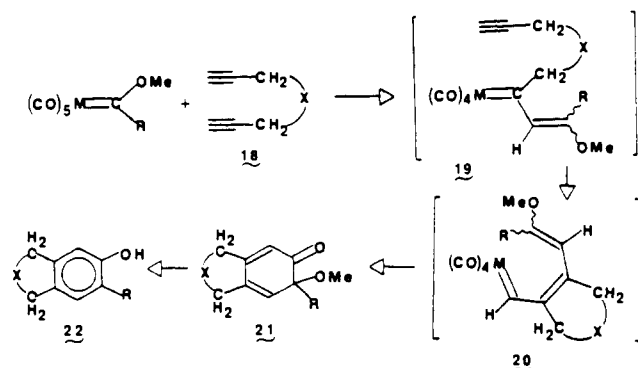


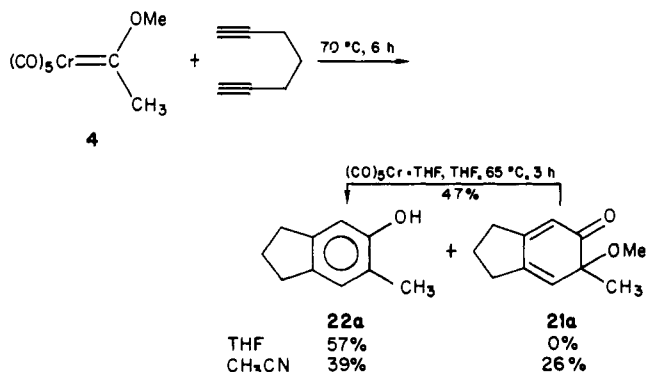
Scheme III



that from the intermolecular reactions.

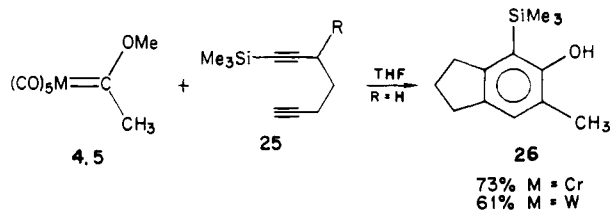
The success of the intramolecular version of the two-alkyne annulation is illustrated for several diynes in Table I. The chromium complex **4** reacts with 1,6-heptadiyne to give the indanol **22a** in 57% yield. As anticipated, these intramolecular reactions are sensitive to alkyne concentrations and a drop in yield of **22a** from 57% to 20% is observed when the concentration is raised from 0.0044 to 0.1 M. For practical considerations the use of lower concentrations can be obviated by employing a slow addition (84 h) of 1,6-heptadiyne to a 0.1 M solution of **4** providing a 52% yield of **22a**.

The cyclohexadienone **21a** can be isolated from the reaction of **4** with 1,6-heptadiyne in acetonitrile, which may be attributed



to the solvent's ability to more strongly coordinate to any chromium(0) species before reduction to the indanol can occur. The dienone **21a** can be reduced to the indanol **22a** with excess (tetrahydrofuran)pentacarbonylchromium(0)¹⁵ lending credence to the suggestion that the phenol products are a result of an in situ reduction of the expected cyclohexadienones by chromium(0).

An important issue in the development of these reactions is the control of the regiochemistry of addition of unsymmetrical diynes. A possible solution is to employ a monosilylated diene such as **25**. The two-alkyne annulation of complex **4** with **25** occurs regioselectively with the incorporation of first the terminal and then the silylated alkyne to give a single isomer of indanol **26** in 73% yield. The same reaction of the tungsten complex **5**⁷ gives a 61% yield **26**.¹⁶



(15) The reduction of a 0.0044 M solution of **21a** in acetonitrile with (acetonitrile)pentacarbonylchromium(0) is much slower resulting in a 1.9:1.0 mixture of **22a** and **21a** in 45% overall yield at 70°C in 40 h.

(16) Chromium complex **4** reacted completely with 1.2 equiv of the diene **25**, whereas the reaction of the tungsten complex **5** required 10 equiv of **25**.

The yields of the reactions of the tungsten complexes with diynes **18a-d** (Table I) are generally slightly higher than for the chromium complexes despite the fact that substantial polymer formation occurs, thus requiring 5-7 equiv of diene to drive the reaction to completion. This, however, can be reduced to $2^{1/2}$ equiv in the photoinduced reaction of the tungsten complex **5** with diene **18a**. It was quite surprising that the tungsten complexes also gave the indanols **22** since it has never been observed for tungsten complexes that a cyclized product can be obtained with terminal acetylenes¹⁴ nor that cyclized products are formed with the incorporation of a carbon monoxide ligand.^{14,17}

The continued investigation of the synthetic potential of the reactions of transition-metal carbene complexes¹⁸ with diynes¹⁹ is warranted particularly with regard to examining more functionalized acetylenes and optimization of the reaction for the formation of cyclohexadienones.

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Supplementary Material Available: Spectral and physical data for **15a-c**, **16**, **21a**, **22a-e**, and **26** (3 pages). Ordering information is given on any current masthead page.

(17) Tungsten complex **5** (0.05 M in THF) was found to react with 1-pentyne (10 equiv) to give a 35% yield of **15b** in 18 h at 90°C .

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A Tungsten-Bismuth Cluster Featuring Dibismuth as a Four-Electron Donor and a Bridging Bismuthinidene

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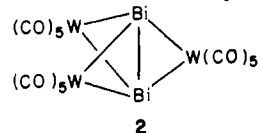
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The use of bulky ligands has permitted the isolation of compounds with $\text{P}=\text{P}$, $\text{P}=\text{As}$, and $\text{As}=\text{As}$ bonds.¹ However, attempts to prepare analogous compounds with $\text{Sb}=\text{Sb}$ or $\text{Bi}=\text{Bi}$ bonds have been unsuccessful. We have therefore turned our attention to stabilizing such species by the attachment of transition-metal fragments. We describe the preparation and structure of a complex that involves (i) the first instance of Bi_2 functioning as a four-electron donor and (ii) the first example of a monomeric ligated bismuthinidene (RBi).

The bismuthine $(\text{Me}_3\text{Si})_2\text{CHBiCl}_2$ (**1**) was prepared as a yellow oil (bp $108-110^\circ\text{C}$ at 10^{-4} torr) in 51% yield in a similar fashion to the corresponding stibine.² Bismuthine **1** was treated with $\text{Na}_2[\text{W}(\text{CO})_5]$ (5.0 mmol) in 30 mL of THF at 25°C . After evaporation of the solvent, the crude product was separated by column chromatography (silica gel, 1:1 toluene/*n*-hexane) to afford a 5% yield of $[\{\text{W}(\text{CO})_5\}_2(\mu_3-\eta^2-\text{Bi}_2)]$ (**2**) and a 12% yield of $[\text{W}_2(\text{CO})_8(\mu_2-\eta^2-\text{Bi}_2)(\mu-\text{BiMeW}(\text{CO})_5)]$ (**3**). Compounds **2** and **3** were recrystallized from toluene/*n*-hexane and benzene, respectively.

As shown by Huttner et al.³ the triangulated structure of **2**



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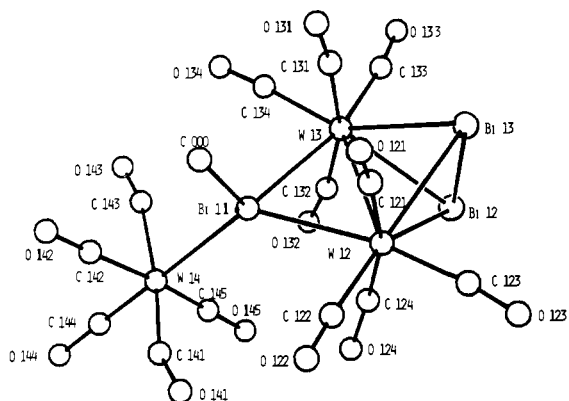


Figure 1. ORTEP view of $[W_2(CO)_8(\mu_2\text{-}\eta^2\text{-Bi}_2)(\mu\text{-Bi})MeW(CO)_5]$ (**3**). Pertinent metric parameters: $W(12)\text{-}W(13) = 3.142(3)$, $Bi(12)\text{-}W(12) = 2.987(3)$, $Bi(13)\text{-}W(12) = 2.990(2)$, $Bi(12)\text{-}W(13) = 3.001(3)$, $Bi(13)\text{-}W(13) = 2.997(3)$, $Bi(11)\text{-}W(13) = 2.865(2)$, $Bi(11)\text{-}W(12) = 2.882(2)$, $Bi(11)\text{-}W(14) = 2.851(2)$ Å, $W(12)\text{-}Bi(11)\text{-}W(13) = 66.33(6)^\circ$.

possess approximately D_{3h} skeletal symmetry and involves the lateral attachment of three $\mu_2\text{-}W(CO)_5$ moieties to a Bi_2 molecule which therefore functions as a six-electron donor. Compound **3** also contains a Bi_2 molecule (Figure 1),⁴ however, in this instance it acts as a four-electron donor in a manner reminiscent of a transversely bridging alkyne. The Bi-Bi bond lengths in **2** (2.815 (1) Å) and **3** (2.795 (3) Å) are considerably shorter than those in single-bonded structures, e.g., Ph_4Bi_2 (2.990 (2) Å),⁵ Bi_4^{2-} (2.936 (2) and 2.941 (2) Å),⁶ and elemental Bi (nearest neighbor, 3.071 (1) Å).⁷ For diphosphenes and diarsenes, the E-E bond lengths are ~ 0.2 Å shorter than those of the corresponding single bonds.¹ If the same decrement applies to the heavier group 5 elements the Bi-Bi bond lengths in **2** and **3** correspond to a bond order of approximately 2. The observation of a slightly shorter Bi-Bi bond lengths for **3** is possibly a consequence of the noninvolvement of the Bi-Bi σ -bonding electron in the coordination.⁸ However, additional experiments are necessary to define more precisely the nature of the bismuth-bismuth interaction.

The methylbismuthinidene unit of **3** is also remarkable. The only previous bismuthinidene complex, $[(C_5H_5(CO)_2Mn)_2BiCl]_2$ (**4**),⁹ is a Bi_2Cl_2 -bridged dimer. Furthermore, **4** is an "open" structure in the sense that it does not contain a metal-metal bond. By contrast, **3** features a W-W bond and is thus a "closed" structure. "Open" RE-bridged compounds, $RE(ML)_2$, are Lewis acidic at the E center,¹⁰ which accounts for the dimeric nature of **4**. Note, however, that the corresponding "closed" compounds possess a lone pair at the E center.¹¹ As a consequence, **3** is able to coordinate to a $W(CO)_5$ group. Finally, we speculate that the methyl group¹² arises via successive Cl^- attacks at a $(Me_3Si)_2C-$

(H)Bi moiety followed by protonation of the resulting carbanions.¹³

Acknowledgment. We are grateful to the National Science Foundation and the Robert A. Welch Foundation for financial support.

Supplementary Material Available: Tables of bond lengths, bond angles, atomic coordinates, thermal parameters, and structure factors for **3** (18 pages). Ordering information is given on any current masthead page.

(13) A similar process has been invoked to explain the transformation of a $(Me_3Si)_3CP$ to a $(Me_3Si)_2C(H)P$ moiety: Cowley, A. H.; Kilduff, J. E.; Mehrotra, S. K.; Norman, N. C.; Pakulski, M. *J. Chem. Soc., Chem. Commun.* **1983**, 520.

Meso Deuterium NMR Hyperfine Shift as a Probe for Determining Five- or Six-Coordination at Heme Iron Binding Site in Ferric High-Spin Hemoproteins

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In the oxidized (ferric) high-spin form of hemoproteins, the heme iron sixth coordination site is either occupied by water or vacant, depending on their heme microenvironmental structures. In ferric high-spin myoglobin and hemoglobin (aquometMb and -Hb), an oxygen atom, presumably from water, lies close to the heme iron, as visualized by the X-ray crystallographic analysis.¹ This water has been believed to be bound to the heme iron in these hemoproteins, on the basis of the X-ray result of the iron-oxygen interatomic distance (2.0 Å), the bulk water proton relaxation time measurements,² the ESR line-width change in H_2O and $H_2^{17}O$,³ and recent studies of proton ENDOR⁴ and spin-echo measurements⁵ for the electron-proton (or deuterium) coupling. In ferric high-spin horseradish peroxidase (HRP), however, the heme iron has been suggested to be five-coordinate from the proton relaxation measurements^{6,7} and the ESR line-width studies in H_2O and $H_2^{17}O$.⁶ We have recently shown⁸ that the chemical modi-

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(8) Shiro, Y.; Morishima, I. *Biochemistry* **1984**, *23*, 4879-4884. Cyanogen bromide (BrCN) modifies the distal histidylimidazole of Mb. The BrCN-modified metMb exhibited proton NMR and absorption spectra characteristic of a ferric high-spin hemoprotein. However, the significant difference in the Soret region between native and modified metMb's was noticeable. The absorption spectrum of the BrCN-modified metMb was almost superimposable to that of HRP or *Aplysia* Mb, and its absorptivity at maximum absorption ($\epsilon_{397\text{ nm}} 103\text{ mM}^{-1}\text{ cm}^{-1}$) was comparable with that of HRP ($\epsilon_{403\text{ nm}} 102\text{ mM}^{-1}\text{ cm}^{-1}$) which is significantly different from those of hemoproteins having a bound water as a sixth ligand. On the basis of these results, the heme environmental structure of the BrCN-modified metMb would demand the absence of a coordinate water molecule.

(3) This compound has been prepared by Huttner et al. (Huttner, G.; Weber, U.; Zsolnai, L. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *B37*, 707) via the reaction of $BiCl_3$ with $[W(CO)_5]^{2-}$.

(4) Compound **3** ($C_{14}H_3Bi_2O_{13}W_3$) M_r 1557.66. Crystal data: (triclinic; $P\bar{1}$; $a = 9.595(5)$ Å, $b = 16.130(8)$ Å, $c = 10.520(2)$ Å, $\alpha = 81.99(3)^\circ$, $\beta = 111.84(3)^\circ$, $\gamma = 94.90(4)^\circ$; $V = 1494.9$ Å³; $Z = 2$; $d(\text{calcd}) = 3.454$ g cm^{-3} . Intensity data (25 °C): Enraf-Nonius CAD4-F diffractometer, Mo K α radiation, ω - 2θ scan mode in the range $3.0 \leq 2\theta \leq 46.0$; 4818 unique reflections. The structure of **3** was solved (Patterson and difference Fourier) and refined by using 2523 data with $I > 3.0\sigma(I)$. Final residuals: $R = 0.055$, $R_w = 0.0672$.

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