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Alkylation of Methylene- and Ylide-Bridged Binuclear Gold(III) Complexes

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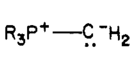
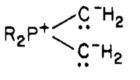
A-Frame complexes of the type $[R_2P(CH_2)_2]_2(AuX)_2CH_2$, where R = CH_3 or C_6H_5 and X = Br or I (**2a–c**) obtained by CH_2X_2 addition to the parent ylide complexes, were alkylated through the reaction with organolithium compounds under carefully controlled conditions. The complexes $[(CH_3)_2P(CH_2)_2]_2(Au\text{-}n\text{-}C_4H_9)_2CH_2$ (**3a**) and $[(C_6H_5)_2P(CH_2)_2]_2(AuCH_3)_2CH_2$ (**3b**) could be isolated and fully characterized. A partially alkylated intermediate $[(C_6H_5)_2P(CH_2)_2]_2(AuCH_3)(AuBr)CH_2$ (**5**) was also separated from the reaction mixture. A single-crystal X-ray structure analysis of **3b**·$C_6H_5CH_3$ confirmed the proposed A-frame constitution based on a boat conformation of the gold ylide heterocycle with the two gold(III) centers in a square-planar environment of four aliphatic carbon atoms ($P\bar{1}$, a = 11.852 (2), b = 13.120 (2), c = 13.715 (1) Å; α = 119.98 (1), β = 97.50 (1), γ = 102.71 (1)°; V = 1727.5 Å^3; d_{calcd} = 1.839 g/cm^3 for Z = 2; R_w = 0.053 for 332 refined parameters and 5038 observations with $F_o \geq 4.0\sigma(F_o)$). Complexes of the composition $[R_2P(CH_2)_2]_2Au_2(CH_3)_2$ are observed as byproducts, but no structural details are available as yet. Thermal decomposition of **3a,b** leads to clean reductive elimination of propane from **3b** but gives a mixture of products from **3a**. The ylide complexes are regenerated in the process.

Introduction

Phosphorus ylides A and their corresponding anions B are powerful ligands for organometallic compounds derived from elements of all parts of the periodic table.[1] A particularly great variety of model compounds has been obtained with gold in its common oxidation states (+I and +III) and even for the more unusual oxidation number +II.[1,2] Special attention has been attributed to novel binuclear species C, in which two gold atoms are held in close transannular proximity by the two bridging ligands of type B.[3-22] Structural[4-6] and reactivity studies[3,7,12]—supported by theoretical calculations[23]—suggest an attractive interaction of the two $5d^{10}6s^0$ metal centers due to a small HOMO–LUMO separation of relativistic origin.[24,25]

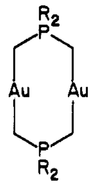

$R_3P^+—\underset{..}{C}{}^-H_2$

A

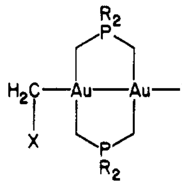


B

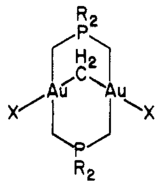
This metal–metal interaction, however weak, is probably also responsible for the ease with which oxidative addition reactions take place that involve both metal atoms.[1-5,12,14-19] Among these the addition of dihalomethanes leading to the bicyclic products E is most remarkable.[26,27] This addition is now known to proceed in two steps. Both the intermediates D and the final products E could be isolated and structurally characterized.[13,26] As part of a continuing study of the chemistry of species C–E, an attempt was made to fully alkylate the two Au(III) metals in compounds E (R = CH_3, C_6H_5). The resulting compounds would contain two tetraorganogold(III) centers which should undergo reductive elimination more readily than the halogenated precursors. Previous experiments with noncyclic mononuclear analogues[2,28] gave clear decomposition



C



D



E

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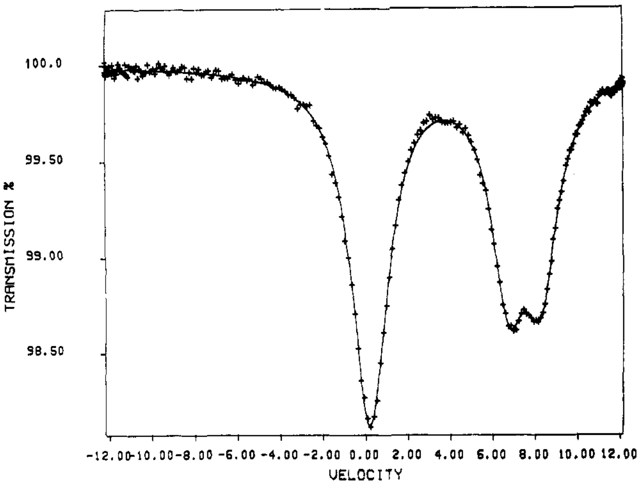
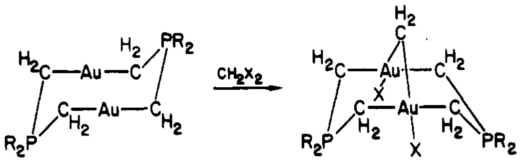


Figure 1. ^{197}Au Mössbauer spectrum of **5** (4 K).

patterns and suggested the experiments with binuclear materials now described in this paper.

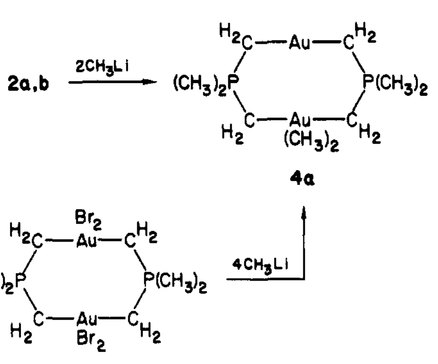


1a, R = CH_3
b, R = C_6H_5

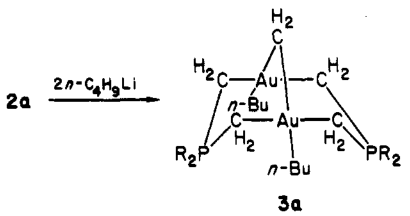
2a, R = CH_3, X = Br
b, R = CH_3, X = I
c, R = C_6H_5, X = Br

Results

Synthesis of Binuclear Complexes. The dimeric compounds **1a,b** are readily available by using established methods.[29] The tetraphenylated homologue **1b** was not fully characterized in previous studies, and some additional spectral data are given in the Experimental Section. The addition of CH_2X_2 also follows published procedures[26,27] (**2a–c**). Alkylation experiments with the dimethylphosphonium bis(methylide) complexes **2a,b** and CH_3Li in tetrahydrofuran did not yield the expected products of a simple halogen substitution at both metal centers. The process is obviously followed by an elimination process. Surprisingly, a mixed-valence dimer **4a** is obtained in good yield. The fate of the CH_2 entity lost in the reaction is as yet unknown. The same compound was also generated a few years ago from the reaction of $[(CH_3)_2P(CH_2)_2AuBr_2]_2$ with 4 equivalents of CH_3Li.[3] Treatment of **2a** with n-C_4H_9Li in tetrahydrofuran at −70 °C finally afforded the desired double alkylation without elimination of the CH_2 bridge. Compound **3a** is a colorless crystalline solid with a melting point of 120 °C, which is easily characterized by analytical and spectroscopic data (Experimental Section).

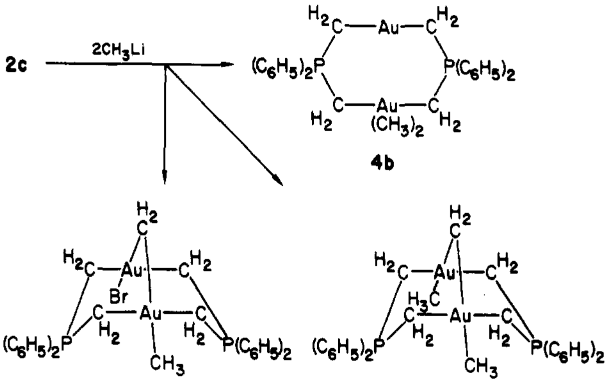


4a



3a

Experiments with the *tetraphenylated* precursor **2c** and CH_3Li as the methylating agent (in tetrahydrofuran at −70 °C) gave a mixture of three products, all of which could be isolated and identified. The dimethylated species **3b** is obtained in 46% yield (71% of total conversion), accompanied by the monomethylated compound **5** (13%) and again a mixed-valence species (**4b**, 16%) in which the CH_2 bridge is absent. The ^1H and ^{13}C NMR spectra of all three compounds are fully consistent with the proposed structures, though the relative orientation of the two CH_3 groups in **4b** (cis or trans) remains to be determined. For **3b** a time-averaged C_{2v} symmetry is indicated in solution, which could be confirmed for the crystalline state by an X-ray diffraction analysis (below). The PCH_2Au hydrogen atoms are inequivalent, as are the phenyl groups attached to phosphorus. The position of the $AuCH_2Au$ group relative to the symmetry elements renders its hydrogen atoms equivalent.



4b

5

3b

For compound **5** the molecular symmetry in solution is reduced to C_s. Accordingly, the PCH_2Au groups give rise to complex ^1H spin multiplets and two ^{13}C resonances as AXX′ sets, but the hydrogen equivalence of the $AuCH_2Au$ group is retained. The postulated inequivalence of the *gold* atoms is borne out by the ^{197}Au Mössbauer spectrum, which features two partially overlapping quadrupole doublets (Figure 1). The values of isomeric shifts and quadrupole coupling constants are in the range expected for this family of compounds.[11,12]

Compound **5** clearly is an intermediate in the synthesis of **3b** from **2c**. Reduced molar quantities of CH_3Li therefore lead to increased yields of this monosubstitution product, but nevertheless an almost constant proportion of **4b** is observed in all runs with different ratios of reactants.

The Molecular Structure of Complex 3b. The structure determination of **3b**·$C_6H_5CH_3$ firmly establishes it as the first methylene-bridged dinuclear Au(III) ylide complex with both Au atoms being exclusively bonded to alkyl groups (Figure 2; Tables I–III). The familiar "A-frame" geometry consists of two exactly planar tetraalkylgold(III) units which form a dihedral angle of 84.7°.

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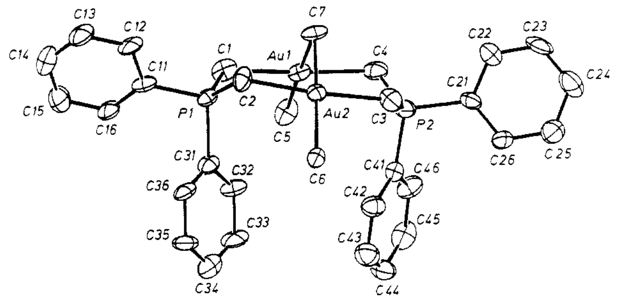


Figure 2. Molecular structure of **3b** and numbering scheme used (ORTEP, thermal ellipsoids at the 50% probability level; hydrogen atoms omitted for clarity).

Table I. Crystal Structure Data for 3b•$C_6H_5CH_3$

formula	$C_{38}H_{44}Au_2P_2$
fw	956.66
space group	$P\bar{1}$ (no. 2)
a, Å	11.852 (2)
b, Å	13.120 (2)
c, Å	13.715 (1)
α, deg	119.98 (1)
β, deg	97.50 (1)
γ, deg	102.71 (1)
V, Å^3	1727.5
Z	2
d_{calcd}, g/cm^3	1.839
$F(000)$, e	920
μ (Mo $K\alpha$)$_{calcd}$, cm^{-1}	85.7
T, °C	-40
radiatn	Mo $K\alpha$, λ = 0.71069 Å
scan mode	ω
$\Delta\omega$, deg	0.8
scan rate, deg/min	0.9–29.3
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	0.595
hkl range	+14,±15,±16
refl unique	6055
refl obsd	5038
param ref	332
R	0.044
R_w	0.053
max shift/error	0.05
$\Delta_{\rho fin}$ (max/min), e/Å^3	+1.5/-1.3

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors for 3b•$C_6H_5CH_3$[a]

atom	x/a	y/b	z/c	U(eq), Å^2
Au1	0.2286 (1)	0.9658 (1)	0.2539 (1)	0.025
Au2	0.1782 (1)	1.1672 (1)	0.2133 (1)	0.022
P1	-0.0346 (3)	1.0125 (3)	0.2520 (3)	0.024
P2	0.4584 (3)	1.1888 (3)	0.3146 (3)	0.027
C1	0.0421 (11)	0.9049 (12)	0.2343 (11)	0.026
C2	-0.0093 (11)	1.0813 (12)	0.1699 (11)	0.029
C3	0.3665 (11)	1.2380 (13)	0.2441 (11)	0.034
C4	0.4131 (11)	1.0270 (12)	0.2612 (10)	0.030
C5	0.2765 (11)	0.9422 (12)	0.3970 (12)	0.030
C6	0.1641 (10)	1.3521 (11)	0.3221 (10)	0.028
C7	0.1881 (12)	0.9881 (11)	0.1135 (9)	0.026
C11	-0.1946 (11)	0.9336 (11)	0.2117 (10)	0.025
C12	-0.2697 (12)	0.8843 (12)	0.1011 (10)	0.027
C13	-0.3913 (12)	0.8181 (13)	0.0722 (11)	0.036
C14	-0.4384 (12)	0.7998 (13)	0.1490 (14)	0.039
C15	-0.3647 (13)	0.8484 (15)	0.2606 (13)	0.045
C16	-0.2426 (11)	0.9157 (12)	0.2902 (10)	0.030
C31	0.0009 (11)	1.1377 (11)	0.4057 (10)	0.026
C32	0.1011 (12)	1.1601 (11)	0.4879 (10)	0.029
C33	0.1264 (12)	1.2577 (13)	0.6039 (10)	0.031
C34	0.0505 (13)	1.3286 (12)	0.6372 (12)	0.034
C35	-0.0476 (13)	1.3050 (12)	0.5553 (10)	0.032
C36	-0.0719 (11)	1.2081 (11)	0.4387 (10)	0.026
C21	0.6065 (11)	1.2388 (11)	0.2989 (10)	0.026
C22	0.6320 (12)	1.1691 (12)	0.1936 (11)	0.032
C23	0.7356 (14)	1.2083 (15)	0.1712 (11)	0.035
C24	0.8188 (14)	1.3243 (15)	0.2538 (14)	0.044
C25	0.7980 (12)	1.3966 (13)	0.3616 (12)	0.040
C26	0.6910 (11)	1.3533 (11)	0.3833 (11)	0.030
C41	0.4779 (10)	1.2741 (11)	0.4691 (10)	0.027
C42	0.4169 (12)	1.3582 (12)	0.5227 (11)	0.033
C43	0.4369 (13)	1.4251 (13)	0.6432 (13)	0.041
C44	0.5207 (13)	1.4131 (13)	0.7132 (11)	0.037
C45	0.5793 (13)	1.3306 (13)	0.6596 (12)	0.034
C46	0.5606 (12)	1.2595 (12)	0.5409 (12)	0.036
CT1	0.1798 (12)	1.4924 (13)	1.0551 (11)	0.098
CT2	0.1701 (12)	1.6011 (13)	1.0652 (11)	0.076
CT3	0.2248 (12)	1.6444 (13)	1.0027 (11)	0.097
CT4	0.2893 (12)	1.5789 (13)	0.9302 (11)	0.080
CT5	0.2991 (12)	1.4702 (13)	0.9200 (11)	0.093
CT6	0.2443 (12)	1.4269 (13)	0.9825 (11)	0.075
CT7	0.1226 (27)	1.4518 (27)	1.1205 (26)	0.134

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

The four alkyl ligands of each Au atom comprise the methylene group, which links both Au centers as the tip of the "A", a terminal methyl group, and one ylidic function of each of the two anionic diphenylphosphonium bis(methylide) moieties. The Au–C distances to the CH_2 groups are equal within standard deviations and are comparable with those in other A-frame complexes of Au,[2,16,20] particularly in the dichloro compound **2** (R = CH_3, X = Cl).[26] The Au–methyl bonds are slightly, but consistently, longer by ca. 0.05 Å. The phosphonium bis(methylide) groups are part of an eight-membered $Au_2P_2C_4$ heterocycle (Figure 2). This eight-membered ring is in a boat conformation with both PPh_2 moieties being bent toward the open side of the "A", away from the bridging CH_2 group. This is at variance with the conformation observed in some of the unbridged $Au_2P_2C_4$ heterocycles, as, e.g., in the dinuclear Au(I) species **1** (R = Et)[5] or the Au(II) compound $Au_2[(CH_2)_2PMe_2]_2(Me)I$[14] which feature chair conformations. (See ref 6 for a similar boat conformation of an unbridged $Au_2P_2C_4$ ring.) The transannular Au···Au distance (3.118 (1) Å) is not very different from that in unbridged rings containing Au(I)[5,6] but is drastically longer than in the Au(II) species where a strong transannular bond has to be assumed.[4,13,14,16] The ring carbon and gold atoms in **3b** are not strictly coplanar. The planes through Au1, Au2, C1, C2 and Au1, Au2, C3, C4 form an angle of 6.4°. The entire eight-membered ring arrangement including the ipso carbon atoms of the phenyl rings approaches C_{2v} symmetry, the most notable exceptions being the ring angles at C1/C3 and C2/C4 which differ by 8°, thereby reducing the overall symmetry to C_2. In fact, the entire molecule including the phenyl rings may be ascribed C_2 symmetry to a good approximation. Most notably, neither the Au coordination geometry nor the bond distances and angles in **3b** differ from cyclic dinuclear or noncyclic mononuclear tetraalkylgold(III) compounds.[1,2] Apparently, the bicyclic arrangement in the A-frame compounds **2** and **3** is relatively strain-free, thus explaining in part its ease of formation.

Reductive Alkane Elimination. Thermal reductive elimination was probed with two peralkylated compounds, **3a** and **3b**. The gaseous products liberated on heating a sample of **3b** to 50–170 °C were investigated by using mass spectrometry. Propane was the dominant hydrocarbon accounting for more than 95% of the volatile material. The residue was identified, also by mass spectrometry, as the parent eight-membered ring compound **1a**. It therefore appears that there is a clear reductive elimination process following a minimum energy pathway on the energy surface of the system, which allows the combination of the two methyl groups with the methylene group bridging the two gold atoms. This observation (eq 1) is in agreement

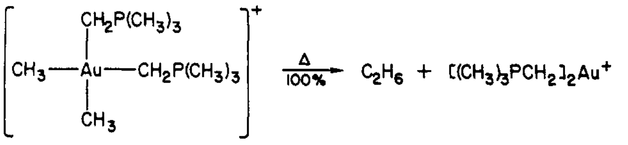
$$\mathbf{3b} \xrightarrow{\Delta} C_3H_6 + [(C_6H_5)_2P(CH_2)_2Au]_2 \qquad (1)$$

Table III. Bond Lengths (Å) and Angles (deg) for 3b[a]

	Bond Distances		
Au1-Au2	3.118 (1)		
Au1-C7	2.10 (1)	Au2-C7	2.09 (1)
Au1-C5	2.16 (1)	Au2-C6	2.18 (1)
Au1-C1	2.11 (1)	Au2-C2	2.11 (1)
Au1-C4	2.13 (1)	Au2-C3	2.11 (1)
P1-C1	1.78 (1)	P2-C3	1.79 (1)
P1-C2	1.78 (1)	P2-C4	1.78 (1)
P1-C11	1.81 (1)	P2-C21	1.81 (1)
P1-C31	1.82 (1)	P2-C41	1.79 (1)
	Bond Angles		
Au1-C7-Au2	96.3 (4)		
C7-Au1-C1	88.7 (5)	C7-Au2-C2	87.1 (5)
C7-Au1-C4	86.8 (5)	C7-Au2-C3	88.0 (5)
C7-Au1-C5	177.9 (5)	C7-Au2-C6	177.6 (5)
C1-Au1-C4	175.5 (5)	C2-Au2-C3	174.8 (5)
C1-Au1-C5	93.2 (5)	C2-Au2-C6	91.6 (5)
C4-Au1-C5	91.3 (5)	C3-Au2-C6	93.4 (5)
Au1-C1-P1	116.4 (7)	Au2-C2-P1	108.1 (6)
Au1-C4-P2	108.8 (6)	Au2-C3-P2	116.4 (7)
C1-P1-C2	115.5 (6)	C3-P2-C4	117.5 (6)
C1-P1-C11	108.5 (6)	C3-P2-C21	104.2 (6)
C1-P1-C31	111.7 (6)	C3-P2-C41	111.2 (6)
C2-P1-C11	108.6 (6)	C4-P2-C21	110.2 (6)
C2-P1-C31	108.0 (6)	C4-P2-C41	108.0 (6)
C11-P1-C31	103.8 (5)	C21-P2-C41	105.0 (5)

[a] Esd's in units of the last significant figure are given in parentheses.

with the decomposition pattern of mononuclear dialkylbis(ylide)gold(III) salts, where ethane gas is formed exclusively (eq 2).[2,28]



$$\left[CH_3-\overset{\overset{\displaystyle CH_2P(CH_3)_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Au}}-CH_2P(CH_3)_3\right]^+ \xrightarrow[100\%]{\Delta} C_2H_6 + [(CH_3)_3PCH_2]_2Au^+ \quad (2)$$

The thermal decomposition of the di-n-butyl compound **3a** is a much more complex process. Mass spectrometry of the species generated in the temperature range from 50 to 170 °C allowed the identification of a large number of decomposition products, with propane again as the dominating volatile component, however. n-Nonane, the combination product of two n-butyl groups and one methylene moiety, was not detected at all. It is unclear as yet how propane and the other hydrocarbons present in the product mixture are formed from **3a**. Highly sophisticated labeling and dilution experiments would be necessary to clarify this point. The clean RCH_2R production in the thermal cleavage of **3b** is therefore unique for this molecule ($R = CH_3$), where β-elimination and other fragmentations are excluded. The propane elimination from **3b** would mechanistically follow the retro pathway suggested by the CH_2X_2 addition to **1b**, where an intermediate with an Au–Au bond (D) is known to play a key role (E → C). Intermolecular mechanisms—possibly involving radicals—can not be excluded at this stage.

Experimental Section

General Data. All experiments were carried out under a pure dried nitrogen atmosphere. Glassware was oven-dried and filled with nitrogen; solvents were dried, distilled, and saturated with nitrogen. The preparation of complexes **1a,b** followed previously published methods[14,29] and was based on pure salt-free ylides $(CH_3)_3PCH_2$ and $CH_3(C_6H_5)_2PCH_2$.[28-30] All other chemicals were purchased or obtained as gifts from chemical industry (see Acknowledgment).

μ,μ'-Bis[diphenylphosphonium bis(methylido)]digold(I) (1b). Obtained from $(CH_3)_3PAuCl$ and $CH_3(C_6H_5)_2P{=}CH_2$ in the molar ratio 1:2 (yield 81%, mp. 226 °C), the compound has the following spectroscopic data: ^1H NMR ($CDCl_3$)[15] δ 1.30 (A_2XX', $N = 13$ Hz, 8 H), 7.15–7.82 (m, 20 H); ^{31}P NMR δ 34.2 (s) $\{^1H\}$; ^{13}C NMR δ 12.4 (AXX′, $N = 57.6$ Hz, CH_2), 128.3 (AXX′, $N = 9.8$ Hz, C_2), 130.6 (AXX′, $N = 7.8$ Hz, C_3), 130.9 (s, C_4), 135.4 (AXX′, $N = 76.2$ Hz, C_1).

(μ-Methylene)-μ,μ'-bis[diphenylphosphonium bis(methylido)]dibromodigold(III) (2c). The compound was prepared from **1b** and excess CH_2Br_2 at 20 °C. The yield was 95% after 30 h: mp 240 °C dec; ^1H NMR ($CDCl_3$)[13] δ 1.65 and 2.52 (ABXX′, $N = 12.0$ and 13.2 Hz, CH_2P), 2.40 (s, CH_2Au_2), 7.0–8.1 (m, C_6H_5); ^{31}P NMR δ 36.4 (s) $\{^1H\}$; ^{13}C NMR δ 14.2, (AXX′, $N = 50.8$ Hz, CH_2P), 32.4 (t, $^3J(PC) = 4.9$ Hz, CH_2Au_2); the C_6H_5 resonances were not resolved (δ 120.8–136.7).

μ,μ'-Bis[dimethylphosphonium bis(methylido)][dimethylgold(III)]gold(I) (4a). Compound **2b** (310 mg, 0.37 mmol) was dissolved in 15 mL of tetrahydrofuran and treated with 0.75 mmol of CH_3Li in diethyl ether at −70 °C. The color changed from orange to yellow. The mixture was allowed to warm to room temperature over a period of 8 h. After evaporation of the solvent under vacuum, a yellow solid remained, which was extracted with toluene; yield 135 mg (61%). The properties and the ^1H NMR spectrum were similar to those of an authentic sample:[1,3] ^{31}P NMR ($CDCl_3$) δ 30.1 (s) $\{^1H\}$; ^{13}C NMR δ 8.5 (s, CH_3Au), 12.2 and 15.9 (AXX′, $N = 51.8$ and 50.8 Hz, respectively, CH_2P), 18.2 (d, $^1J(PC) = 50.8$ Hz, CH_3P).

(μ-Methylene)-μ,μ'-bis[dimethylphosphonium bis(methylido)]di-n-butyldigold(III) (3a). A suspension of 690 mg of compound **2a** (0.925 mmol) in 30 mL of tetrahydrofuran was treated with 1.85 mmol of n-C_4H_9Li in n-hexane at −70 °C. A colorless solution was formed on warming to room temperature. After evaporation of the solvent under vacuum, the residue was extracted four times with 25 mL of pentane. The combined extracts yielded 215 mg of the product (32%), colorless crystals (mp 120 °C) which turn yellow on exposure to air. It is freely soluble in pentane, benzene, diethyl ether, and chloroform: mass spectrum (EI, 70 eV), m/e 700.8 (M^+); ^1H NMR (C_6D_6) δ 0.0–1.65 (m); ^{31}P NMR δ 31.2 (s) $\{^1H\}$; ^{13}C NMR δ 14.7, 29.2, 30.9, 34.1 (s for C_1–C_4 of butyl), 12.0 (AXX′, $N = 53.7$ Hz, CH_2P), 13.3 and 20.3 (AXX′, $N = 67.4$ and 43.9 Hz, respectively, CH_3P), 44.1 (t, $^3J(PC) = 6.8$ Hz, CH_2Au_2). Anal. Calcd for $C_{17}H_{40}Au_2P_2$ (705.4): C, 29.15; H, 5.76; P, 8.84. Found: C, 28.52; H, 5.55; P, 8.76.

(μ-Methylene)-μ,μ'-bis[diphenylphosphonium bis(methylido)]dimethyldigold(III) (3b). **2c** (1.68 g, 1.69 mmol) was dissolved in 15 mL of tetrahydrofuran and treated with 3.53 mmol of CH_3Li in diethyl ether at −70 °C. A clear solution was obtained upon warming the mixture to ambient temperature. A solid remained after evaporation of the solvents, which contained three products (**3b, 5, 4b**). The first of these could be readily extracted with three 10-mL portions of ether (see below). The residue was then extracted with more boiling ether in a Soxhlet apparatus. After 6 h the ether volume contained 674 mg (46%) of product **3b**: yellow-green crystals; mp 145–150 °C dec; mass spectrum (FD, 70 eV), m/e 864 (M^+); ^1H NMR ($CDCl_3$) δ −0.21 (s, CH_3Au), 1.09 (s, CH_2Au_2), 1.50–2.42 (m, CH_2P), 7.06–7.85 (m, C_6H_5); ^{31}P NMR δ 38.7 (s) $\{^1H\}$; ^{13}C NMR (C_6D_6) δ 8.6 (AXX′, $N = 49.8$ Hz, CH_2P), 12.3 (s, CH_3Au), 47.8 (t, $^3J(PC) = 7.8$ Hz, CH_2Au_2), 128.3–132.5 (m, C_6H_5). Anal. Calcd for $C_{31}H_{36}Au_2P_2$ (864.1): Au, 45.57; P, 7.17. Found: Au, 45.05; P, 6.76.

(μ-Methylene)-μ,μ'-bis[diphenylphosphonium bis(methylido)][bromogold(III)]methylgold(III) (5). The residue of the continuous ether extraction (to give **3b**, above) was recrystallized from benzene. Pure **5** (98 mg, 6%) was obtained as a colorless solid: mp 191–192 °C dec; mass spectrum (EI, 70 eV), m/e 912, 914 ($M^+ - CH_4$); ^1H NMR ($CDCl_3$) δ −0.15 (s, $AuCH_3$), 2.07 (s, CH_2Au_2), 1.27–2.67 (two ABXX′ multiplets, CH_2P), 7.0–8.1 (m, C_6H_5); ^{31}P NMR δ 37.8 (s) $\{^1H\}$; ^{13}C NMR 7.7 (s, CH_3Au), 8.5 and 14.5 (AXX′, $N = 49.8$ and 50.8 Hz, respectively, CH_2P), 50.8 (t, $^3J(PC) = 6.35$ Hz, CH_2Au_2), 127.9–132.3 (m, C_6H_5); ^{197}Au

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Mössbauer spectrum (4 K) IS = 3.47 mm s^{-1} and QS 6.52 mm s^{-1}, IS = 4.24 mm s^{-1} and QS = 8.06 mm s^{-1}. Anal. Calcd for $C_{30}H_{33}Au_2BrP_2$ (929.4): Au, 42.39; P, 6.67. Found: Au, 40.61; P, 6.71.

μ,μ′-Bis[diphenylphosphonium bis(methylido)][dimethylgold(III)]gold(I) (4b). The primary ether extract in the preparation of **3b** (above) contained mainly **4b**, which could be recrystallized from toluene: 180 mg (13%) yield; mp 175–180 °C dec; ^1H NMR ($CDCl_3$) δ –0.35 (s, $AuCH_3$), 1.24 and 1.85 ($A_2A'_2XX'$, N = 13.0 and 13.4 Hz, respectively, CH_2P), 7.25–8.05 (m, C_6H_5); ^{31}P NMR δ 32.0 (s) {^1H}; ^{13}C NMR δ 8.0 (s, CH_3Au); 8.4 and 11.4 (AXX′, N = 47.9 and 48.8 Hz, respectively, CH_2P), 127.2–131.7 (m, C_6H_5). Anal. Calcd for $C_{30}H_{34}Au_2P_2$ (850.5): C, 42.37; H, 4.03. Found: C, 42.50; H, 4.19.

Structure Determination of 3b·$C_6H_5CH_3$. Suitable single crystals were obtained from toluene and sealed under argon at dry ice temperature into a glass capillary. Diffractometer measurements (Syntex $P2_1$) indicated a triclinic unit cell which was confirmed by axial photographs. Reduced cell calculations (TRACER) did not indicate any higher symmetry. 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. Pertinent crystal data as well as a summary of intensity data collection and refinement are given in Table I. Data collection and refinement procedures followed closely those described in ref 31.

A total of 6055 unique intensity data were collected on an automated four-circle diffractometer (Syntex $P2_1$) at –40 °C. After correction for Lp effects and for those of absorption (empirical, based on ψ scans of seven reflections near $\chi = 90°$), 964 structure factors with $F_o \le 4.0\sigma(F_o)$ were deemed "unobserved" and not used in all further calculations. A total of 53 structure factors that were evidently mismeasured were additionally suppressed. The structure was solved by Patterson methods and completed by Fourier syntheses. Twelve out of a total of 36 hydrogen atom positions were taken from difference maps, and the rest was calculated at idealized geometrical positions as were those at the toluene molecule (XANADU). Refinement by full-matrix least-squares methods converged at $R = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.044$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF^2]^{1/2} = 0.053$. Thereby all nonhydrogen atoms were refined with anisotropic thermal parameters, with the exception of the toluene molecule which was refined as rigid group with individual isotropic thermal parameters. The H atoms were included in the structure factor calculations as fixed atom contributions and unit weights were used throughout (SHELX 76). A final difference synthesis showed maxima near the toluene and the Au atoms and was otherwise featureless. Reference 31 also contains the sources of the scattering factors and references to the programs used. Table II contains the atomic coordinates; Table III summarizes important distances and angles. Figure 2 gives a view of the molecular structure.

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Registry No. **1b**, 81457-56-9; **2a**, 80387-84-4; **2b**, 80387-83-3; **2c**, 90742-64-6; **3a**, 102133-45-9; **3b**, 102133-46-0; **3b**·$C_6H_5CH_3$, 102133-49-3; **4a**, 55744-47-3; **4b**, 102133-48-2; **5**, 102133-47-1; $(CH_3)_3PAuCl$, 15278-97-4; $CH_3(C_6H_5)_2P{=}CH_2$, 4554-22-7; CH_2Br_2, 74-95-3.

Supplementary Material Available: Tables of anisotropic temperature factors, H atom coordinates, and observed and calculated structure factor amplitudes for **3b**·$C_6H_5CH_3$ (28 pages). Ordering information is given on any current masthead page.

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X-ray Crystal Structure and Molecular Dynamics of (Indenyl)bis(ethylene)rhodium(I): 500-MHz NMR Spectra and EHMO Calculations

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(Indenyl)bis(ethylene)rhodium(I) crystallizes in the monoclinic space group $P2_1/n$ with a = 7.8387 (19) Å, b = 10.9886 (22) Å, c = 25.9379 (78) Å, β = 98.178 (22)°, V = 2211.5 (10) $Å^3$, and Z = 8. The $Rh(C_2H_4)_2$ moiety is displaced from the center of the five-membered ring toward an η^3-bonding mode. The 500-MHz DNMR spectra of the 1-methylindenyl analogue allow an evaluation of the ethylene rotation barrier and also of ML_2 rotation about the Rh–indenyl axis. Extended Hückel molecular orbital calculations were used to probe the mechanisms of these rotation processes.

Introduction

The use of NMR spectroscopy to measure rotational barriers in metal–olefin complexes was first discussed more than 20 years ago in a now classic paper by Cramer.[1] He noted that in the molecule $(C_5H_5)Rh(C_2H_4)_2$ (**1**) the alkene protons could be distinguished by their relative orientations with respect to the cyclopentadienyl ring. Thus the "outside" and "inside" protons could, in principle, be interconverted by a formal rotation about an axis joining the rhodium to the center of the carbon–carbon double bond.

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