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.

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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 carbon dioxide partial pressure in methanol synthesis with commercial CuO/ZnO catalyst[2] (eq 2), and the direct catalytic methanation[3] (eq 3) possibly employing hydrogen thermally generated from nuclear reactors.[4] An important 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.

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

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

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

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

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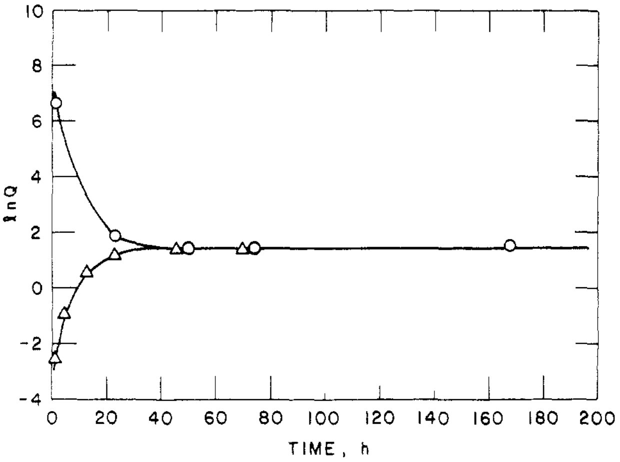

Figure 1. The natural logarithm of the experimental reaction quotients, $Q = [Bu_3SnO_2CH]/[Bu_3SnH]\cdot P_{CO_2}$, vs. time in tetrahydrofuran solution at 150 °C: △, $[Bu_3SnH]_i$ = 0.29 M, $[CO_2]_i$ = 4.5 atm; ○, $[Bu_3SnO_2CH]_i$ = 0.29 M.

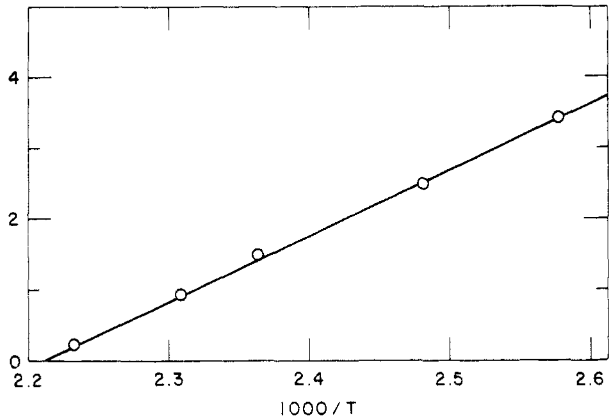

Figure 2. The natural logarithm of the equilibrium constants for tributyltin hydride addition to carbon dioxide in tetrahydrofuran solution vs. the inverse of the temperature over the range 115–175 °C.

Our recent involvement in formate ion disproportionation reactions[6] and a literature report on the synthesis of tin hydride[7] suggested that the tributyltin system (eq 5)

$$Bu_3SnH + CO_2 \rightleftharpoons Bu_3SnO_2CH \qquad (5)$$

might be sufficiently well behaved[8] to obtain accurate equilibrium data. Indeed, the results obtained in tetrahydrofuran solution at 150 °C in Figure 1 (where the experimental reaction quotients[10] defined in eq 6 are plotted

$$Q = [Bu_3SnO_2CH]/[Bu_3SnH]\cdot P_{CO_2} \qquad (6)$$

vs. time) demonstrate that the same equilibrium mixture is obtained by starting with either carbon dioxide plus hydride, triangles, or the corresponding formate ion, circles. Analysis of the temperature dependence of the equilibrium constants thus obtained over the interval 115–175 °C according to the van't Hoff equation in Figure 2 yields $\Delta H = -18.3 \pm 0.2$ kcal mol^{-1} and $\Delta S = -20.2 \pm 0.2$ cal mol^{-1} deg^{-1} from the slope and intercept, respectively. The entropy change is consistent with a condensation reaction which consumed 1 equiv of gas.[12] Interestingly, the enthalpy change for the hydride addition to carbon dioxide (eq 5) is remarkably close to the analogous addition to an olefin[13] (eq 7) for which $\Delta H = -21$ kcal. More important

$$(i\text{-Bu})_2Al\text{-}H + CH_2 = C(CH_3)_2 \rightleftharpoons Al(i\text{-Bu})_3 \qquad (7)$$

however, the enthalpy change for the partial reduction of carbon dioxide according to eq 5 is indeed quite favorable despite *the fact that carbon dioxide is the thermodynamic* end product of many facile reactions. Therefore, carbon dioxide may be a highly reactive component serving to control a steady-state formate ion[14] concentration even in processes which do not result in a net consumption of carbon dioxide. For example, at 200 °C a carbon dioxide partial pressure of only 2 atm is sufficient to maintain roughly equal concentrations of tributyltin formate and tributyltin hydride.[15] It is hoped that by studying homogeneous systems such as that in eq 5 a better understanding of the process in eq 2 may be obtained.[16]

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Registry No. Bu_3SnH, 688-73-3; CO_2, 124-38-9; Bu_3SnO_2CH, 5847-51-8.

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[8] A 300-mL Autoclave Engineers vessel was modified such that all components which contact the solution are made of glass. Tributyltin hydride is decomposed to dihydrogen and hexabutylditin on the surface of metals.[9]

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[10] Tributyltin hydride and tributyltin formate were analyzed by measuring the Sn— and C═O stretching frequencies[11] at 1804 and 1653 cm^{-1}, respectively, with a Perkin-Elmer Model 1500 FTIR. Carbon dioxide was determined by gas chromatography on a 3.5-ft spherocarb column at 100 °C.

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[14] Recently it has been shown that formate ion is catalytically disproportionated to methanol, carbon monoxide, and carbonate ion with a variety of metal oxide catalysis.[6]

[15] While this is the same carbon dioxide partial pressure which was reported to result in a maximum methanol synthesis rate,[2a] the only clear agreement is that carbon dioxide increases the rate of methanol production over CuO/ZnO catalysts[2b] with syngas in eq 2.

[16] The mechanism for the addition of tributyltin hydride to activated olefins and quinones has been reported[17] and will be compared to that for the reaction in eq 5.

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A Novel Reactivity in the Reaction of Cycloheptatetraene with $Pt(PPh_3)_3$

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Summary: A number of allene complexes of $(PPh_3)_2Pt$ have been reported, but in no case has further reaction to form a metallocyclopentane been reported. Two equivalents of cycloheptatetraene react with $(PPh_3)_3Pt$ to form a metallocyclopentane which has been characterized by spectra and X-ray structure analysis. Benzocycloheptatetraene reacts in a like manner. The regiochemistry of this reaction is novel and is not consistent with predictions based on EHMO calculations. It is proposed that the dimerization step has much radical character.

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