their cleavage by different nucleophiles. The stereochemistries were determined through Walden cycles as shown in Scheme III.

We confirmed that the cleavage takes place by nucleophilic attack at silicon since reaction of $(CO)_5MnSiPh_3$ with $LiAlD_4$ gave only Ph_3SiD. The results obtained for the cleavage reaction with $LiAlH_4$ are reported in Table I. The stereochemistry observed was always predominant retention of configuration whatever the nature of the ligands and the structure of the complex (cis or trans).

We cleaved the optically active complex $(CO)_5MnSiMePh(1\text{-}C_{10}H_7)$ with different nucleophiles. Our results are reported in Table II. The stereochemistry is always predominant retention of configuration. This is the first case in which the stereochemistry of nucleophilic displacement at silicon is quite independent of the electronic features of both leaving group and attacking nucleophile. For complexes such as $(CO)_5MnSiR_3$, the leaving group $(CO)_5Mn$, like $(CO)_4Co$, is a poor nucleophile.[8] It should be a good leaving group, and inversion of configuration is the normally expected stereochemistry.[1,2] The replacement of a CO ligand by electron-donating ligands does not change the stereochemistry of the cleavage reaction in contrast to the cobalt–silicon cleavage.[6]

When the electronic character of the nucleophilic reagent was changed, no change in stereochemistry was observed. In particular, we have selected two known examples: (i) the use of $LiAlH_4/LiBr$, instead of $LiAlH_4$, which causes a change in the stereochemistry from predominant inversion to retention of configuration for some fluorosilanes[17] (Table II) and (ii) the addition of MeONa to MeOH, which displaces the stereochemistry from predominant inversion to retention[18] (Table II). Such effects are not observed in the case of the manganese complexes. In all cases a low retention of configuration was obtained. The main difference between cobalt and manganese (or rhenium or tungsten) compounds is their geometry: cobalt complexes are trigonal bipyramidal; the others are octahedral. We believe that this first reported exception to the leaving group rule, observed for octahedral complexes, is certainly connected with their geometry.

Further work is in progress in order to determine whether or not the mechanism is actually the same in the two cases.

Registry No. (*S*)-(−)-$(CO)_5MnSiMePh(1\text{-}C_{10}H_7)$, 81476-81-5; (*R*)-(+)-$(CO)_5MnGeMePh(1\text{-}C_{10}H_7)$, 81476-82-6; *trans*-(*S*)-(−)-$PPh_3(CO)_4MnSiMePh(1\text{-}C_{10}H_7)$, 81476-83-7; *cis*-(*S*)-(−)-$(CO)_4[C(OEt)Me]MnGeMePh(1\text{-}C_{10}H_7)$, 81476-84-8; *cis*-(*S*)-(−)-$(CO)_4[C(OEt)Me]ReGeMePh(1\text{-}C_{10}H_7)$, 81476-85-9; (*R*)-(+)-$MePh(1\text{-}C_{10}H_7)SiH$, 1025-08-7; (*S*)-(−)-$MePh(1\text{-}C_{10}H_7)GeH$, 22430-39-3; $Mn_2(CO)_{10}$, 10170-69-1.

---

(11) $(CO)_5MnM'R_3$ (M′ = Si, Ge) were prepared by thermal reaction at 150° between $(CO)_{10}Mn_2$ and optically active $MePh(1\text{-}C_{10}H_7)M'H$ according to: Jetz, W.; Simons, P. B.; Thompson, J. A. G.; Graham, W. A. G. *Inorg. Chem.* **1966**, *5*, 2217. These compounds were oils, and their optical purity is therefore unknown. Starting with (*R*)-(+)-$MePh(1\text{-}C_{10}H_7)SiH$,[12] we obtained (*S*)-(−)-$(CO)_5MnSiMePh(1\text{-}C_{10}H_7)$ $[\alpha]^{25}_D$ −107° (pentane), and with (*S*)-(−)-$MePh(1\text{-}C_{10}H_7)GeH$,[13] we obtained (*R*)-(+)-$(CO)_5MnGeMePh(1\text{-}C_{10}H_7)$ $[\alpha]^{25}_D$ +60.5° (pentane). We assume in our calculations that these maximum rotations correspond to the optically pure compounds. *trans*-(*S*)-(−)-$PPh_3(CO)_4MnSiR_3$, $[\alpha]^{25}_D$ −150°, was obtained as orange crystals, mp 201–203 °C, from (*R*)-(+)-R_3SiH, according to: Schrieke, R. R.; West, B. O. *Aust. J. Chem.* **1969**, *22*, 49. *cis*-(*S*)-(−)-$(CO)_4[C(OEt)Me]MGeR_3$ (M = Mn, Re) was prepared as in ref 14. All complexes have the same absolute configuration as the starting materials for the same reasons invoked in ref 5 and 6. New complexes gave satisfactory elemental analyses (±0.4 %).

(12) Corriu, R. J. P.; Moreau, J. J. E. *Bull. Soc. Chim. Fr.* **1975**, 901.

(13) Brook, A. G.; Peddle, G. J. D. *J. Am. Chem. Soc.* **1963**, *85*, 1869.

(14) Carré, F.; Cerveau, G.; Colomer, E.; Corriu, R. J. P. *J. Organomet. Chem.*, in press.

(15) Sommer, L. H.; Citron, J. D.; Parker, G. A. *J. Am. Chem. Soc.* **1969**, *91*, 4729.

(16) Cleavage reactions were performed as in ref 4.

(17) Corriu, R. J. P.; Fernandez, J. M.; Guérin, C. *Tetrahedron Lett.* **1978**, 3391.

(18) Sommer, L. H.; Fujimoto, H. *J. Am. Chem. Soc.* **1969**, *91*, 7040.

(19) Reference 1, p 73.

Carbon Monoxide Insertion into a Uranium–Carbon Double Bond. The Structure of $(\eta^5\text{-}C_5H_5)_3U(\eta^2\text{-}OCCH)P(CH_3)(C_6H_5)_2$

Roger E. Cramer,* Richard B. Maynard, Josephine C. Paw, and John W. Gilje*

Department of Chemistry, University of Hawaii
Honolulu, Hawaii 96822

Received December 4, 1981

Summary: The complex $(\eta^5\text{-}C_5H_5)_3U(\eta^2\text{-}OCCH)P(CH_3)(C_6H_5)_2$ crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell of dimensions a = 16.54 (2) Å, b = 10.31 (1) Å, c = 17.372 (9) Å, β = 117.60 (6)°, V = 2962 (4) Å^3, and ρ_{calcd} = 1.51 g/cm^3. The structure has been refined by the least-squares method to the final error indices on F of R_1 = 0.053 and R_2 = 0.063 with 112 variables and 1536 data. The three η^5-cyclopentadienyl ligands and a η^2-β-ketoylide coordinate tetrahedrally about the uranium(IV) ion. Within the η^2-CO unit, the U–O distance 2.27 (1) Å is shorter than the U–C distance 2.37 (2) Å.

We have recently prepared and determined the structure of $(\eta^5\text{-}C_5H_5)_3U{=}CHPR_3$ (1),[1] in which the uranium–carbon bond can be ascribed multiple bond character.[2] Since the availability of 1 presents an opportunity to examine the behavior of the heretofore unknown uranium carbon double bond, we have begun to investigate the chemistry of 1. We report here a facile CO insertion into this bond.

Solutions of 1 in toluene react with CO under atmospheric pressure. At ambient temperature, green toluene solutions of 1 become red within 0.5 h. After concentration and addition of heptane, red crystalline 2 precipitates at −15 °C. Spectroscopic and chemical analysis indicate the formulation shown in eq 1.[3] NMR demonstrates that the Cp_3U and $CHPR_3$ groups retain their integrity and molecular weight measurements show **2a** to be monomeric in benzene solution. Since these data do not determine the details of the carbon monoxide binding, a single-crystal

$$1 + CO(1\text{ atm}) \xrightarrow[25\ ^\circ C]{\text{toluene}} (\eta^5\text{-}C_5H_5)_3U(\eta^2\text{-}OCCH)PR_1R_2R_3 \qquad (1)$$
$$\textbf{2a},\ R_1 = CH_3,\ R_2 = R_3 = C_6H_5$$
$$\textbf{2b},\ R_1 = R_2 = CH_3,\ R_3 = C_6H_5$$

---

(1) Cramer, R. E.; Maynard, R. B.; Gilje, J. W. *Inorg. Chem.* **1981**, *20*, 2466–2470.

(2) Cramer, R. E.; Paw, J. C.; Maynard, R. B.; Gilje, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 3589–3590.

(3) 2a: NMR (^{1}H in C_6D_6, chemical shifts relative to internal C_6H_6, positive shifts downfield) +53.64 (1 H, d, J_{HCP} = 35 Hz), −0.40 (4 H, dd, J_{HCP} = 12 Hz, J_{HCCH} = 7 Hz), −1.09 (2 H, t, J_{HCCH} = 7 Hz, −1.51 (4 H, t, J_{HCCH} = 7 Hz), −6.88 (3 H, d, J_{HCP} = 14 Hz), −18.61 ppm (15 H, s). Anal. Calcd for $UPOC_{30}H_{29}$: C, 53.41; H, 4.34; P, 4.59; mol wt 675. Found: C, 55.65; H, 4.45; P, 4.60; mol wt 719 (cryoscopic in benzene). 2b: NMR (^{1}H in C_6D_6, chemical shifts relative to internal C_6H_6, positive shifts downfield) +56.30 (1 H, d, J_{HCP} = 36 Hz), −0.80 (2 H, dd, J_{HCP} = 12 Hz, J_{HCCH} = 7 Hz), −1.31 (1 H, t, J_{HCCH} = 7 Hz), −1.85 (2 H, t, J_{HCCH} = 7 Hz), −6.07 (6 H, d, J_{HCP} = 14 Hz), −18.58 ppm (15 H, s). Anal. Calcd for $UPOC_{25}H_{27}$: C, 49.02; H, 4.45; P, 5.06. Found: C, 48.09; H, 4.47; P, 5.05.

0276-7333/82/2301-0869$01.25/0

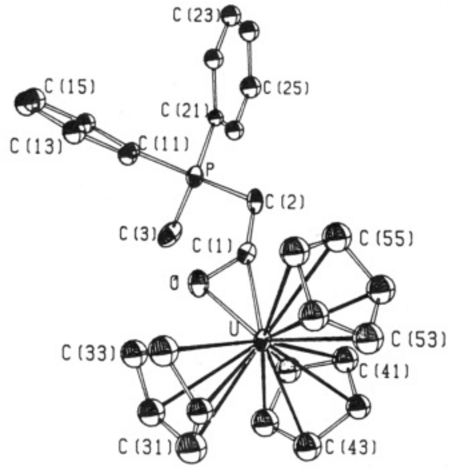


Figure 1. An ORTEP perspective drawing of $(Cp)_3U(OCCH)P(CH_3)(C_6H_5)_2$.

Table II. Bond Lengths (Å) and Angles (Deg) for $(\eta^5\text{-}C_5H_5)_3U(\eta^2\text{-}OCCH)P(CH_3)(C_6H_5)_2$

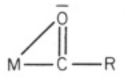
	Bond Lengths		
U-O	2.27 (1)	P-C(2)	1.77 (2)
U-C(1)	2.37 (2)	P-C(3)	1.85 (2)
U-Cp[a]	2.81 (3)	P-C(11)	1.79 (1)
C(1)-O	1.27 (3)	P-C(21)	1.79 (1)
C(1)-C(2)	1.37 (3)		
	Bond Angles		
U-C(1)-C(2)	162 (2)	O-U-C(1)	32 (1)
U-C(1)-O	69 (1)	O-C(1)-C(2)	128 (2)
U-O-C(1)	79 (1)	P-C(2)-C(1)	116 (2)

[a] Average U-C distance for the 15 carbons of the η^5-C_5H_5 rings.

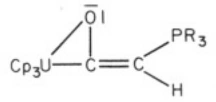
X-ray diffraction study of **2a** was undertaken.

The structure was solved and refined routinely to yield $R_1 = 0.053$ and $R_2 = 0.063$, using procedures and programs which have been previously described.[2] The C_6H_5 and C_5H_5 rings were refined as rigid groups, with individual isotropic thermal parameters, while all other atoms were refined with anisotropic thermal parameters. A summary of X-ray data and results is given in Table I, the molecular structure is shown in Figure 1, and the more important bond lengths and angles are given in Table II. The positional and thermal parameters for the nongroup atoms are listed in Table III, while those for group atoms are listed in Table IV. Figure 1 shows that the carbon monoxide has inserted into the uranium carbon bond forming a β-ketoylide derivative. The CO functionality is η^2 bonded, and, as with many organoactinide complexes, the geometry about uranium is roughly tetrahedral if the Cp centroids and midpoint of the C(1)–O bond are taken to represent vertices of a polyhedron.

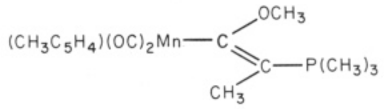
The structure of *2* bears superficial resemblance to $Th[\eta^5\text{-}(CH_3)_5C_5]_2[\eta^2\text{-}(OCCH_2)C(CH_3)_3]Cl$,[4] **3**, $Zr(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}OCCH_3)(CH_3)$,[5] **4**, $Ti(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}OCCH_3)Cl$,[6] **5**, and $[Mo(Cl)(CO)_2[P(CH_3)_3][\eta^2\text{-}(OCCH_2)Si(CH_3)_3]]_2$,[7] **6**, all of which are acyls formed by the insertion of a CO into a metal carbon single bond. Bond lengths in **3**, **4**, **5**, and **6** are consistent with electronic structure A. In the case of **2** insertion has occurred into a four-electron bond permitting the formation of a double C(1)–C(2) bond, 1.37 (3) Å in length. A single proton is observed on C(2) in the NMR and the P–C(2) distance, 1.77 (2) Å, indicates little double or ylidic character.[8] This suggests that a resonance form, B, is important for **2**. However the C(1)–O bond, 1.27 (3) Å, in **2**, while at least 2σ longer than those found for **3**, 1.18 (3) Å,[4] **4**, 1.18 (2) Å,[6] or **5**, 1.211 (8) Å,[5] does not approach the 1.40 Å expected for a C–O single bond, as is found,[8] for example, in This, together with the planarity of atoms U, O, C(1), C(2), and P, suggests a delocalized system and indicates that C, in addition to B, is a contributing resonance form for **2**.

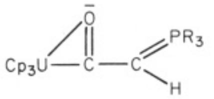


A



B

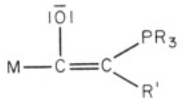




C

As with **3**, and in contrast to **4**, **5**, or **6**,[4] the U–O bond in **2** is shorter than the U–C bond. The U–C distance, 2.37 (2) Å, is comparable to the Th–C distance in **3**, 2.44 (2) Å,[4] after correction is made for the 0.07 Å larger ionic radius of Th(IV).[9] However, the U–O bond in **2**, 2.27 (1) Å,[4] is about 2σ shorter than the similar bond in **3**, 2.37 (2) Å, after correcting for the difference in size of U(IV) and Th(IV). This is consistent with the longer C(1)–O bond in **2**, a greater negative charge on O in **2** than **3**, and a stronger U–O bond in **2**.

While β-ketoylide metal complexes have not yet been prepared via direct reaction of a β-ketoylide with an organometallic reagent, a number of such complexes of the later transition metals have recently been prepared by indirect means.[8,10–13] The bonding in these molecules has been described [8,10] in terms of D on the basis of X-ray structural data. This bears a close resemblance to C except that in **2** both carbon and oxygen coordinate the metal, reflecting the high affinity of actinides toward oxygen.



D

To our knowledge two CO insertion reactions with early transition-metal complexes containing metal–carbon double bonds have been reported. One of these products,

---

(4) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, V. W.; Vollmer, S. H.; Day, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 5393–96.

(5) Fachinetti, G; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946–1950.

(6) Fachinetti, G.; Floriani, C.; Stoeckli-Evans, H. *J. Chem. Soc., Dalton Trans.* **1977**, 2297–2302.

(7) Guzman, C. E.; Wilkinson, G.; Atwood, J. L.; Rogers, R. D.; Hunter, W. E.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1978**, 465–466.

(8) Blau, H.; Malish, W. *Angew. Chem.* **1980**, *92*, 1065–6.

(9) Raymond, K. *Acc. Chem. Res.* **1980**, *13*, 276–283.

(10) Blau, H.; Malish, W.; Voran, S.; Blank, K.; Krüger, C. *J. Organomet. Chem.* **1980**, *202*, C33–C38.

(11) Malish, W.; Blau, H.; Schubert, U. *Angew. Chem.* **1980**, *92*, 1063–5.

(12) Knoll, L. *Chem. Ber.* **1978**, *111*, 814–816.

(13) Malish, W.; Blau, H.; Voran, S. *Angew. Chem.* **1978**, *90*, 827–8.

$(\eta^5\text{-}C_5H_5)_2(Cl)Zr[(OCCH)P(C_6H_5)_3]$,[14] which has been chemically but not structurally characterized would seem to be a close analogue of **2**. The second is an incompletely characterized product formed from the reaction of $(\eta^5\text{-}C_5H_5)_2(Cl)Ta{=}CH(C(CH_3)_3)$ with CO.[15] Since a structure of this molecule is not available, we can not yet compare our product with those from analogous reactions with alkylidenes.

Registry No. 1a, 77357-86-9; **1b**, 77357-85-8; **2a**, 81388-97-8; **2b**, 81388-96-7.

Supplementary Material Available: Crystal and data collection data (Table I), nongroup atom positional and thermal parameters with standard deviations for $(\eta^5\text{-}C_5H_5)_3U(OCCH)P(CH_3)_2(C_6H_5)$ (Table III), positional and thermal parameters for group atoms (Table IV), and observed and calculated structure factors (Table V) (10 pages). Ordering information is given on any current masthead page.

---

[14] Baldwin, J. C.; Keder, N. L.; Strouse, C. E.; Kaska, W. C. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1980**, *35B*, 1289–1297.

[15] Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104.

Oxidative Addition of Methyl Iodide to a Dinuclear Gold(I) Complex. The X-ray Crystal Structure of Bis[μ-(dimethyldimethylenephosphoranyl-*C*,*C*)]-iodomethyldigold(II)(*Au*-*Au*), $Au_2[(CH_2)_2P(CH_3)_2]_2(CH_3)I$

John P. Fackler, Jr.,* and John D. Basil

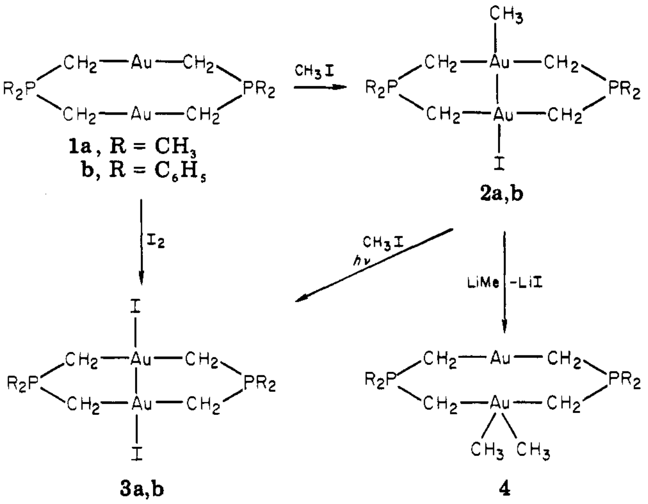
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

Received November 30, 1981

Summary: The oxidative addition of alkyl halides to dinuclear species may produce two-electron oxidation at a single center or one-electron oxidation at each of the two centers. X-ray crystallographic structural studies show that the product of CH_3I addition to dinuclear gold(I) ylide complexes occurs with the formation of one-electron oxidation at each center and a Au-Au band (2.695 (4) Å).

The oxidative addition of alkyl halides and related species to transition-metal complexes plays an important role in many M–C bond-forming reactions and transition-metal-mediated catalytic processes.[1] While oxidative addition has been studied in detail for reactions which occur at a single metal center,[1] few well defined examples involving two or more metal atom centers can be found. Gray and co-workers[2] have reported the oxidative addition of CH_3I to $Rh_2(bridge)_4^{2+}$, but only spectroscopic data exist concerning the nature of the product. Similarly Schmidbaur and co-workers[3] have reported that CH_3I adds to **1a** to produce **2a**. Due to the photosensitivity of the product, our initial attempts to reproduce these results (to obtain a crystalline product) failed. Instead **3a** was obtained along with **1a** and methylated products. The structures of both **1a** and **3a** have been determined previously in our laboratory.[4]

Scheme I



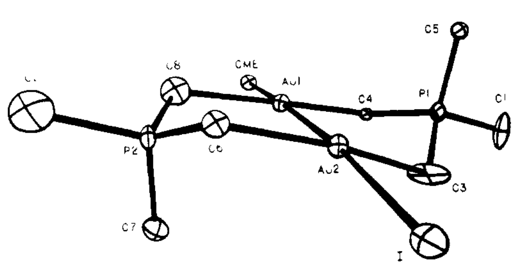


Figure 1. ORTEP drawing (50% probability) of bis[μ-(dimethyldimethylenephosphoranyl-*c*,*c*)]-iodomethyldigold(II)(Au–Au). Important distances (in Å): Au(1)–Au(2) = 2.695 (4); Au(1)–CMe = 2.13 (5); Au(2)–I = 2.894 (5); Au–CH_2(av) = 2.14; P–CH_2(av) = 1.70; P–CH_3(av) = 1.79. Some angles (in deg): CMe–Au(1)–Au(2) = 177.5 (1.9); Au(1)–Au(2)–I = 175.1 (2); C(4)–Au(1)–Au(2) = 90.4 (1.7); C(6)–Au(2)–Au(1) = 91.0 (2.0); C(6)–P(2)–C(8) = 112 (3).

Added incentive for a detailed structural characterization of **2** stems from the reported observation[19] that **2** reacts with $LiCH_3$ to produce the asymmetric mixed-valent species **4**.

Synthesis. The dimer **1a** was prepared by established methods.[3,5] Using the same procedure with Ph_2PMe (Strem), **1b** was also synthesized. The synthesis of **2a** and **2b** proceeded essentially as described,[3] except that rigorous precautions were taken to prevent solutions of the products from being exposed to light. Dry 1,2-dichloroethane (stored over P_4O_{10}) was used as the solvent. Products were isolated by first filtering, adding a twofold excess of dry ($CaCl_2$) heptane, and cooling the solution to −18 °C overnight. The resulting yellow crystalline products were washed (in air) with a few milliliters of cold toluene and then with diethyl ether: yield 60–70%; for **2a** mp 142–145 °C (lit.[3] 143 °C); for **2b** mp 172 °C dec. Anal. Calcd for

---

[1] Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980.

[2] Lewis, N. S.; Mann, K. R.; Gordon II, J. G.; Gray, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 7461–7463.

[3] Schmidbaur, H.; Franke, R. *Inorg. Chim. Acta* **1975**, *13*, 85–89.

[4] H.-W. Chen, C. Paparizos, and J. P. Fackler, Jr., to be submitted for publication. Crystallographic data: **1a**, $[CH_3)_2P(CH_2)_2Au^I]_2$, monoclinic space group C_2/c, $a = 10.292$ (4) Å, $b = 9.622$ (4) Å, $c = 13.063$ (3) Å, $\beta = 95.27$ (2)°, $Z = 4$, 985 data with $\theta \leq 25°$, and I/σ (I) ≥ 3.0, $\mu = 236.4$ cm^{-1}, $R = 12.8\%$ with anistropic Au and no absorption correction; **3a**, $[(CH_3)_2P(CH_2)_2Au^{II}I]_2$, monoclinic space group $P2_1/c$, $a = 6.252$ (3) Å, $b = 12.064$ (7) Å, $c = 11.559$ (3) Å, $\beta = 101.20$ (3)°, $Z = 2$, 1164 data with $I/\sigma(\mathrm{I}) \geq 3.0$, $\mu = 214.58$ cm^{-1}, $R = 14.5\%$ with anisotropic Au and I and no absorption correction. Bond distances (Å): for **1a**, Au–Au = 3.005 (3), Au–CH_2 = 2.23 and 2.16; for **3a**, Au–Au = 2.654 (4), Au–I = 2.699 (8), Au–CH_2 = 2.23 and 2.10.

[5] Schmidbaur, H. "Inorganic Syntheses"; Douglas, B. E., Ed.; Wiley Interscience: New York, 1978; Vol. XVIII, p 138.

0276-7333/82/2301-0871$01.25/0