somerized. This finding in conjunction with the absence of positional isomerization in product as well as starting materials narrows any available mechanistic options. Path a should have generated only one product isomer; bath **b** would have necessitated positional isomerization. Path c requires configurational nonintegrity around the metal in C, a possibility made unlikely by earlier results.[4b] Thus, although by no means proven to be correct, d is left as the currently most appealing mechanistic candidate, involving the postulate of the reversible generation of a configurationally unstable (and rapidly disastereoisomerizing) initial intermediate D, providing the rationale for both stereochemical observations. The reason for the contrasting barriers to inversion at cobalt in C vs. D might be attributed to the presumed "antiaromatic" transition state involved when isomerizing the former. Further mechanistic and theoretical work is in order to clarify these points.

Nevertheless, and in summary, we have uncovered a new organometallic reaction which is likely to proceed through novel organometallic intermediates. These findings might be of some stimulus to mechanistic and synthetic chemists in general and those interested in particular in sulfur removal from thiophenic contaminants of industrial liquids.

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Registry No. **1**, 83152-10-7; **2**, 83152-11-8; **3**, 83152-12-9; **4**, 83152-13-0; **5**, 83152-14-1; **6**, 83152-15-2; **7**, 83152-16-3; **8**, 83152-17-4; **9a**, 83152-18-5; **9b**, 83198-81-6; **10a**, 83152-19-6; **10b**, 83198-82-7.

Group 6B Complexes Containing Arsenic–Arsenic Double Bonds. Synthesis and Crystallographic Characterization of $[\eta^5\text{-}C_5H_5M(CO)_2]_2(\mu\text{-}\eta^2\text{-}As_2)$ (M = Mo or W)

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Summary: Hexaphenylcyclohexaarsine when heated with $[CpMo(CO)_3]_2$ or $CpW(CO)_3H$ forms the new cluster compounds $[CpM(CO)_2]_2(\mu\text{-}\eta^2\text{-}As_2)$ (M = Mo (**1**) or W (**2**)). Both **1** and **2** have been characterized by X-ray crystallographic methods; they are isomorphous and belong to the monoclinic space group $P2/n$. For **1**: a = 13.594 (6) Å, b = 7.559 (2) Å, c = 15.862 (8) Å, β = 95.94 (4)°, V = 1621.2 (12) Å^3, Z = 4, and R = 6.17%. For **2**: a = 13.505 (3) Å, b = 7.543 (1) Å, c = 15.845 (4) Å, β = 95.57 (2)°, V = 1606.6 (6) Å^3, Z = 4, and R = 6.91%. Two independent, but not significantly different, half molecules form the asymmetric unit. The heavy atoms form distorted tetrahedral frames characterized by very short As–As bond distances ⟨average⟩ = 2.312 (3) Å (**1**) and ⟨average⟩ = 2.323 (5) Å (**2**) (approximate bond order = 2) and normal, single M–M bond distances ⟨average⟩ = 3.039 (2) Å (**1**) and ⟨average⟩ = 3.020 (2) Å (**2**).

In comparison to the extensive attention given in the last decade to metal clusters containing multiple metal–metal bonds,[1] little effort has been devoted to the preparation of metal clusters containing bridges with multiple nonmetal–nonmetal bonds. Nonetheless, sufficient knowledge exists to demonstrate unquestionably that such bonds should provide new reaction pathways in metal cluster chemistry and provide a basis for the design of new structural classes of compounds. The E–E single bond in $Fe_2(CO)_6(\mu\text{-}E_2)$, E = S[2] or Se or Te,[3] undergoes a diverse range of bond cleavage reactions. Many different modes and bond orders of S–S bridging have been observed and the subject recently surveyed.[4] In comparison, far less is known about P–P, As–As, and Sb–Sb bridging. Prior to the present study, the only confirmed structures were derivatives of $[Co(CO)_3]_3E_2$ (E = P or As) formed via carbonyl group replacement[5] and $[W(CO)_5]_3E_2$, E = As[6] or Sb.[7] These compounds are characterized by a very short $\mu\text{-}\eta^2$ or $\mu_3\text{-}\eta^2$ (E_2) bond leading to the conclusion that they may be treated as complexes of "E≡E". As a part of our continuing survey of the reactions of cyclopolyarsines with cyclopentadienylmetal carbonyls, we have investigated the thermal reactions of hexaphenylcyclohexaarsine, $(AsC_6H_5)_6$, with $[CpMo(CO)_3]_2$ and $CpW(CO)_3H$. In both cases, the compound $[CpM(CO)_2]_2(\mu\text{-}\eta^2\text{-}As_2)$ (M = Mo (**1**) or W (**2**)) is formed.

Table I. Data Collection and Refinement Parameters for $[CpMo(CO)_2]_2As_2$ and $[CpW(CO)_2]_2As_2$

	$[CpMo(CO)_2]_2As_2$ (1)	$[CpW(CO)_2]As_2$ (2)
mol formula	$C_{14}H_{10}As_2Mo_2O_4$	$C_{14}H_{10}As_2O_4W_2$
fw	583.94	759.76
crystl system	monoclinic	
space group	$P2/n$	
a, Å	13.594 (6)	13.505 (3)
b, Å	7.559 (2)	7.543 (1)
c, Å	15.862 (8)	15.845 (4)
β, deg	95.94 (4)	95.57 (2)
V, Å^3	1621.2 (12)	1606.6 (6)
Z	4	
d_{calcd}, g cm^{-3}	2.17	2.86
μ, cm^{-1} (Mo Kα)	55.68	187.16
crystal size (mm), color	0.21 × 0.23 × 0.40, red-orange	0.16 × 0.29 × 0.37, red
reflns measured	$\pm h,k,l$	
scan type	$\theta-2\theta$	
scan range	3–45°	3–50°
scan speed, deg/min	variable 3–15	
std reflns	3/141	
unique data	2124	2832
unique data ($F_o \geqslant 3\sigma(F_o)$)	1574	2147
R_F, %	6.17	6.91
R_{wF}, %	5.30	6.56

All manipulations were carried out in a glovebox or carried out by using Schlenk techniques. Compound **1** was prepared by combining cyclopentadienylmolybdenum

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Table II. Selected Bond Distances and Angles for $[CpM(CO)_2]_2As_2$ with a Comparison to $Co_2(CO)_5[P(C_6H_5)_3]As_2$ [a]

	M = Mo (1)		M = W (2)		$Co_2(CO)_5$-$[P(C_6H_5)_3]As_2$ [5]
	mol a	mol b	mol a	mol b	
			Bond Distances (Å)		
M-M′	3.039 (2)	3.038 (2)	3.026 (2)	3.013 (2)	2.594 (3)
As-As′	2.311 (3)	2.312 (3)	2.326 (5)	2.319 (5)	2.273 (3)
M-As	2.676 (2)	2.663 (2)	2.682 (3)	2.663 (3)	2.386 (3) (av)
M-As′	2.569 (2)	2.567 (2)	2.573 (3)	2.571 (3)	
			Bond Angles (Deg)		
M-M′-As	53.0 (0)	53.0 (0)	53.2 (1)	53.4 (1)	57.1 (av)
M′-M-As′	56.3 (0)	56.0 (0)	56.5 (1)	56.3 (1)	
M-As-M′	70.8 (1)	71.0 (1)	70.3 (1)	70.3 (1)	65.8 (av)
M-As-As′	61.5 (1)	61.6 (1)	61.3 (1)	61.7 (1)	61.5 (av)
M′-As-As′	66.3 (1)	65.9 (1)	66.2 (1)	65.8 (1)	
As-M-As′	52.2 (1)	52.4 (1)	52.5 (1)	52.6 (1)	56.9 (av)
C_1-M-C_2	88.0 (5)	88.8 (5)	87.9 (10)	88.2 (9)	
C_1-M-As	70.9 (4)	70.9 (4)	71.4 (7)	71.3 (7)	
C_2-M-As	77.5 (4)	78.3 (4)	77.1 (8)	78.3 (7)	
C_1-M-As′	122.7 (4)	123.1 (4)	123.5 (7)	123.6 (7)	
C_2-M-As′	86.1 (4)	85.0 (4)	86.5 (7)	86.0 (6)	
C_1-M-M′	86.3 (3)	87.9 (3)	86.2 (7)	87.8 (6)	
C_2-M-M′	129.1 (4)	129.3 (4)	129.1 (8)	130.1 (7)	

[a] Mol = molecule. Av = average.

tricarbonyl dimer (1 mmol) with hexaphenylcyclohexaarsine (1 mmol) dissolved in dried toluene (3 mL), in a sealed, evacuated Carius tube for 24 h at 180 °C. The tube was then slowly cooled to room temperature where upon red crystals formed on the walls of the tube. The tube was cooled to −196 °C, opened, and allowed to warm slowly at room temperature. The crystals were redissolved in warm toluene. The solution was then concentrated and cooled to 0 °C. Crystals suitable for X-ray diffraction were isolated and washed with dry hexane. The crystals isolated were red-orange and air stable out of solution (mp 145 °C (d, open tube)).

The analogous tungsten complex **2** was prepared in a similar fashion to **1**, except cyclopentadienyltungsten tricarbonyl hydride was substituted for the molybdenum dimer. The isolation of air-stable, dark red crystals was executed as described above. Both compounds were only slightly soluble in common solvents. The yields for **1** and **2** were similar: 20–25%.

$$[CpMo(CO)_3]_2 \text{ or } CpW(CO)_3H \xrightarrow[\substack{180\ °C\ 24\ h \\ \text{toluene, sealed tube} \\ (P(\text{est}) = 6.5\ \text{atm})}]{(AsC_6H_5)_6} \begin{array}{c} [CpM(CO)_2]_2As_2 \\ \mathbf{1},\ M = Mo \\ \mathbf{2},\ M = W \end{array}$$

In comparison, the alkylcyclopolyarsine, $(CH_3As)_5$, upon reaction with $[CpMo(CO)_2]_2$ at 140 °C retained its organic substitution and formed the bridged binuclear complex $[CpMo(CO)_2]_2[\mu\text{-}\eta^2\text{-}(AsCH_3)_5]$ which does not have a Mo–Mo bond;[9] at 190 °C, all organic substitution and carbonyl groups are lost to form $(CpMo)_2(\mu\text{-}\eta^4\text{-}As_5)$, containing a Mo═Mo bond and a planar As_5 ring divisible into $\mu\text{-}\eta^2\text{-}As_2$ and $\mu\text{-}\eta^2\text{-}As_3$ ligands.[10]

1 and **2** have been characterized by X-ray crystallography. The unit-cell parameters given in Table I were obtained from the angular settings of 25 reflections (25° ≤ 2θ ≤ 30°).

Empirical corrections for absorption based upon ψ scan reflections were applied to the data. The two compounds are isomorphous. The structure of compound **1** was solved by direct methods and subsequent difference Fourier syntheses; the completed structure for **1** proved an adequate model for **2** and only the metal atom identity needed to be changed prior to final refinement. Both structures were refined by using blocked-cascade, least-squares routines to the residuals given in Table I, along with other data collection and refinement parameters. The asymmetric unit consists of two independent half molecules (two M, two As, two Cp rings, and four CO groups). Whole molecules are constructed from the halves by rotation about a 2-fold crystallographic axis passing through the midpoints of the As–As′ and M–M′ vectors. The structure and labeling scheme are provided in Figure 1, and selected bond distances and angles are listed in Table II which also includes comparison data for $Co_2(CO)_5[P(C_6H_5)_3]As_2$.

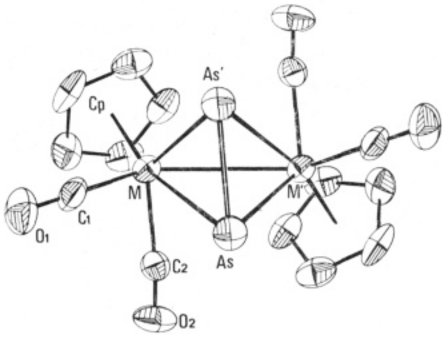

Figure 1. Thermal ellipsoid diagram and labeling scheme for $[CpMo(CO)_2]_2(\mu\text{-}\eta^2\text{-}As_2)$, M = Mo (**1**) and M = W (**2**). The compounds crystallize in isomorphous structures each containing two independent molecules. Differences between **1** and **2** and between the independent molecules are too slight to warrant separate depiction. Hydrogen atoms have been delected for clarity.

Both **1** and **2** crystallize as discrete, well-separated molecules; the two independent molecules differ only slightly as is evident from an inspection of the bond parameters in Table II. The heavy atoms form distorted tetrahedral frames; the localized metal atom environments are not readily assignable to a common coordination geometry. Both possess extremely short As–As bonds, ⟨average⟩ = 2.312 (3) Å for **1** and ⟨average⟩ = 2.323 (5) Å for **2**; these distances may be compared to an As–As distance of 2.273 (3) Å in $Co_2(CO)_5[P(C_6H_5)_3]As_2$ (the shortest known As–As bond),[5] to an As–As distance of 2.279 (4) Å in $[W(CO)_5]_3As_2$,[6] and to a "normal" As–As single-bond

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distance of 2.43–2.46 Å.[11] Dahl et al. have suggested that an As–As distance of ~2.3 Å corresponds approximately to a double-bond length, and that in complexes of this type, the ligand bond order is decreased from 3 (free state as N_2 homologue) to 2 (on coordination) by the synergic combination of (1) the donation of electron density from the filled π orbitals of As_2 to the metal orbitals and (2) back-bonding involving the transfer of electron density from the metal orbitals into empty π^* orbitals of As_2.[5]

The two new compounds, **1** and **2**, provide a confirmation of Dahl's bonding description. Since the moieties $Co(CO)_3$ and $CpM(CO)_2$ (M = Mo or W) are isoelectronic, differences in the basicities of these groups should be reflected in the As–As bond distances. In fact, a comparison of $Co(CO)_4$ and $CpM(CO)_3$ (M = Mo or W) suggests that $Co(CO)_3$ should be a much poorer base[12] and, therefore, contribute less electron density to the As_2 π^* orbital, in keeping with Dahl's expectations.

The metal–metal bond distances ⟨average⟩ (Mo–Mo) = 3.039 (2) Å and ⟨average⟩ (W–W) = 3.020 (2) Å are within the range expected for single bonds between these elements.[13] Other bond distances and angles in **1** and **2** when compared to $Co_2(CO)_5[P(C_6H_5)_3]As_2$ agree with expectations based upon longer metal–metal bonds in **1** and **2**. Thus, the As–M–As′ angles are predictably smaller in **1** and **2**: ⟨average⟩ = 52.3 (1) and ⟨average⟩ = 52.6 (1)°, respectively, vs. 57.4 (1)° in the Co compound.

Of the known structures of complexes containing multiple As–As bonds, those involving 15-electron metal groups, i.e., $Co(CO)_3$,[5] $CpMo(CO)_2$, and $CpW(CO)_2$, bond two metal groups, form metal–metal bonds, and utilize the As_2 ligand as a four-electron donor. In contrast, the one example of a 16-electron metal group, $W(CO)_5$,[6] bonds three metal groups, does not form metal–metal bonds, and utilizes the As_2 ligand as a six-electron donor.

Recently new interest[14] in reactions of the isoelectronic cobalt carbonyl analogues of **1** and **2** has been stimulated, in part, by the observation that isolobal replacements of each of the four tetrahedral apical groups is possible. Thus, Dahl et al. have shown[5] that all members of the series $E_n[Co(CO)_3]_m$ ($n + m = 4$) can be prepared, and Seyferth et al. have shown that μ_3-alkylidyne groups also may replace either unit.[14] The possibility for substitutional replacements either for the $CpM(CO)_2$ group or the As atoms in **1** or **2** will become a subject for future study.

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Registry No. 1, 83025-09-6; 2, 83025-08-5; $[CpMo(CO)_3]_2$, 12091-64-4; $CpW(CO)_3H$, 12128-26-6; $(AsC_6H_5)_6$, 20738-31-2.

Supplementary Material Available: Tables of final fractionsl atomic coordinates, bond distances and angles, and structure factors (34 pages). Ordering information is given on any current masthead page.

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cis-Hydridoacylrhodium(III) Complexes Not Stabilized by Chelation. Reductive Elimination and Decarbonylation[†]

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Summary: Stable *cis*-hydridoacylrhodium complexes, *cis*-HRh(COR)$(PMe_3)_3$Cl (R = Me, Ph, 4-C_6H_4F, OMe), are obtained by oxidative addition of RCHO to RhCl $(PMe_3)_3$ (**1**). Upon heating, these complexes undergo competing intramolecular reductive elimination of the aldehyde and decarbonylation to the alkane; the former process prevails if RCHO is removed as formed. Both these processes proceed from a common unsaturated intermediate, formation of which is probably rate determining.

Although hydridoacylmetal complexes have been postulated as intermediates in a number of very important transformations,[1] only a few such complexes have been reported.[2,3] Of particular interest are hydridoacylrhodium complexes since rhodium compounds are useful homogeneous catalysts for hydroformylation,[4] aldehyde decarbonylation,[2,5] and aldehyde hydroacylation of olefins,[2,6,7] all of which are thought to involve these complexes as intermediates. The only hydridoacylrhodium complex reported is a chelation-stabilized oxidative addition product of 8-quinolinecarboxaldehyde to RhCl $(PPh_3)_3$,[2] despite attempts to isolate such complexes.[7] We have recently found that *cis*-hydridoalkylrhodium(III) trimethylphosphine compounds are relatively stable and isolable as a result of very slow PMe_3 dissociation from them.[8] This suggests that hydridoacylrhodium trimethylphosphine complexes may be stabilized toward migratory deinsertion as well as reductive elimination, both of which probably require ligand dissociation.

Indeed, we have found that simple aldehydes undergo cis oxidative addition to $RhCl(PMe_3)_3$[9] (**1**) to afford the first stable *cis*-hydridoacylrhodium complexes not stabilized by chelation and have directly observed for the first

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[†] Contribution No. 3068.

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