sp^3-hybridized geometry and fixed C-H bond lengths of 0.960 Å. Anisotropic thermal parameters were used for all atoms except hydrogens.

Au(I) and Au(III) centers belonging to the same molecule remain in close proximity (3.184 Å), despite lack of ligand constraints. There are no intermolecular gold-gold interactions. The closest distance is 4.67 Å between two Au(I) centers. The geometry around Au(III) is square planar and around Au(I) is linear, as expected. The Au(2), Au(1), Cl(2), C(1), C(2), and C(3) atoms are almost planar. There is a slight twist of 10° between the Cl(2)-Au(2)-C(2) and C(3)-Au(1)-C(1) linear arrangements.

Acknowledgment. The National Science Foundation (CHE-8408414) has supported this work. We also thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support and the Welch Foundation for some supplies.

Registry No. **2**-Cl_2, 97571-09-0; **4**, 97571-10-3.

Supplementary Material Available: Tables of atomic positional and thermal parameters and a listing of structure factor amplitudes for **4** (22 pages). Ordering information is given on any current masthead page.

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(5) Dudis, D.; Fackler, J. P., Jr., accepted for publication in *Inorg. Chem.*

(6) H. H. Murray and J. P. Fackler Jr., to be published, have completed the X-ray structure of **2**-Cl_2.

Thermodynamics for the Addition of a Tin Hydride to Carbon Dioxide

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Summary: Tributyltin hydride reacts reversibly with carbon dioxide to yield tributyltin formate. Measurement of the equilibrium constant over the temperature interval 115-175 °C provides $\Delta H = -18.3 \pm 0.2$ kcal mol^{-1} and $\Delta S = -20.2 \pm 0.2$ cal mol^{-1} deg^{-1}.

The organometallic activation of carbon dioxide is currently an active area of interest bearing critically on three diverse areas of catalysis: the mechanism of the water-gas shift reaction[1] (eq 1), the kinetic dependence on

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad (1)$$

carbon dioxide partial pressure in methanol synthesis with commercial CuO/ZnO catalyst[2] (eq 2), and the direct

$$CO + 2H_2 \rightarrow CH_3OH \qquad (2)$$

catalytic methanation[3] (eq 3) possibly employing hydrogen thermally generated from nuclear reactors.[4] An important

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (3)$$

facet of the catalytic chemistry of carbon dioxide is the partial reduction with metal hydride to yield formate ion as indicated in eq 4. Numerous examples of this type of reaction exist[5] yet no thermodynamic data are currently available.

$$M{-}H + CO_2 \rightarrow M{-}OC({=}O)H \qquad (4)$$

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