reported in the literature involving metal carbonyls containing phosphine oxides and formate ligands.[12] Further evidence was found in the substitution of acyl complexes as observed by Brown and Bellus.[13] Lin and Lu[14] also observed a similar labilizing effect in their study of the addition of iodine to the metal-metal bond of a (carboxamido)triosmium cluster.

It is interesting that complex **3** is converted into the hydrido complexes (μ-H)$Os_3(CO)_9$(μ_2-CONHR')(CNR) (**4a,b**)[15] with the elimination of amine when passed through silica gel. It is most likely that the protonation of **3** by the acidic sites on silica gel, with a consequent elimination of amine, and protonation of the metal-metal bond followed by deprotonation of aminocarbyne lead to the formation of the bridging hydrido complex **4**. Preliminary results obtained when **3** was treated with acetic acid in CH_2Cl_2 at room temperature show that **4** is formed in 50-60% yield. This result is in agreement with the suggestion that the acidic sites on silica may be responsible for the transformation observed. The process of protonation/elimination of amine ultimately creates a vacant site on the Os atom which accommodates the isocyanide ligand. The ^{1}H NMR spectrum of **4a** showed there are three hydride peaks at δ −13.62, −14.24, and −15.06, which may be attributed to the three isomers with different locations of the bridging hydride. The interesting feature of this transformation is that it led to the re-formation of an Os-Os bond which was initially broken. The ready elimination of amine instead of CO during the regeneration of the isocyanide ligand supports the fact that the Os-N bond is weaker than the Os-C bond.

In conclusion, the coordinated isocyanide ligand was observed to mediate the reactivity of the osmium cluster throughout the cluster's reaction with amines. When the isocyanide accepts a hydrogen atom to form the bridging carbyne and the carbamoyl ligand converts to the bridging carboxamido group, the osmium cluster is doubly bridged and cleavage of the Os-Os bond takes place instead of CO elimination. In these reactions the transformations of the coordinated isocyanide, first into the bridging carbyne and then back into the isocyanide with the cleavage and re-formation of the Os-Os bond, most likely play an important role in the reactivity of these osmium clusters. Further investigation regardig the labilizing behavior of the O-attacked μ-carboxamido ligand in osmium isocyanide complexes as well as the reactions of these complexes with nucleophilic reagents is in progress.

Acknowledgment. We thank the National Science Council of the Republic of China for financial support. Valuable suggestions from the reviewers are appreciated.

Registry No. **1a**, 138957-26-3; **1b**, 138957-27-4; **1c**, 61993-50-8; **2a** (*E* isomer), 138957-28-5; **2a** (*Z* isomer), 138957-29-6; **2b** (*E* isomer), 138957-30-9; **2b** (*Z* isomer), 138957-31-0; **2c** (*E* isomer), 138957-32-1; **2c** (*Z* isomer), 138957-33-2; **3a** (*Z* isomer), 138957-34-3; **3a** (*E* isomer), 138957-34-3; **3b** (*E* isomer), 138957-35-4; **3b** (*Z* isomer), 138957-36-5; **3c** (*E* isomer), 138957-37-6; **3c** (*Z* isomer), 138957-38-7; **4a**, 138957-39-8; **4b**, 138957-40-1; NH_2Pr, 75-31-0.

Supplementary Material Available: A table of analytical and spectroscopic data and tables of atomic coordinates, crystal and intensity collection data, anisotropic thermal parameters, and bond lengths and angles (8 pages); a table of structure factors (13 pages). Ordering information is given on any current masthead page.

---

(12) (a) Darensbourg, D. J.; Walker, N.; Darensburg, M. Y. *J. Am. Chem. Soc.* **1980**, *102*, 1213. (b) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S.; Kuddararoski, R. *Inorg. Chem.* **1982**, *21*, 1656. (c) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3155.

(13) Brown, T. L.; Bellus, P. A. *Inorg. Chem.* **1978**, *17*, 3726.

(14) Lu, K. L.; Lin, Y. C.; Wang, Y. *Organometallics* **1990**, *9*, 1320.

(15) (μ-H)$Os_3(CO)_9$(μ_2-CONHPr^i)(CNPh) (**4a**): The complex **3a** (100 mg, 0.10 mmol) was chromatographed on a silica gel column with CH_2Cl_2/hexane (10:90) as eluent to afford **4a** (73 mg, 0.07 mmol, 75%). Anal. Calcd for $C_{20}H_{14}N_2O_{10}Os_3$: C, 23.72; H, 1.39. Found: C, 23.62; H, 1.35. IR (*n*-hex): ν_{CN} = 2158 (w), ν_{CO} = 2053 (s), 2033 (s), 1994 (br), 1961 (sh) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.14-7.39 (Ph), 5.56 (d, 1 H, μ_2-CON*H*), 3.90 (m, 1 H, C*H*Me$_2$), 0.98 (d, 6 H, C*H*$_3$), −15.06, −14.24, −13.62 (s, Os-H-Os, three isomers). MS (EI): *m/z* 1017 (M^+), 988 (M^+ − CO), 960 (M^+ − 2CO), 931 (M^+ − 3CO), 911 (M^+ − CO − Ph), 886 (M^+ − 2CO − Ph).

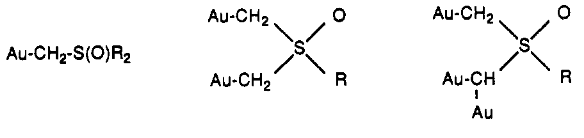
Synthesis of Bi- and Tetranuclear Sulfur Ylide Complexes of Gold(I) by Phase-Transfer-Catalysis Techniques

Ivan J. B. Lin,*,† C. W. Liu,† Ling-Kang Liu,*,‡ and Yuh-Sheng Wen‡
Department of Chemistry, Fu Jen Catholic University, Hsinchuang, Taipei 242, Taiwan, and Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan

Received December 23, 1991

Summary: The luminescent binuclear sulfur ylide gold compound {Au_2(dppm)[$(CH_2)_2S(O)N(CH_3)_2$]}BF_4 (**1**; dppm = $Ph_2PCH_2PPh_2$) and the tetranuclear sulfur ylide gold compound {Au_4(dppm)($Ph_2PCHPPh_2$)[(μ-CH)(CH_2)S(O)N(CH_3)$_2$]}BF_4 (**2**) have been synthesized by phase-transfer-catalysis techniques. Crystal structure studies show that the molecules of **1** are packed pairwise with shorter inter- than intramolecular Au···Au distances and that **2** has triply bridging $Ph_2PCHPPh_2^-$ and (CH)(CH_2)S(O)N(CH_3)$_2^{2-}$ ligands.

In contrast to the analogous phosphorus ylide complexes,[1] sulfur ylide complexes of gold are rare.[2] In the known gold complexes,[2] sulfur ylide coordinated as a terminal ligand (type A). To our knowledge, a gold com-



A B C

plex with a type B or C bonding mode has never been reported. Type C bonding is not even known for other

---

[†] Fu Jen Catholic University.

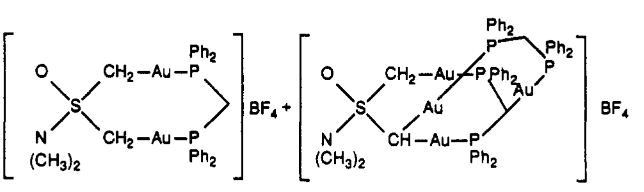
[‡] Academia Sinica.

(1) (a) Schmidbaur, H. *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 907. (b) Kaska, W. C. *Coord. Chem. Rev.* **1983**, *48*, 1.

(2) (a) Fackler, J. P., Jr.; Paparizos, C. *J. Am. Chem. Soc.* **1977**, *99*, 2363. (b) Stein, J., Fackler, J. P., Jr.; Paparizos, C.; Chen, H. W. *J. Am. Chem. Soc.* **1981**, *103*, 2192. (c) Weber, L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 516. (d) Yamamoto, Y. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1189. (e) Konno, H.; Yamamoto, Y. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2561.

0276-7333/92/2311-1447$03.00/0

metal complexes. We have recently reported the use of phase-transfer-catalysis (PTC) techniques in the synthesis of sulfur and mixed sulfur–phosphorus ylide complexes of palladium and platinum.[3-5] This technique is especially useful in the synthesis of sulfur ylide complexes in which the sulfur ylide behaves either as a chelating ligand or as a monodentate ligand. We have also noted that if dppm (dppm = $Ph_2PCH_2PPh_2$) was present in the above reaction, base hydrolysis of the P–C bond in dppm complexes was observed.[6] In this paper we wish to report an interesting result in the reaction of $Au_2(dppm)Cl_2$ with $[(CH_3)_2S(O)N(CH_3)_2]BF_4$ under PTC conditions. In this reaction the dppm ligand was not hydrolyzed and the sulfur ylide with type B or C bonding mode was obtained (eq 1). One of the compounds, having shorter inter- than intramolecular Au···Au distances in the solid, shows luminescent properties in both the solid and solution states.



1 2 (1)

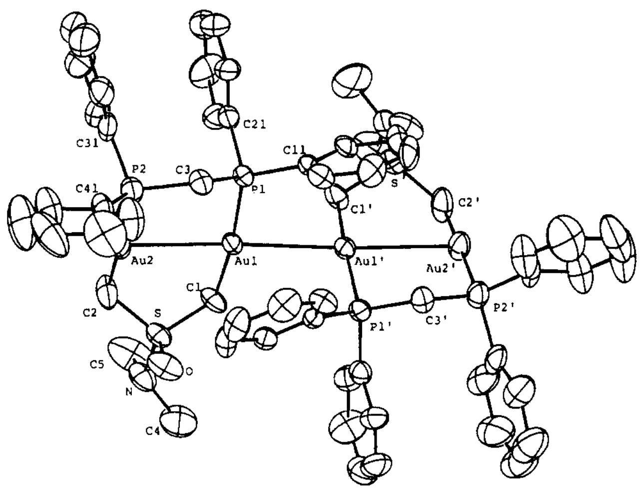


Figure 1. ORTEP drawing of 1. Selected structural parameters are as follows. Bond distances (Å): Au1–P1, 2.289 (3); Au1–C1, 2.088 (12); Au2–P2, 2.274 (4); Au2–C2, 2.097 (14); Au1···Au1′, 2.959 (1); Au1···Au2, 2.984 (1). Bond angles (deg): P1–Au1–C1, 172.8 (4); P2–Au2–C2, 176.7 (4). Torsional angles (deg): P1–Au2···Au2–P2, −11.1 (1); P1–Au1···Au2–C2, 165.7 (4); C1–Au1···Au2–P2, 174.4 (3); C1–Au1···Au2–C2, −8.9 (5); P1–Au1···Au1′–P1′, 94.5 (1); P1–Au1···Au1′–C1′, −90.6 (3); C1–Au1···Au1′–C1′, 84.3 (4).

Reaction of $Au_2(dppm)Cl_2$[7] (0.7 mmol) with $[(CH_3)_2S(O)N(CH_3)_2]BF_4$[8] (0.84 mmol) in CH_2Cl_2 (10 mL) under basic PTC conditions produced the greenish binuclear compound $\{Au_2(dppm)[(CH_2)_2S(O)N(CH_3)_2]\}BF_4$, (1; 52% yield)[9] and the white tetranuclear compound $\{Au_4(dppm)(Ph_2PCHPPh_2)[(\mu\text{-}CH)(CH_2)S(O)N(CH_3)_2]\}BF_4$, (2; 20% yield).[9] Compounds 1 and 2 were characterized[10] by UV–vis and ^1H and ^{31}P NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction.[11] The crystal structure of 1, consisting of discrete digold cations, is shown in Figure 1. The cation is an eight-membered dimetallacycle with two Au atoms being doubly bridged by a $(CH_2)_2S(O)NMe_2^-$ ligand and a dppm ligand; the C–Au–P fragments are linear. To our knowledge, this is the first example of a gold compound having a bridging $(CH_2)_2S(O)NMe_2^-$ ligand. The eight-membered ring is in a boat conformation with the S atom and methylene C atom of dppm as the head and tail. The most interesting features of the structure are that two C_2-related cations are packed together such that four Au atoms are in a row, with the intermolecular Au1···Au1′ distance (2.959 Å) shorter than the intramolecular Au1···Au2 distance (2.984 Å), and the six-atom plane (Au1, Au2, P1, P2, C1, and C2) in one cation is perpendicular to the corresponding plane in the C_2-related cation. Compound 1 with a PF_6 anion instead of a BF_4 anion was also structurally determined by X-ray diffraction. The intermolecular Au···Au distance is also shorter than the intramolecular one (2.913 vs 2.956 Å). Eight-membered digold ring compounds having short Au···Au distances are known;[12] however, the presence of shorter inter- than intramolecular Au···Au distances is rather unusual.[12d] For instance, a chainlike tetragold(I)

---

[3] (a) Lin, I. J. B.; Lai, H. Y. C.; Wu, S. C.; Hwan, L. *J. Organomet. Chem.* **1986**, *309*, 225. (b) Wu, R. F.; Lin, I. J. B.; Lee, G. H.; Cheng, M. C.; Wang, Y. *Organometallics* **1990**, *9*, 126.

[4] Lin, I. J. B.; Shy, H. C.; Liu, C. W.; Liu, L.-K.; Yeh, S.-K. *J. Chem. Soc., Dalton Trans.* **1990**, 2509.

[5] Lai, J. S.; Wu, R. F.; Lin, I. J. B.; Cheng, M. C.; Wang, Y. *J. Organomet. Chem.* **1990**, *393*, 433.

[6] (a) Lin, I. J. B.; Lai, J. S.; Liu, C. W. *Organometallics* **1990**, *9*, 530. (b) Lin, I. J. B.; Lai, J. S.; Wen, Y. S.; Liu, L.-K. *J. Organomet. Chem.* **1990**, *399*, 361.

[7] Schmidbaur, H.; Wohlleben, A.; Wagner, F.; Orama, O.; Huttner, G. *Chem. Ber.* **1977**, *110*, 1748.

[8] Johnson, C. R.; Rogers, P. E. *J. Org. Chem.* **1973**, *38*, 1793.

[9] To $Au_2(dppm)Cl_2$ (0.70 mmol) and $[(CH_3)_2S(O)N(CH_3)_2]BF_4$ (0.84 mmol) in 10 mL of CH_2Cl_2 was added 0.04 mmol of $(n\text{-}Bu)_4NCl$ as the phase-transferring agent followed by 3 mL of NaOH (0.46 N). The resultant solution was stirred at room temperature for 8 h. The organic layer was then separated, washed with 10 mL of H_2O four times, and dried by a vacuum rotary evaporator. The crude product (yield >80%) was recrystallized from a CH_3OH–CH_2Cl_2 mixture (20:1 by volume). White crystals (compound **2**) precipitating in the early stages were filtered (20% yield), and the filtrate was slowly evaporated to give a 52% yield of greenish yellow crystals (compound 1) appropriate for an X-ray diffraction study. Crystals of **2** suitable for an X-ray diffraction study were obtained from the slow diffusion of ether into the CH_2Cl_2 solution of 1.

[10] Compound 1: mp 220 °C dec; ^{31}P NMR ($CDCl_3$, 85% H_3PO_4 standard) δ 36.4 ppm; ^1H NMR ($CDCl_3$, TMS standard) δ 7.6 (m, 20 H, C_6H_5), 3.67 (m, 2 H, SCH_2), 3.41, 3.24 (t, d, 2 H, $J(HH) = 13.9$ Hz, $J(HP) = 12.0$ Hz, P_2CH_2), 2.94 (s, 6 H, NCH_3), 2.70 (m, 2 H, SCH_2); UV–vis (CH_2Cl_2) λ_{max} 279 nm (ϵ_{max} 4×10^5 M^{-1} cm^{-1}), λ_{max} 478 nm (ϵ_{max} 4×10^3 M^{-1} cm^{-1}), emission 435 and 500 nm (CH_2Cl_2); FAB/MS *m/e* 898 (M − BF_4). Anal. Calcd for $C_{29}H_{32}BF_4NOP_2SAu_2$: C, 35.3; H, 3.3; N, 1.4. Found: C, 35.3; H, 3.2; N, 1.3. Compound 2: ^{31}P NMR ($CDCl_3$, 85% H_3PO_4 standard) δ 36.4 (d, $J(PP) = 14$ Hz), 36.3 (d, $J(PP) = 14$ Hz), 32.9 (d, t, $J(PP) = 52, 14$ Hz), 28.0 (d, $J(PP) = 52$ Hz); ^1H NMR ($CDCl_3$, TMS standard) δ 8.0–6.8 (m, 40 H, C_6H_5), 3.9–3.5 (m, 4 H, PCH_2, PCH, SCH), 3.03 (s, 6 H, NCH_3), 2.54 (m, 1 H, SCH), 2.34 (m, 1 H, SCH); FAB/MS *m/e* 1674 [M − (BF_4 + H_2O)]. Anal. Calcd for $C_{54}H_{54}BF_4NO_2P_4SAu_4$: C, 36.5; H, 3.1; N, 0.8. Found: C, 36.6; H, 3.0; N, 0.8.

[11] Crystal data for 1: $C_{29}H_{32}Au_2NOP_2SBF_4$; formula weight 985.31; monoclinic, space group *C*2/*c*; $a = 22.799$ (3) Å, $b = 11.590$ (2) Å, $c = 24.662$ (5) Å; $\beta = 104.80$ (1)°; $V = 6300.4$ (18) Å^3; $Z = 8$; $D_c = 2.078$ g/cm^3; $F(000) = 1923.51$; Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation, $\lambda = 0.7093$ Å; $\mu = 4.77$ mm^{-1}; minimum and maximum transmission factors 0.607 and 0.999; 4113 unique reflections; 2079 observations with $I_o > 2.5\sigma(I_o)$; refinement of 73 atoms and 325 parameters with non-H atoms varied anisotropically, BF_4 positions fixed but thermal parameters varied isotropically, and H atoms fixed ideally converging to $R = 0.034$, $R_w = 0.040$, GOF = 1.80. Crystal data for **2**: $C_{54}H_{52}Au_4NOP_4SBF_4 \cdot H_2O$; formula weight 1779.65; triclinic space group $P\bar{1}$, $a = 13.063$ (3) Å, $b = 13.584$ (3) Å, $c = 16.876$ (3) Å; $\alpha = 95.93$ (2)°, $\beta = 89.90$ (2)°, $\gamma = 103.47$ (2)°; V 2896.0 (10) Å^3; $Z = 2$; $D_c = 2.041$ g/cm^{-3}, $F(000) = 1667.54$, Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation, $\lambda = 0.7093$ Å; $\mu = 10.27$ mm^{-1}; minimum and maximum transmission factors 0.640 and 1.000; 7425 unique reflections; 4867 reflections with $I_o > 2.06\sigma(I_o)$ used in refinement; non-H atoms refined anisotropically, except anionic BF_4 and hydrate O atoms; final block-diagonal least-squares cycle of 125 atoms and 826 parameters converged to $R = 0.057$, $R_w = 0.067$, GOF = 2.48.

[12] (a) Jones, P. G. *Gold Bull.* **1981**, *14*, 102. (b) Jones, P. G. *Gold Bull.* **1983**, *16*, 114. (c) Jones, P. G. *Gold Bull.* **1986**, *19*, 46. (d) Schmidbaur, H. *Gold Bull.* **1990**, *23*, 11. (e) Balch, A. L.; Fung, E. Y.; Olmstead, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 5181.

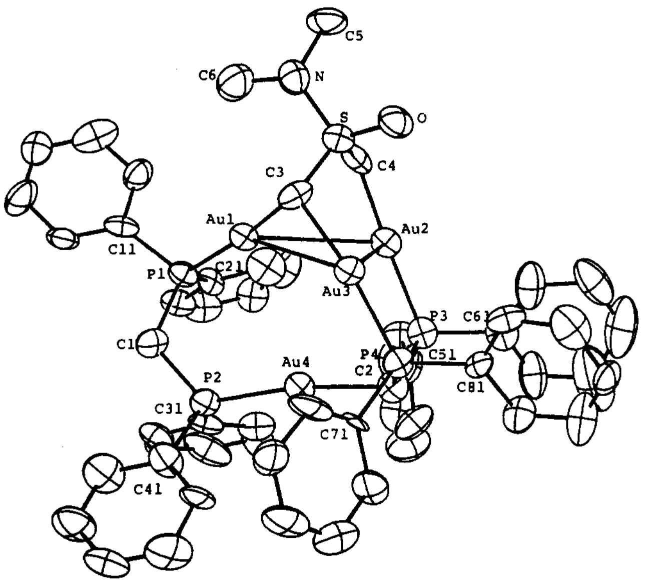


Figure 2. ORTEP drawing of 2. Selected bond lengths and angles are as follows. Bond distances (Å): Au1–P1, 2.264 (7); Au1–C3, 2.05 (3); Au2–P3, 2.305 (8); Au2–C4, 2.11 (3); Au3–P4, 2.293 (7); Au3–C3, 2.084 (24); Au4–P2, 2.295 (7); Au4–C2, 2.15 (3); Au1···Au2, 3.394 (2); Au1···Au3, 3.305 (2); Au1···Au4, 3.711 (2); Au2···Au3, 2.993 (2); Au2···Au4, 3.922 (2); Au3···Au4, 3.635 (2). Bond angles (deg): P1–Au1–C3, 174.2 (7); P3–Au2–C4, 176.6 (8), P4–Au3–C3, 167.5 (7); P2–Au4–C2, 170.2 (8); Au1–C3–Au3, 94.4 (10).

compound reported by Balch et al.[12e] has a constrained central Au···Au interaction (2.965 Å) shorter than the nonconstrained external Au···Au separation (3.096 Å). 1 exhibits green luminescence in the solid state but yellow luminescence in CH_2Cl_2 solution. It is likely that the intermolecular interaction may be responsible for the green luminescent behavior of solid 1. In solution, the emission consists of a broad band with a maximum at 435 and 500 nm; the corresponding excitation maximum is at 279 and 478 nm. Study of the luminescent properties of organometallic complexes is a rapidly growing area of interest,[13] especially complexes with d^{10} or s^2 electronic configurations.[14]

The formation of 2 can be explained by eq 2. Once

$$Au_2(dppm)Cl_2 + 1 \xrightarrow{PTC/OH^-} 2 \qquad (2)$$

compound 1 is formed, deprotonation of the dppm and sulfoxonium ylide methylene groups, followed by reaction with $Au_2(dppm)Cl_2$, can produce compound 2. Indeed, in a separate experiment, reaction of 1 with $Au_2(dppm)Cl_2$ under PTC/OH^- conditions produced compound 2. The structure of compound 2, as determined by X-ray crystallography, is shown in Figure 2. A dppm ligand triply bridges three Au atoms (Au2, Au3, and Au4) through two P atoms (P3 and P4) and one methylene C atom (C2), and a sulfur ylide dianion also triply bridges three Au atoms through ylidic atoms C3 and C4 (C3 bonded to both Au1 and Au3 and C4 to Au2). This results in a triangular gold geometry (Au1, Au2, and Au3) with Au···Au contacts of 2.993, 3.035, and 3.394 Å. The fourth Au atom (Au4) is at much longer Au···Au contacts with the above three (>3.635 Å). Bridging triangular Au(I)/Au(III) complexes have been reported.[15] The Au···Au distances are normally in the range of 3.2–3.4 Å. If we disregard the Au···Au contacts, each Au atom is seen to connect one C atom and one P atom, with C–Au–P angles ranging from 167.5 (7) to 176.6 (8)°. A highly strained ylidic C3 is revealed (angle Au1–C3–Au3 = 94.4 (10)°). Although we have reported that sulfur ylide complexes can be prepared by using PTC techniques, a dianionic sulfur ylide bridging three gold atoms by removing three protons from the sulfoxonium salt has up to now been unknown. This is also the first example of deprotonation of a dppm CH_2 group using PTC techniques, although non-PTC reactions are known.[16]

In conclusion, we have demonstrated that, under PTC/OH^- conditions, we are able to obtain the first luminescent binuclear gold compound containing a bridging sulfur ylide and a tetranuclear gold compound containing a tridentate bridging dppm and sulfur ylide. The formation of 2 from further reaction of 1 indicates that the PTC/OH^- system is a reasonably strong base and that the tendency toward an Au···Au interaction may be one of the important factors for the formation of 2. Further application of PTC techniques in the synthesis of other gold compounds and a detailed spectroscopic study are underway.

Acknowledgment. We thank the National Science Council of Taiwan (ROC; Grant No. NSC81-0208-M030-08) for financial support.

Supplementary Material Available: Tables of crystal data, positional parameters, anisotropic thermal parameters, and bond distances and angles for both of the structural analyses (14 pages). Ordering information is given on any current masthead page.

---

[13] Lee, A. J. *Chem. Rev.* **1987**, *87*, 711.

[14] (a) Che, C.-M.; Wong, W.-T.; Lai, T.-F.; Kwong, H.-L. *J. Chem. Soc., Chem. Commun.* **1989**, 243. (b) Wang, S.; Fackler, J. P., Jr.; King, C.; Wang, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 3308. (c) Balch, A. L.; Davis, B. J.; Olmstead, M. M. *Inorg. Chem.* **1989**, *28*, 3148. (d) Balch, A. L.; Nagle, J. K.; Oram, D. E.; Reedy, P. E., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 454.

[15] (a) Minghetti, G.; Bonati, F. *Inorg. Chem.* **1974**, *13*, 1600. (b) Tiripicchio, A.; Tiripicchio-Camellini, M.; Minghetti, G. *J. Organomet. Chem.* **1979**, *171*, 399. (c) Murray, H. H.; Raptis, R. G.; Fackler, J. P., Jr. *Inorg. Chem.* **1988**, *27*, 26. (d) Raptis, R. G.; Fackler, J. P., Jr. *Inorg. Chem.* **1990**, *29*, 5003.

[16] (a) van der Velden, J. W. A.; Bour, J. J.; Vollenbrock, Beurskens, P. T.; Smiths, J. M. M. *J. Chem. Soc., Chem. Commun.* **1979**, 1162. (b) Uson, R.; Laguna, A.; Laguna, M.; Manzano, B. R.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1984**, 839. (c) Uson, R.; Laguna, A.; Laguna, M.; Gimeno, M. C.; Jones, P. G.; Fittschen, C.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1986**, 509. (d) Uson, R.; Laguna, A.; Laguna, M.; Lazaro, I.; Jones, P. G. *Organometallics* **1987**, *6*, 2326.