$$3\mathbf{b} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{I_2}} \underset{30\text{–}40\%}{[\mathrm{CO_2C_2H_5}]_2} + \underset{40\%}{\mathrm{C_{10}H_{15}{\cdot}CO_2C_2H_5}} + \underset{\text{trace}}{\mathrm{H_5C_2OC({=}O)OC_2H_5}} \qquad (4)$$

subjecting the product mixture to GLPC/mass spectral analysis, diethyl oxalate[28] was observed in a 30–40% yield. The other organic products which contained "CO" were diethyl carbonate (trace) and a compound with the formula $C_{10}H_{15}{\cdot}CO_2C_2H_5$ (4) (~40%).[29] Upon changing the reaction solvent from CH_2Cl_2 to diethyl ether, only 4 was produced. The mechanism of this iodine promoted carbon–carbon bond forming reaction is under current investigation and will be reported at a later date.

The carbon–carbon bond-forming step in oxalate synthesis from CO and alcohol has now been demonstrated for the metals rhodium and palladium to involve a dicarboalkoxy mononuclear intermediate. Current studies are under way to further elucidate the chemistry of these and other cobalt triad complexes which contain two alkoxycarbonyl ligands.

Acknowledgment. We wish to thank R. L. Pruett, S. L. Soled, and J. S. Merola for helpful discussions. We also thank C. S. Hsu for assistance in obtaining the GLPC/mass spectra and R. V. Kastrup for the ^{13}C NMR spectra.

Registry No. 2, 12354-85-7; 3a, 88825-23-4; 3b, 88841-56-9; 4, 35211-68-8; $[CO_2C_2H_5]_2$, 95-92-1.

Supplementary Material Available: Tables of interatomic distances and angles, fractional coordinates, F_o/F_c, and thermal parameters for $Me_5CpRh(CO)(CO_2Me)$ (9 pages). Ordering information is given on any current masthead page.

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[28] The obtained diethyl oxalate spectrum was consistent with published spectra: "EPA/NIH Mass Spectral Data Base"; Heller, S. R.; Mime, G. W. A., Eds.; National Bureau of Standards: Washington, DC, 1978; Vol. 1, p 410.

[29] The base peak in the mass spectrum of 4 at 135 corresponded to $M^+ - CO_2C_2H_5$, which strongly suggests this compound is ethyl pentamethylcyclopentadiene carboxylate.

Synthesis of 2,2′,5,5′-Tetramethylbibismole. A Thermochromic Dibismuthine

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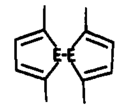
Summary: The reaction of 1,1-dibutyl-2,5-dimethylstannole with iodine gave 2(*Z*),5(*Z*)-diiodohexa-2,4-diene, which on treatment with butyllithium followed by phenylbismuth diiodide afforded 1-phenyl-2,5-dimethylbismole. The bismole was converted to the thermochromic 2,2′,5,5′-tetramethylbibismole by reaction of sodium in liquid ammonia followed by treatment with 1,2-dichloroethane.

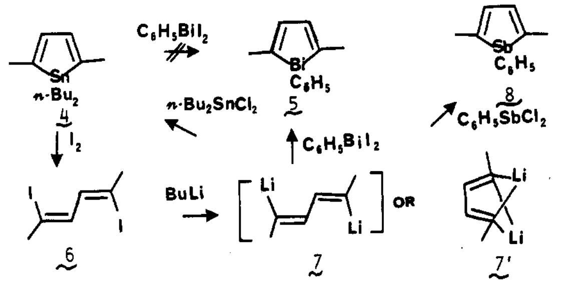
The thermochromic distibine 2,2′,5,5′-tetramethylbistibole (1) forms intensely colored blue crystals which melt to a pale yellow oil and form yellow solutions in organic solvents.[1] The crystal structure of 1 shows that the antimony atoms are aligned in linear chains with very short Sb–Sb··Sb–Sb separations. A molecular orbital treatment by Hoffmann et al. suggests that the solid-phase color is due to intermolecular interaction involving the Sb–Sb σ-bonds.[2]



1, E = Sb
2, E = As
3, E = Bi

In order to explore the generality of this effect, we have investigated a variety of dipnicogen compounds including the arsenic and antimony analogues of 1.[3-5] The synthesis of the nonthermochromic 2,2′,5,5′-tetramethylbiarsole (2) was recently reported.[6] We now wish to report a synthesis of the thermochromic 2,2′,5,5′-tetramethylbibismole (3) that involves several intermediates of theoretical interest.

The attempted exchange reaction between 1,1-dibutyl-2,5-dimethylstannole (4)[7] and phenylbismuth diiodide gave only an intractable black material. This failure may be due to the known great sensitivity of vinylbismuth compounds to acidic conditions.[8] Alternatively, treating stannole 4 with iodine in carbon disulfide afforded 2(Z),5(Z)-diiodohexa-2,4-diene (6): mp 36–39 °C; ^1H NMR ($CDCl_3$) δ 2.60 (s, 6 H), 6.20 (s, 2 H).[9] Metalation of 6 with butyllithium gave a solution of 7, a 1,4-dilithiobutadiene. This reagent may be used to prepare a variety of five-membered ring heterocycles.[10] Thus treating 7 with dibutyltin dichloride affords 4, while reaction with phenylantimony dichloride gave the known 1-phenyl-2,5-dimethylstibole (8).[7] On theoretical grounds it has been suggested that 1,4-dilithiobutadienes have bridged structures.[11] Whether 7 has bridged structure 7′ is currently under investigation.



The reaction of 7 with a suspension of phenylbismuth diiodide in diethyl ether gave 28% of the desired 1-phenyl-2,5-dimethylbismole (5): ^1H NMR (CD_2Cl_2) δ 2.35

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[7] Ashe, A. J., III; Diephouse, T. R. *J. Organomet. Chem.* **1980**, *202*, C95.

[8] Ashe, A. J., III; Diephouse, T. R.; El-Sheikh, M. Y. *J. Am. Chem. Soc.* **1982**, *104*, 5693.

[9] For a similar procedure see: Jutzi, P.; Baumgärtner, J. *J. Organomet. Chem.* **1978**, *148*, 247.

[10] See: Leavitt, F. C.; Manuel, T. A.; Johnson, F. *J. Am. Chem. Soc.* **1959**, *81*, 3163. Leavitt, F. C.; Manuel, T. A.; Johnson, F.; Matternas, L. U.; Lehman, D. S. *Ibid.* **1960**, *82*, 5099.

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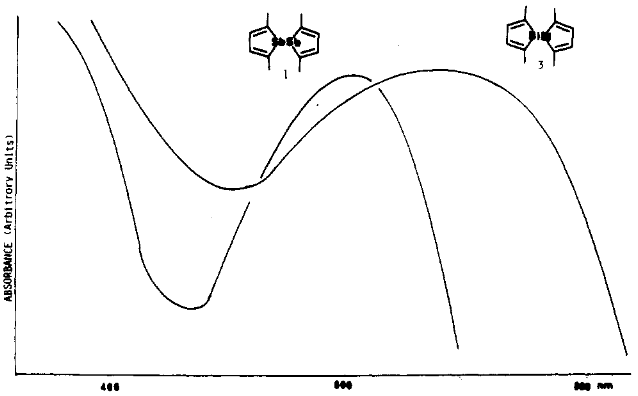
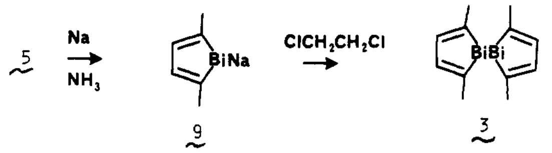


Figure 1. A comparison of the diffuse reflectance spectra of solid 2,2′,5,5′-tetramethylbistibole (1) and 2,2′,5,5′-tetramethylbibismole (3). The vertical scale is arbitrary.

(s, 6 H), 7.28–7.45 (m, 3 H), 7.98 (d, $J = 6.5$ Hz, 2 H), 8.53 (s, 2 H); MS *m/e* (relative intensity) 366 (1, M^+ for $C_{12}H_{13}Bi$), 209 (60, Bi^+), 157 (100, $M^+ - Bi$). Because of its lability the bismole was used directly without extensive purification. Like its pnicogen analogues, 1-phenyl-2,5-dimethylbismole undergoes facile phenyl cleavage on treatment with active metals.[7,12] The reaction of 5 with sodium in liquid ammonia gave the potentially aromatic 2,5-dimethylbismolyl anion 9. Coupling of 9 with 1,2-dichloroethane afforded the desired 2,2′,5,5′-tetramethylbibismole (3): mp > 95 °C dec; ^1H NMR (C_7D_8) δ 2.41 (s, 6 H), 8.43 (s, 2 H); ^{13}C NMR (C_7D_8) δ 28.5 (CH_3), 152.3 (CH), 162.6 (CBi); MS (CI–CH_4) *m/e* (relative intensity) 579 (0.5, $M^+ + 1$ for $C_{12}H_{16}Bi_2$), 209 (16), 160 (100, $M^+ - Bi_2$). Anal. Calcd for $C_{12}H_{10}Bi_2$: C, 24.93; H, 2.79. Found: C, 24.81; H, 2.77.



This dibismuthine is air sensitive but in the solid state can be stored at room temperature. The dibismuthine is obtained as black crystals with a greenish luster. The diffuse reflectance spectrum of crystalline 3 (illustrated in Figure 1) shows a broad absorption maximum centered at 690 nm. On the other hand, solutions of 3 in cyclohexane are red ($\lambda_{max} = 230$ nm (ϵ 14 600), sh 320 nm (5600) with a low intensity tail out to 700 nm). This large red shift between solution and solid is similar to that observed for 1. Consequently, we believe that the crystal packing of 1 and 3 must be similar.

Hoffmann et al. have suggested that the solid-phase color of 1 is due to a $\sigma \rightarrow \pi^*$ excitation.[2] One expects the lowest π^* orbital of 1 and 3 to be of very similar energy. On the other hand, the Bi–Bi σ bond of 3 is likely to be of higher energy than the Sb–Sb σ bond of 1.[4] Thus the observed red shift between 3 and 1 is consistent with the smaller band gap predicted from the Hoffmann model.

Acknowledgment. Support of our work by the A.F. O.S.R. (Grant No. 81-099) is gratefully acknowledged.

Registry No. 3, 88635-82-9; 4, 77214-60-9; 5, 88635-81-8; 6, 88635-79-4; 7, 88635-80-7; 9, 88644-52-4; $C_6H_5BiI_2$, 39110-03-7.

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Mixed-Metal Cluster Carbides and a Mixed-Metal Ketenylidene with Nucleophilic Carbide Sites

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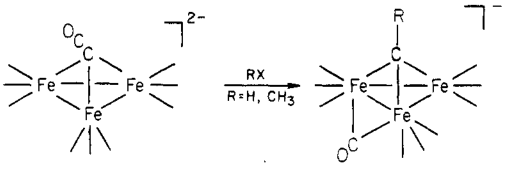
Summary: The nucleophilic ketenylidene $[Fe_3(CO)_9(CCO)]^{2-}$ (III) serves as a convenient mixed-metal carbide precursor. Compound III reacts readily with labile metal carbonyl fragments such as $M(CO)_3(NCCH_3)_3$ (M = Cr, W) to generate the new clusters $[Fe_3MC(CO)_{13}]^{2-}$ which contain a nucleophilic carbide ligand similar to that in $[Fe_4C(CO)_{12}]^{2-}$. By contrast, treatment of III with $Co_2(CO)_8$ leads to replacement of one iron vertex, generating a new monoanionic heterometallic ketenylidene $[Fe_2Co(CO)_9(CCO)]^-$ which is less reactive but otherwise chemically similar to III. X-ray crystallographic analysis shows the CCO tilt to be considerably less than in the $[Fe_3(CO)_9(CCO)]^{2-}$ species.

Because of the importance of CO cleavage on metal surfaces and the subsequent reduction of the surface carbide, there is considerable interest in the chemistry of metal cluster compounds containing reactive carbide ligands. Metal cluster carbides having more than four metal atoms have repeatedly been observed to lack reactivity at the carbide center.[2,3] To date, reactivity of the carbide ligand has been achieved only for the isoelectronic four-iron butterfly carbides, $Fe_4(CO)_{13}C$ (I) and $[Fe_4(CO)_{12}C]^{2-}$ (II).[4,5] In these compounds the carbide ligand is coordinated to only four iron atoms and it is exposed. Recently, a three-iron cluster $[Fe_3(CO)_9(CCO)]^{2-}$ (III) was synthesized which contains a ketenylidene ligand, CCO, having carbide-like reactivity, and this discovery raises the possibility that ketenylidenes may play a role in the reduction of CO on metal surfaces.[6] The reactivity of III is illustrated by its interaction with methylating agents or acids to produce ethylidyne or methylidyne derivatives (eq 1), with concomitant migration of the ketenyl CO onto the metal cluster. In the present communication we report that III affords a convenient route to new mixed-metal cluster



III (1)

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