the methyl groups will minimize the interactions with the phenyl rings or the THF moiety. This is consistent with some modest steric crowding and, further, may lead to increased energy barriers for rotation of the various groups.

The high reactivity of these compounds indicates possible utility as precursors for organosilane deposition in thin films. This has important applications in the production of semi- and superconducting materials. We are now exploring this general synthesis for mixed organosilylaluminum compounds and are investigating the NMR properties both in solution and in the solid state.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. V.S.J.d.M. acknowledges a Rumble fellowship provided by Wayne State University for support of his graduate studies.

Registry No. 1, 122235-95-4; 2, 122235-96-5; 3, 122235-97-6; 4, 122235-98-7; 5, 122235-99-8; 6, 122236-00-4; 7, 122236-02-6; 8, 122236-04-8; $LiSi(SiMe_3)_3$, 4110-02-5; Al_2Cl_6, 7446-70-0; Me_2AlCl, 1184-58-3; Et_2AlCl, 96-10-6; $EtAlCl_2$, 563-43-9; $AlMe_3$, 75-24-1; $AlEt_3$, 97-93-8.

Supplementary Material Available: Complete listings of torsion angles, least-squares planes, anisotropic thermal parameters, hydrogen atom positional coordinates, and isotropic thermal parameters (16 pages); a listing of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

Complexes of the Allylic Diorganotriarsinidene Ligand, η^3-RAsAsAsR. Syntheses and Crystal Structures of $Cp^*Mo(CO)_2(\eta^3\text{-}PhAsAsAsPh)$ and $Cp^*W(CO)_2(\eta^3\text{-}MeAsAsAsMe)$

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Sealed-tube reactions of $[Cp^*M(CO)_2]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$; M = Mo or W) with the cyclopolyarsines, *cyclo*$(AsR)_n$ (R = Me, $n = 5$; R = Ph, $n = 6$), in toluene at 150–170 °C produce the new complexes $Cp^*M(CO)_2(\eta^3\text{-}RAsAsAsR)$ (1, M = Mo, R = Ph; 2, M = W, R = Me), which are strict isoelectronic and isolobal analogues of π-allyl complexes. As such they constitute the first examples of π-allyl complexes formed without carbon atoms. 1 and 2 have been crystallographically characterized. 1: monoclinic, $P2_1/c$, $a = 20.287$ (6) Å, $b = 9.047$ (2) Å, $c = 13.835$ (3) Å, $\beta = 95.39$ (2)°, $V = 2528.0$ (8) Å^3, $Z = 4$, $R = 5.84\%$. 2: monoclinic, $P2_1/c$, $a = 12.607$ (4) Å, $b = 8.613$ (2) Å, $c = 16.998$ (5) Å, $\beta = 96.21$ (2)°, $V = 1835.0$ (10) Å^3, $Z = 4$, $R = 5.33\%$. All As–As bond distances in both structures are statistically identical; at 2.361 (2) Å, the distance is intermediate between As–As single and double bonds, in keeping with the approximate bond order of 1.5 expected for an allylic analogue. Formation of these allylic complexes is not found when $[CpMo(CO)_3]_2$ replaces $[Cp^*Mo(CO)_2]_2$ in reactions of similar initial As/metal ratios. Rather the closed, tetrahedrane analogues $CpMo(CO)_2(\eta^3\text{-}As_3)$ and $[CpMo(CO)_2]_2(\mu,\eta^2\text{-}As_2)$ are found in which all of the original organic substitution has been lost by disproportionation ($2RAs \rightarrow R_2As + As$).

Introduction

Isolobal analogies have proved to be especially useful in the development of transition-metal/main-group hybrid cluster chemistry. In previous reports[1,2] we have shown that an As atom, as an analogue of the CH group, can form complexes containing the As_2 group in structures closely related to known acetylene complexes, and the *cyclo*-As_5 group, functioning as a cyclopentadienide analogue, can form triple-decker "sandwich" complexes.[3] In an elegant demonstration of the limits to which these analogies can be extended, Scherer and co-workers have shown that the *cyclo*-P_5 group has clear η^5-cyclopentadienyl functionality in forming the ferrocene-like complex $(\eta^5\text{-}P_5)Fe(\eta^5\text{-}C_5Me_5)$.[4] Acetylenic analogues also offer the intriguing possibility of providing insight into the mechanisms for metal-based cyclooligomerization reactions through the isolation of As analogue intermediates. One such As analogue intermediate is $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_2(\mu_2,\eta^2\text{-}As_2)_2]$ which we have isolated and structurally characterized;[2] this diacetylene analogue has been proposed as a cyclooligomerization intermediate, but never isolated.[5] Furthermore, rings and chains of RAs units (isolobally related to CH_2 groups) form complexes with analogues among organic structures such as trishomocubane.[6,7] We have now further extended these analogies to the formation of the first examples of all-arsenic, π-allyl analogue complexes containing the RAsAsAsR group, specifically, $[(\eta^5\text{-}C_5Me_5)M(CO)_2(\eta^3\text{-}RAsAsAsR)]$ (M = Mo or W and R = Me or Ph). We herein report the synthesis and crystal structures of 1 (M = Mo, R = Ph) and 2 (M = W, R = Me). We are aware of no other structures containing an allyl analogue group composed entirely of non-carbon atoms.[8] Appel and co-

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Table I. Crystallographic Data for Cp*M(CO)$_2$[RAsAsAsR] (1, R = Ph, M = Mo; 2, R = Me, M = W)

	1	2
formula	$C_{24}H_{25}As_3MoO_2$	$C_{14}H_{21}As_3O_2W$
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, Å	20.287 (6)	12.607 (4)
b, Å	9.047 (2)	8.613 (2)
c, Å	13.835 (3)	16.998 (5)
β, deg	95.39 (2)	96.21 (2)
V, Å^3	2528.0 (8)	1835.0 (10)
Z	4	4
D(calcd), g cm^{-3}	1.750	2.280
μ(Mo Kα), cm^{-1}	44.1	120.1
temp, K	294	294
color	orange-yellow	yellow
size, mm	0.24 × 0.24 × 0.30	0.20 × 0.30 × 0.37
T_{max}/T_{min}	1.77	5.50
diffractometer	Nicolet R3m	
radiation	Mo Kα (λ = 0.71073 Å)	
monochromator	graphite	
scan limits, deg	$4 \leq 2\theta \leq 45$	$4 \leq 2\theta \leq 52$
scan method	$\theta/2\theta$	Wyckoff
rflns collected	3356	4004
indpdt rflns	3008	3614
obs rflns ($n\sigma(F_o)$)	2240 (n = 4)	2467 (n = 5)
R(merge), %	3.2	4.1
var in std rflns, %	±1	±1
$R(F)$, $R(wF)$, %	5.84, 5.94	5.33, 6.31
GOF	1.582	1.334
Δ/σ (final)	0.049	0.005
$\Delta(\rho)$, e Å^{-3}	0.48	1.95
N_o/N_v	8.1	13.6

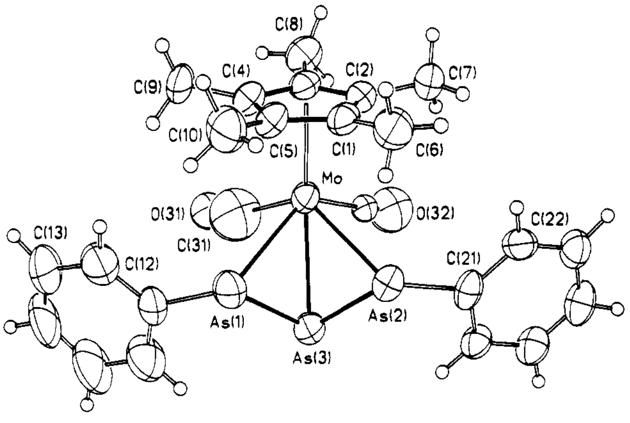

Figure 1. Molecular structure and labeling scheme for Cp*Mo(CO)$_2$(η^3-PhAsAsAsPh) (1) drawn with 40% probability thermal ellipsoids. Distortions in the CO ligand ellipsoids are due to disorder (see Figure 2).

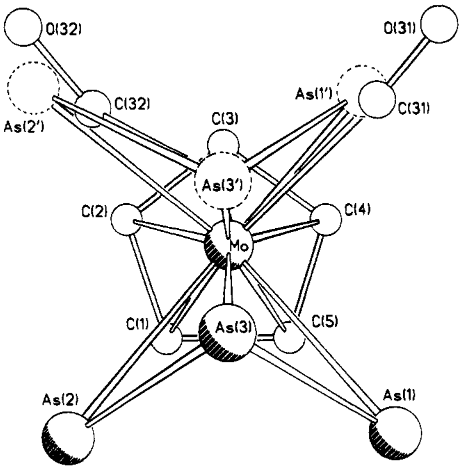

Figure 2. A view of 1 showing the colocation of two of the three minor (~10%) As atom sites and the major CO ligand sites.

workers[9] have reported a complex containing a 1,3-diphosphallyl ligand, viz., Co(CO)$_3$(η^3-RPCHPR) (R = 2,4,6-*tert*-butylphenyl), and allylic coordination has been suggested for the phosphaamidine anion in [(η^3-PhPC(CMe$_3$)NPh)PtCl]$_2$.[10]

Experimental Section

General Procedures. All reactions and manipulations were carried out in an atmosphere of purified N$_2$ or in evacuated Carius tubes. Melting points were measured on a Mel-Temp apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Nicolet 50XB FTIR spectrophotometer as solutions in either CDCl$_3$ or CH$_2$Cl$_2$. ^{1}H NMR spectra were obtained on a Bruker 250-MHz spectrometer with Me$_4$Si as an internal reference.

Materials. Toluene was freshly distilled from sodium benzophenone ketyl under N$_2$. Hexane and methylene chloride were freshly distilled from CaH$_2$ under N$_2$. Mo(CO)$_6$ (Aldrich) and W(CO)$_6$ (Climax) were sublimed prior to use. Pentamethylcyclopentadiene (Aldrich) was used as received. [Cp*M(CO)$_2$]$_2$ (M = Mo, W),[11] *cyclo*(CH$_3$As)$_5$,[12] and *cyclo*(PhAs)$_6$[13] were prepared by published procedures.

Preparation of Cp*W(CO)$_2${[As(CH$_3$)]$_2$As} (2). [Cp*W(CO)$_2$]$_2$ (0.30 g, 0.40 mmol) was dissolved into 15 mL of a dry, degassed toluene solution containing 0.217 g (0.48 mmol) of pentamethylcyclopentaarsine in a medium-wall Carius tube (15-mm diameter, 25 mL). The tube was evacuated with three freeze–pump–thaw cycles, flame-sealed under vacuum, and heated at 170 °C for 22 h in an oven. (*Caution*: *Pressures of 20–30 atm are generated during the heating process; therefore, the tube should be protected by an end-capped, perforated steel tube.*) After being cooled slowly to room temperature, the tube was opened with a moderate pop (evolution of CO) and yellow needle-shaped crystals were separated by filtration. The remaining deep-orange solution was evaporated to dryness and chromatographed on alumina (activity grade I, 70/30 hexanes/methylene chloride) which eluted as a bright yellow band. Recrystallization from cold methylene chloride yielded yellow diffraction-grade crystals (40% yield): mp 240–242 °C; ^{1}H NMR (CDCl$_3$) Cp* δ 2.154 (15 H), As–CH$_3$ 1.141 (6 H); IR (CDCl$_3$) ν(CO) 1969 (s), 1915 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{21}As_3O_2W$: C, 26.69; H, 3.36. Found: C, 27.01; H, 3.28.

Preparation of Cp*Mo(CO)$_2${As(C$_6$H$_5$)]$_2$As} (1). [Cp*Mo(CO)$_2$]$_2$ (1.85 g, 3.20 mmol) and 1.66 g (1.80 mmol) of hexaphenylcyclohexaarsine were placed in a Carius tube and dissolved in 15 mL of toluene. The solution was degassed with three freeze–pump–thaw cycles; the tube was sealed under vacuum and placed in an oven at 150 °C for 22 h. See *Caution* above. Chromatography of the product on alumina (activity grade I, pentane) yielded unreacted starting materials. On deactivation of the column with methanol, a yellow band was obtained. Evaporation and recrystallization from ethyl acetate/octane gave yellow crystals (26% yield): mp 240–245 °C; ^{1}H NMR (CDCl$_3$) δ 2.00 (s, 15 H), 7.10–7.90 (m, 10 H); IR (CH$_2$Cl$_2$) ν(CO) 1969 (s), 1923 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{25}AsMoO_2$: C, 43.33; H, 3.79; As, 33.79; Mo, 14.27. Found: C, 42.97; H, 3.88; As, 33.21; Mo, 14.62.

Crystal Structure Determinations. Data relating to the crystal structure determinations for structures 1 and 2 are sum-

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(8) The planar ring of five As atoms in (CpMo)$_2$(μ,η^4-As$_5$)^3 is distorted to produce As$_3$ and As$_2$ units; in an extreme description of the μ,η^2-As$_3$ group, it could be termed "allylic". Additionally, phosphinidene complexes such as CpMn(CO)$_2$PPhFe(CO)$_4$ form compounds with Fe(CO)$_3$ with allyl-like structures but lack the strictly comparable electron counts for true allyl complexes that the RAsAsAsR complexes exhibit. Huttner, G.; Mohr, G.; Frank, A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 682. Huttner, G.; Evertz, K. *Acc. Chem. Res.* **1986**, *19*, 406. The triphosphacyclobutenide anion, P$_3$CH$_2^-$, is a potential ligand directly related to RAsAsAsR, but no complexes of it have been reported. Baudler, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 419.

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Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for 1

	x	*y*	*z*	*U*
Mo	7360.8 (5)	−139 (1)	895.2 (7)	61.1 (4)[a]
As(1)	8521.1 (7)	−318 (2)	1964 (1)	83.2 (6)[a]
As(2)	7137.5 (7)	−1215 (2)	2621.8 (9)	69.1 (5)[a]
As(3)	7694.3 (7)	1077 (2)	2643 (1)	76.9 (6)[a]
C(1)	7122 (6)	−2612 (13)	379 (7)	67 (5)[a]
C(2)	6642 (6)	−1636 (14)	−83 (7)	66 (5)[a]
C(3)	6959 (6)	−670 (13)	−674 (7)	66 (4)[a]
C(4)	7651 (6)	−1058 (14)	−580 (8)	74 (5)[a]
C(5)	7742 (6)	−2244 (13)	71 (7)	67 (5)[a]
C(6)	6981 (7)	−3964 (14)	958 (9)	98 (6)[a]
C(7)	5905 (6)	−1755 (14)	−43 (8)	85 (5)[a]
C(8)	6609 (7)	396 (14)	−1393 (9)	90 (6)[a]
C(9)	8153 (6)	−436 (15)	−1181 (9)	92 (6)[a]
C(10)	8364 (6)	−3170 (16)	249 (10)	102 (6)[a]
C(11)	9085 (7)	1386 (20)	1636 (11)	102 (7)[a]
C(12)	9424 (9)	1336 (27)	831 (14)	149 (11)[a]
C(13)	9837 (10)	2469 (29)	505 (16)	186 (13)[a]
C(14)	9944 (9)	3527 (26)	1092 (17)	150 (12)[a]
C(15)	9659 (10)	3590 (25)	1970 (19)	180 (13)[a]
C(16)	9218 (9)	2564 (22)	2205 (14)	139 (10)[a]
C(21)	6245 (7)	−586 (15)	2957 (9)	72 (5)[a]
C(22)	5692 (7)	−1421 (16)	2621 (9)	79 (6)[a]
C(23)	5061 (7)	−1102 (17)	2875 (10)	85 (6)[a]
C(24)	5010 (7)	−25 (14)	3558 (11)	88 (6)[a]
C(25)	5551 (7)	753 (15)	3900 (10)	83 (6)[a]
C(26)	6165 (7)	561 (14)	3607 (9)	71 (5)[a]
As(1′)	7691 (9)	1983 (26)	441 (13)	65 (5)[a]
As(2′)	6280 (11)	1280 (24)	1208 (12)	143 (10)[a]
As(3′)	7395 (8)	2035 (16)	2024 (10)	88 (6)[a]
C(31)	7776 (19)	2007 (52)	496 (28)	189 (17)
C(32)	6553 (6)	1148 (13)	1068 (7)	50 (3)
O(31)	7902 (5)	2862 (11)	176 (6)	94 (3)
O(32)	6140 (7)	1836 (16)	1085 (9)	145 (5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for 2

	x	*y*	*z*	*U*[a]
W	2663.4 (4)	6383.7 (7)	6419.2 (3)	49.3 (2)
As(1)	685 (1)	7439 (2)	6046 (1)	72.3 (6)
As(2)	1297 (1)	4259 (2)	6863.1 (9)	69.2 (6)
As(3)	1120 (1)	6772 (2)	7388 (1)	72.7 (6)
O(1)	3222 (10)	9737 (15)	6967 (8)	104 (6)
O(2)	4002 (9)	5551 (15)	8013 (6)	88 (5)
C(1)	667 (15)	9805 (29)	6122 (13)	123 (10)
C(2)	1985 (14)	3112 (21)	7803 (10)	82 (7)
C(3)	2980 (12)	8513 (16)	6784 (9)	66 (5)
C(4)	3452 (11)	5794 (18)	7454 (9)	63 (5)
C(5)	2889 (12)	4591 (21)	5382 (9)	72 (6)
C(6)	2598 (14)	5969 (23)	5044 (9)	79 (7)
C(7)	3364 (16)	7084 (21)	5276 (11)	86 (7)
C(8)	4179 (12)	6309 (23)	5809 (10)	76 (6)
C(9)	3854 (11)	4783 (21)	5869 (9)	71 (6)
C(10)	2343 (19)	2996 (28)	5202 (14)	129 (11)
C(11)	1629 (22)	6079 (40)	4405 (11)	186 (17)
C(12)	3429 (28)	8763 (26)	4941 (17)	181 (17)
C(13)	5229 (15)	6982 (36)	6118 (16)	161 (14)
C(14)	4459 (19)	3483 (28)	6293 (11)	129 (11)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table IV. Bond Distances, Angles, and Dihedral Angle for 1

(a) Bond Distances (Å)			
Mo–As(1)	2.665 (2)	As(2)–As(3)	2.360 (2)
Mo–As(2)	2.657 (2)	Mo–CENT[a]	2.014 (9)
Mo–As(3)	2.685 (2)	Mo–C(31)	2.21 (4)
As(1)–As(3)	2.363 (2)	Mo–C(32)	2.04 (1)
(b) Bond Angles (deg)			
As(1)–As(3)–As(2)	83.2 (1)	CENT–Mo–C(31)	116.1 (6)
As(1)–Mo–As(3)	52.4 (1)	CENT–Mo–C(32)	114.5 (6)
As(1)–Mo–As(2)	72.2 (1)	Mo–As(1)–C(11)	108.8 (4)
As(3)–Mo–As(2)	52.4 (1)	Mo–As(2)–C(21)	109.9 (4)
CENT–Mo–As(1)	114.9 (3)	As(3)–As(1)–C(11)	96.9 (5)
CENT–Mo–As(2)	113.0 (3)	As(3)–As(2)–C(21)	101.0 (4)
CENT–Mo–As(3)	161.2 (3)		
(c) Dihedral Angle (deg)			
[As(1)–As(3)–Mo]–[As(2)–As(3)–Mo]	96.1		

[a] CENT = centroid of Cp ring.

Table V. Bond Distances, Angles, and Dihedral Angle for 2

(a) Bond Distances (Å)			
W–As(1)	2.665 (2)	As(2)–As(3)	2.361 (3)
W–As(2)	2.678 (2)	W–CENT[a]	1.998 (7)
W–As(3)	2.702 (2)	W–C(3)	1.963 (14)
As(1)–As(3)	2.358 (2)	W–C(4)	1.990 (14)
(b) Bond Angles (deg)			
As(1)–As(3)–As(2)	83.1 (1)	CENT–W–C(3)	114.4 (7)
As(1)–W–As(3)	52.1 (1)	CENT–W–C(4)	114.6 (7)
As(1)–W–As(2)	71.7 (1)	W–As(1)–C(1)	110.0 (5)
As(2)–W–As(3)	52.1 (1)	W–As(2)–C(2)	109.1 (5)
CENT–W–As(1)	113.2 (4)	As(3)–As(1)–C(1)	100.7 (6)
CENT–W–As(2)	113.4 (3)	As(3)–As(2)–C(2)	101.7 (5)
CENT–W–As(3)	159.9 (4)		
(c) Dihedral Angle (deg)			
[As(1)–As(3)–W]–[As(2)–As(3)–W]	95.9		

[a] CENT = centroid of Cp ring.

marized in Table I. The crystal selected for data collection were mounted in epoxy on glass fibers. The monoclinic space group $P2_1/c$ was uniquely determined for both structures from photographic evidence and systematic absences in the diffraction data. Both data sets were empirically corrected for absorption. 1 was solved by direct methods and 2 from a Patterson projection. In the development of structure 1, it was found that the three As atoms were disordered at two sites: As(1), As(2), and As(3) at ~90% occupancy and As(1′), As(2′), and As(3′) at ~10% occupancy. The minor sites are undoubtedly accompanied by minor sites for other, lighter atoms as well, but these aspects of the structure could not be resolved. Since the major site CO groups and minor site As atoms occupy interpenetrating space, considerable distortion of the CO thermal parameters and bond metrics have resulted, evident in Figure 1 as physically unreasonable CO thermal ellipsoids and in Figure 2 which shows the positional overlap.

Except for the CO groups of 1, all non-hydrogen atoms were anisotropically refined. Hydrogen atom locations in the Cp* methyl groups are based on partial lists of found positions but, like the remainder of the hydrogen atoms, were ultimately included as updated, idealized isotropic contributions (d(CH) = 0.96 Å).

Tables II and III contain the atom coordinates for 1 and 2, respectively, and Tables IV and V, selected bond distances and angles.

SHELXTL (5.1) software was used for all calculations (G. Sheldrick, Nicolet XRD, Madison, WI).

Results and Discussion

We have previously shown that $[CpM(CO)_3]_2$ or $CpM(CO)_3H$ (Cp = η^5-C_5H_5; M = Mo or W) reacts with the cyclopolyarsines *cyclo*$[AsCH_3)_5$ and *cyclo*$(AsC_6H_5)_6$ in toluene between 120 and 160 °C to form tetrahedrane analogue clusters, viz., $[CpM(CO)_2]_3(\mu_3$-As), $[CpM(CO)_2]_2(\mu,\eta^2$-$As_2)$, and $[CpM(CO)_2](\eta^3$-$As_3)$.[1a] Initial M/As ratios could be varied to favor specific clusters, and, in general, *cyclo*$(AsCH_3)_5$ reacted at temperatures 15–30 °C below that required for *cyclo*$(AsC_6H_5)_6$. If the temperature is raised rapidly to 175 °C in the reaction of $[CpMo(CO)_3]_2$ with *cyclo*$(AsCH_3)_5$, the catenated complex $[CpMo(CO)_2]_2[\mu,\eta^2$-$(AsCH_3)_5]$ is formed.[14] Thus, at lower tem-

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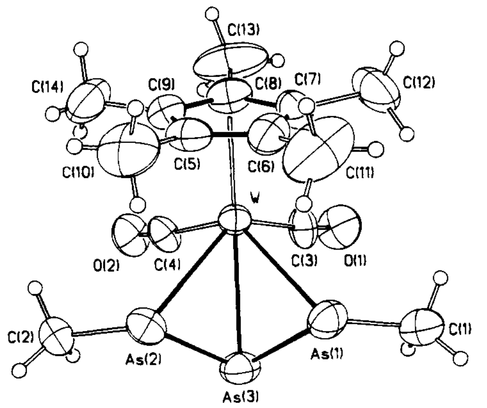

Figure 3. Molecular structure and labeling scheme for Cp*W-$(CO)_2(\eta^3$-MeAsAsAsMe) (2) drawn with 40% probability thermal ellipsoids.

peratures where thermal decarbonylation is slow, extensive formation of elemental arsenic via disproportionation, $2RAs \rightarrow R_2As + As$, occurs leading to As atom clusters.[15] At higher temperatures, where thermal decarbonylation is rapid, complexes are formed with retention of organic substitution. If the $[CpMo(CO)_2]_2(\mu,\eta^2$-As) cluster is heated with additional *cyclo*$(AsCH_3)_5$ at 150°, further arsenic enrichment occurs to form $[CpMo(CO)]_2(\mu,\eta^2\text{-}As_2)_2$[2] and $(CpMo)_2(\mu,\eta^5\text{-}As_5)$.[3]

Under these same reaction conditions, substitution of $[Cp^*M(CO)_2]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$) for $[CpM(CO)_3]_2$ produces no M_2As_2 clusters with either cyclopolyarsine. This result does not appear to be the result of any inherent instability of the M_2As_2 product as $[Cp^*Mo(CO)_2]_2[\mu,\eta^2\text{-}As_2]$ has been previously obtained in very low yield from the reaction of $[Cp^*Mo(CO)_2]_2$ with either As_4[16a] or As_4S_4.[16b] Instead of M_2As_2 species, we find that $[Cp^*M(CO)_2]_3(\mu_3\text{-}As)$, the MAs_3 tetrahedrane analogues, and the allyl analogue species $[Cp^*M(CO)_2](\eta^3$-RAsAsAsR) (**1**, M = Mo, R = Ph; **2**, M = W, R = Me) are the major products formed. The structures of **1** and **2** have been crystallographically confirmed.

The structures of **1** and **2**, which are shown in Figures 1 and 3, are very similar. Both may be regarded as CpM-$(CO)_2$ complexes of the η^3-RAsAsAsR group[17] which, by strict analogy to π-allyl ligands, serve as three-electron donors. The resulting complexes are, therefore, electron-precise and diamagnetic. The tetrahedral complexes $[CpM(CO)_2]As_3$ are related to **1** and **2** as tetrahedrane is related to bicyclobutane. The four As–As bonds in the two structures are statistically identical (average 2.361 (2) Å) and are intermediate between values normal for As–As single bonds ($\sim$2.45 Å)[18] and that reported for the As=As double bond in $(2,4,6\text{-}(t\text{-}Bu)_3C_6H_2)As{=}AsCH(SiMe_3)_2$[19] (2.224 (2) Å). They are similar to the tetrahedrane complexes $[CpM(CO)_2]_2(\mu_2\text{-}As_2)$ [M = Mo, 2.312 (3) Å; M = W, 2.323 (3) Å].[1a] Thus, an As–As distance of $\sim$2.36 Å represents an approximate bond order of 1.5 in keeping with an allylic description.

Both structures contain the η^3-RAsAsAsR group in endo conformations regarding the central As atom. CpMo-$(CO)_2(\eta^3\text{-}C_3H_5)$ crystallizes exclusively in the exo conformation, but both endo and exo conformations are found in solution.[20] Structures of both *endo*-CpMo(MO)I(η^3-C_3H_5)[20] and *exo*-CpW(NO)I(η^3-C_3H_5)[21] are reported. We see evidence for only a single allylic species in solution, a result of the higher inversional energy for As. Additional conformational isomerization is possible at the outer As atoms, but this is likely to result in unacceptable steric crowding for all conformations except for the one shown (i.e., exo,exo with regard to the As_3M butterfly).[22]

The As–metal distances are very nearly equal with the central distance being 0.02 to 0.03 Å longer than the average of the outer As–metal distances; in $[CpMo(CO)_2](\eta^3\text{-}C_3H_5)$, with an exo allyl group, this effect is reversed: central Mo–C, 2.236 (4) Å, and outer Mo–C, 2.359 (3) Å.[20] There have been no structural reports of symmetrical CpMo–carbaallyl complexes in an endo configuration.

The two major products at 150–170 °C for reactions of $[Cp^*M(CO)_2]_2$ (M = Mo or W) with cyclopolyarsines in autopressurized sealed systems are the M_3As tetrahedrane and the allyl analogue complexes typified by **1** and **2**. If an electron-precise tetrahedral cluster has 60 valence electrons, then all of the M_3As, M_2As_2, and MAs_3 cluste are electron-precise.[24] Thus the 62-electron complexes and **2** are formally related to the 60-electron MAs_3 tetrahedrane analogues by the opening of one tetrahedron edge and the addition of two organic radicals at each exposed vertex.

We have been unable to affect the reverse process (closure of the opened butterfly) for **1** by thermolysis (up to the mp of $\sim$240 °C) or by chemical treatment with either excess cyclopolyarsine (as an organic radical abstractor) or, for R = Ph, with Li to form a dianion followed by 1,2-dibromoethane. It is unlikely, therefore, that the allylic complexes are precursors to the 60-electron MAs_3 clusters although we are continuing to study this for **2**. In reactions of $[Cp^*Mo(CO)_2]_2$ with yellow arsenic (As_4) as the pnictogen source, $[Cp^*Mo(CO)_2(\eta^3\text{-}As_3)]$ is obtained in 15% yield at 140 °C,[16a] and with As_4S_4, it is obtained in 12% yield at 100 °C.[16b] Both reactions were in arene solvents, and its formation, in both cases, was accompanied by trace formation of $[Cp^*Mo(CO)_2]_2(\mu,\eta^2\text{-}As_2)$.

Although undoubtedly more complex in mechanism, one can envision thermal scission of the M≡M bond in the metal carbonyl precursor to form the 15-electron fragment $Cp^*M(CO)_2$, which in the presence of naked arsenic species, e.g., As_4 or As_4S_4, regains an 18-electron environment by acquiring a three-electron-donating $\eta^3\text{-}As_3$ group, whereas with *cyclo*$(RAs)_x$ precursors the partially "unclothed" three-electron RAsAsAsR allylic group is apparently more readily accessible. Thus, as seems reasonable, only a sufficient number of organic substituents are lost to fulfill the metal's electronic requirements. Once formed, the allylic group is sufficiently stable to resist further loss of organic substitution.

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We have seen exactly this process in earlier work with cyclopolyarsine reactions of $M_2(CO)_{10}$ (M = Mn and Re),[7] in which a chain of eight CH_3As groups loses just one methyl group to form a trishomocubane structure to satisfy the electronic requirements of the Re atom to which the naked As atom is attached. There is at present insufficient evidence to determine whether the essential difference between Cp and Cp* precursors are sterically determined, a function of the M–M bond order, or both. We are currently studying comparable reactions of $[CpMo(CO)_2]_2$ and $[Cp^*Mo(CO)_3]_2$ to examine these factors. Our preliminary results suggest that the M≡M bond order may prove more important.[25] This would suggest that when the metal precursor is triply bonded, decarbonylation no longer competes with loss of organic substitution in the arsenic precursor. Initial metal–arsenic coordination occurs more rapidly at the coordinatively unsaturated metal centers in the triply bonded precursors promoting metal–metal bond scission, fragmentation of the cycloarsines, and loss of organic substitution.

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Registry No. 1, 122270-44-4; **2**, 122270-45-5; $[Cp^*W(CO)_2]_2$, 70634-77-4; *cyclo*$(CH_3As)_5$, 20550-47-4; $[Cp^*Mo(CO)_2]_2$, 12132-04-6; *cyclo*$(PhAs)_6$, 20738-31-2.

Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates (9 pages); listing of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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(25) In fact, we may speculate that the low yield of M_2As_2 species from As_4 and As_4S_4 sources may be due to traces of the singly bonded metal precursor which accompany the preparation of $[Cp^*Mo(CO)_2]_2$.

Bonding in Transition-Metal–Silyl Dimers. Molecular Orbital Theory

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Molecular orbital studies of $Mn_2(CO)_8(Si(C_6H_5)_2)_2$ and $Pt_2(H_3P)_4(Si(C_6H_5)Cl)_2$ have been made by interacting disilene fragments with transition-metal dimers. In the former complex, it is found that the Mn–Mn distance is close to the sum of the atomic radii because the Mn–Mn bond order is 1. This leads to a long Si–Si distance and allows strong Si–Mn bond formation. In the latter complex, the Pt–Pt bond order is 0, so the disilene, with the Si–Si bond intact, binds to the Pt atoms by means of ordinary π donation and back-donation to π^*. On the basis of these findings, the M–M and Si–Si distances in other known transition-metal–silyl four-membered rings are discussed.

The applications of polysilanes[1] have produced considerable interest in their synthesis by transition-metal catalysis.[2-4] Attempts to isolate compounds from such catalytic mixtures have led to the isolation of bimetallic (M_2Si) or dimeric $(MSi)_2$ transition-metal–silyl complexes.[3,4] Several different types of structures have been found for metal–silyl dimers,[3-12] but no attempt has been made to describe the bonding in these species. To address this need and to begin to understand structure/bonding/cat-

Table I. Structures of Transition-Metal–Silyl Four-Membered Rings Based on Data in Ref 1–8[a]

compd	ref	d^n	dist, Å M–M	dist, Å Si–Si	angle, deg Si–M–Si	angle, deg M–Si–M
$Pt_2((C_2H_5)_3P)_4(Si(C_6H_5)Cl)_2$	3	d^{10}	3.973	2.602	67	114
$Pt_2(P(C_6H_{11})_3)_2H_2(Si(CH_3)_2)_2$	5	d^9	2.708	3.896	110	70
$Ru_2(Si(CH_3)_3)_2(CO)_6(Si(CH_3)_3)_2$	6	d^7	2.959	3.886	105	75
$Mn_2(CO)_8(Si(C_6H_5)_2)_2$	7	d^7	2.871	3.852	107	73
$Re_2(CO)_7H_2(Si(C_2H_5)_2)_2$	8	d^6	3.052	4.075	106	74
$Re_2(CO)_6H_4(Si(C_2H_5)_2)_2$	9	d^5	3.084	4.023	105	75
$W_2(CO)_8H_2(Si(C_2H_5)_2)_2$	10	d^5	3.183	4.225	106	74
$Ti_2(C_5H_5)_4H_2(Si(C_6H_5)H)_2$	4a	d^1	3.890	3.820	88	91
					89	90

[a] d electron count is for M in M_2 fragment.

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