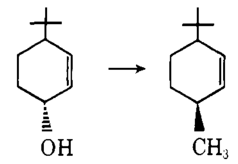

5 6 (75%)

isolated yield)(entry 16) and cyclopropylphenylmethane (73%) (entry 17), respectively, upon treatment with the corresponding organolithium compounds under the same reaction conditions.[11]

The following procedure for the synthesis of 1-phenyl-*cis*-1-heptene (**8**) is representative (entry 4). To a suspension of cuprous iodide (3.82 g, 20 mmol) in dry THF (50 mL) was added a solution of lithium *cis*-cinnamyl alkoxide (prepared on treatment of *cis*-cinnamyl alcohol (2.68 g, 20 mmol) with ethereal CH_3Li (1.57 M, 12.8 mL) at 0 °C) at room temperature. The mixture was stirred for an additional 30 min before cooling to −78 °C. A hexane solution of *n*-BuLi (39.2 mL, 1.53 M) was added for 10 min, and to the resulting suspension was added a solution of **1** (9.90 g, 20 mmol) in dry DMF (100 mL) for 30 min. The mixture was maintained at the same temperature for 1 h and then warmed to room temperature for 2 h with continuous stirring. After quenching with a saturated NH_4Cl solution (0 °C) the ethereal extract was washed with a 0.2 N HCl solution and dried ($MgSO_4$). To the concentrated solution was added light petroleum ether, and precipitated triphenylphosphine oxide was filtered off. Distillation of the filtrate gave a mixture of 1-phenyl-*cis*-heptene (**8**) and 3-phenyl-1-heptene (**9**) (2.8 g, 80% yield), bp 90-95 °C (4 mmHg). The GLC analysis showed that the relative ratio of **8** and **9** was 96 vs. 4.

The course of the reaction can be readily accounted for, if one assumes that the nucleophilic attack of R^2 of the aminocuprate of the counterion toward the α-carbon of R^1 of **10** in a S_N2 fashion gives R^1-R^2 along with triphenylphosphine oxide and *N,N*-methylphenylaminocuprate.

$$\mathrm{R^1OCuR^2_3Li_3} + \mathbf{1} \longrightarrow [\mathrm{R^1OPPh_3}^+[\mathrm{R^2_3CuN(CH_3)PhLi_2}]^-$$

$$\downarrow \qquad \mathbf{10}$$

$$\mathrm{R^1R^2} + \mathrm{Ph_3P{=}O} + \mathrm{R^2_2CuN(CH_3)PhLi_2}$$

Work is currently in progress on the extension of this reaction to other systems and application to the synthesis of several natural products.

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(2) Prepared as follows: Phenyliminotriphenylphosphorane (mp 128 °C) (L. Horner and H. Oediger, *Justus Liebigs Ann. Chem.*, **627**, 142 (1959)) was reacted with methyl iodide at reflux for 2 h. Removal of excess methyl iodide followed by recrystallization from chloroform-ethyl acetate (1;2) gave **1** quantitatively, mp 238-238.5 °C.

(3) (a) Y. Tanigawa, S.-I. Murahashi, and I. Moritani, *Tetrahedron Lett.*, 471 (1975); (b) Y. Tanigawa, H. Kanamamu, and S.-I. Murahashi, *ibid.*, 4655 (1975).

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(5) When organolithium compounds are valuable or obtainable only by a several-step synthetic process, addition of 2 molar equiv of triphenylphosphine can substitute for excess organolithium compounds (the relative yield of **3**/**4** = 75/25).

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(8) Compound **6**; *m/e* 152; NMR (CCl_4, δ), 2 olefin H at 5.36-5.68 (m), 1 axial, 1 equatorial, and 4 methylene H at 1.22-2.24 (m), 1 axial methyl H at 1.02 (d, J = 3.5 Hz) and 9 methyl H at 0.92 (s), respectively.

(9) When a mixture of 30 vs. 70% of cis and trans alcohols **5** was allowed to react under the same reaction condition, a mixture of cis and trans olefins (**6** and **7**, 70 vs. 30%) was obtained in 68% (bulb-to-bulb distillation, T_{bath} 130 °C (40 mmHg)). Pure **7** was collected by preparative GLC. The spectrum of **7** was as follows (CCl_4, δ); 2 olefin H at 5.24-5.52 (m), 1 axial, 1 equatorial, and 4 methylene H at 1.12-2.32 (m), 1 equatorial methyl H at 0.94 (d, J = 3.5 Hz), and 9 methyl H at 0.92 (s), respectively. Hydrogenation of each of **6** and **7** by utilizing Pd black gave the corresponding cyclohexanes.[10]

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(11) Simple primary alcohols could be used in the reactions with low conversion under the reaction condition. We have not persuited optimization of the yields, since there are many good alternative methods.[4,10]

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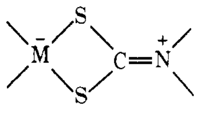
Trimethylgold(III) Complexes of Reactive Sulfoxonium and Sulfonium Ylides

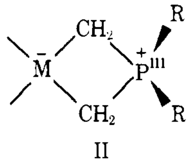
Sir:

Phosphonium ylides have been used for over 20 years[1,2] as reagents for organic synthesis (Wittig reagents). More recently sulfur ylides[3,4] have been found to display important synthetic utility. The pioneering work of Schmidbaur[5] has elucidated the ability of the phosphorus ylides to function as effective organometallic ligands. Recently Kurras et al.[6] and Manzer[7] have extended this work in the transition series of elements.

Our studies[8] and those of others[9,10] have suggested that the ability of dithiocarbamate ligands, I, to delocalize positive charge from the metal center is a determining factor in allowing this ligand to stabilize such unusual oxidation states as Ni^{IV}, Mn^{III}, Cu^{III}, or Fe^{IV}. By analogy we were attracted to Schmidbaur's metal ylide complexes, II, which show remarkable stability for compounds containing transition metal-carbon bonds.[11] Presumably the ability of ylides to remove positive charge from the metal center (reducing the metal) helps to account for their stabilizing influence on metal-carbon bonding. This effect is even more remarkable when one notes that triphenylphosphine does not displace the ylide from $(CH_3)_3AuCH_2P(CH_3)_3$, III



I



II

Sulfur ylides are substantially less stable than phosphorus ylides. However, both $CH_2S(CH_3)_2$ and $CH_2SO(CH_3)_2$ have been generated and utilized[3] in situ. We find that trimethylgold(III) can be used to stabilize these reactive ylides. Furthermore we note that dimethylphenylphosphine can be used

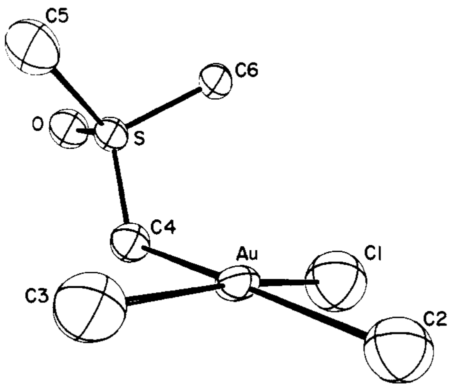
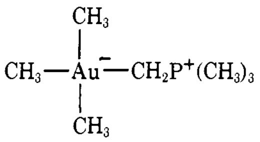


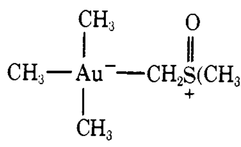
Figure 1. A perspective view of the $(CH_3)_3AuCH_2SO(CH_3)_2$ molecule with the labeling scheme. The atoms are represented by 30% probability thermal ellipsoids.



$$\mathrm{CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Au^-}}{-}CH_2P^+(CH_3)_3}$$

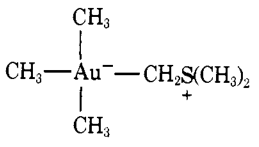
III

to liberate the ylide from the sulfoxonium ylide complex IV (but not from the sulfonium ylide species V).



$$\mathrm{CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Au^-}}{-}CH_2\overset{\displaystyle O}{\underset{+}{S}}(CH_3)_2}$$

IV



$$\mathrm{CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Au^-}}{-}CH_2\underset{+}{S}(CH_3)_2}$$

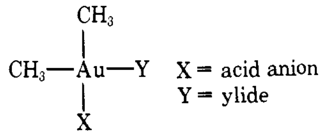
V

Addition of a THF solution of trimethylgold(III) triphenylphosphine to a THF solution of $CH_2SO(CH_3)_2$ under nitrogen results in formation of IV (see Figure 1). After evaporation of the solvent, a white residue remained which was washed with hexane. Recrystallization from $CHCl_3$ gave colorless crystals,[12,13] mp 118-120 °C dec. Anal. Calcd for $AuC_6H_{17}OS$: C, 21.55; H, 5.13; S, 9.58%. Found: C, 21.46; H, 5.14; S, 9.48.

By stirring for 3 days a THF solution containing sodium hydride, trimethylsulfonium chloride, and trimethylgold(III) triphenylphosphine, complex V was obtained. The complex was recrystallized from $CHCl_3$, giving colorless crystals, mp 83-85 °C. Anal. Calcd for $AuC_6H_{17}S$: C, 22.64; H, 5.36; S, 10.09. Found: C, 22.59; H, 5.31; S, 10.01.

Both IV and V are air stable.

Acids selectively eliminate CH_4 from IV and V. In each case a cis product, VI, is formed. With both HCl and CF_3COOH the reaction is very much faster than with CH_3COOH, suggesting that a protonation of the metal may be important. Recently Tobias[15] has demonstrated substantial nucleophilicity for the isoelectronic anions, $Au(CH_3)_4^-$ and $Pt(CH_3)_4^{2-}$. Neither IV nor V reacts with pyridine nor triphenylphosphine.

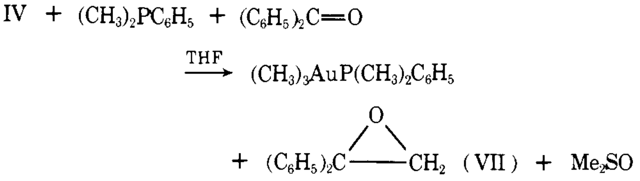


$$\mathrm{CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle X}{Au}}{-}Y}$$

X = acid anion
Y = ylide

VI

Although IV is remarkably easy to handle, we have found that THF solutions smoothly react with $(CH_3)_2PC_6H_5$ to liberate the reactive sulfoxonium ylide at room temperature. With benzophenone quantitative conversion by NMR to the epoxide occurs, VII. The phosphine complex of trimethylgold is readily recovered. Similarly V will react with $(CH_3)_3P$ to liberate the ylide. We have no evidence of reactivity of either IV or V with ketones in the absence of phosphines. The synthetic utility of these reactions is being explored.[16]



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(12) The ylide complex crystallizes in space group $P2_12_12_1$ with cell dimensions $a = 5.277$ (1), $b = 10.953$ (3), and $c = 17.065$ (5) Å; $d_{\mathrm{calcd}} = 2.24$, $d_{\mathrm{obsd}} = 2.20$ gm cm^{-3}, $Z = 4$. With 824 unique Syntex $P2_1$ monochromatic Mo Kα data and 42 variables R refined to 0.09 with $R_w = 0.10$. Some significant distances (Å) and angles (deg): Au–C_1, 2.14 (5); Au–C_2, 2.11 (6); Au–C_3, 2.16 (5); Au–C_4, 2.14 (5); C_4–S, 1.69 (4); S–O, 1.49 (3); S–C_5, 1.74 (5); S–C_6, 1.82 (4); C_1–Au–C_2, 84.8 (27); C_1–Au–C_4, 95.6 (25).

(13) It is crystallographically difficult to distinguish between O and CH_2 coordination to the metal. IR studies show ν_{S-O} to be at 1170 cm^{-1}, a value comparable with ν_{S-O} in $[(CH_3)_3SO]NO_3$ (1210 cm^{-1}) but very different from the ν_{S-O} in $NiCl_2 \cdot 3Me_2SO$, (940 cm^{-1}) wherein oxygen coordination occurs.[14]

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