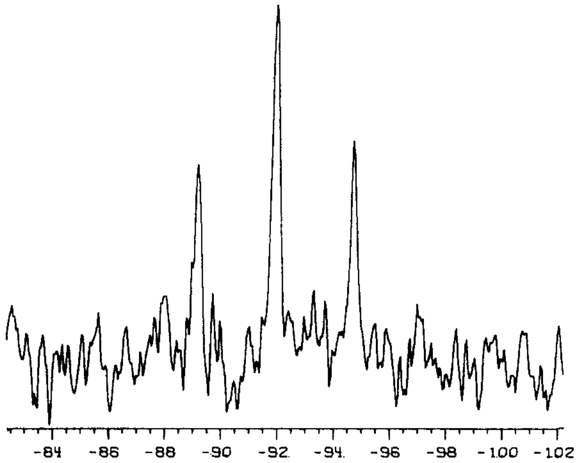

Figure 1. ^{89}Y NMR spectrum of $[(CH_3C_5H_4)_2Y(\mu\text{-}H)(THF)]_2$ in THF (shifts are in ppm vs. aqueous YCl_3; J_{YH} = 27 Hz).

study are representative of well-characterized classes of organoyttrium and organolanthanide species. Methyl-substituted cyclopentadienyl complexes were used in preference to C_5H_5 derivatives because of their enhanced solubility. Saturated solutions were used whenever possible.

The variation in chemical shift for these samples, ca. 400 ppm, is substantial and indicates that the magnetic environment of the metal is significantly affected by the ligands surrounding it. For example, comparison of the shifts of $(CH_3C_5H_4)_3Y(THF)$, $(CH_3C_5H_4)_2YCl(THF)$, and YCl_3 at -371, -101 to -103, and 0 ppm, respectively, demonstrates the effect of a cyclopentadienyl ring on shielding the nucleus. With an increasing number of cyclopentadienyl rings, the resonance is found at higher field (a more negative shift).

The spectrum of $[(CH_3C_5H_4)_2Y(\mu\text{-}H)(THF)]_2$ (Figure 1) deserves special comment in that a 27-Hz ^{89}Y–^{1}H coupling was resolved. In the solid state, this complex exists as a dimer that possesses a crystallographic center of inversion. Two equivalent bridging hydrides hold the monomeric units together. A triplet is observed in the ^{89}Y NMR spectrum of this complex indicating that it is dimeric in solution as well. Consistent with this, the ^{1}H NMR spectrum of $[(CH_3C_5H_4)_2Y(\mu\text{-}H)(THF)]_2$ contained a triplet for the bridge hydrogens.[5]

^{89}Y–^{1}H coupling is also observed in the spectrum of $\{[(C_5H_5)_2Y(\mu\text{-}H)]_3(\mu_3\text{-}H)\}\{Li(THF)_4\}$, but the low solubility of this sample and the fact that the signal is split into six lines by the coupling gave a signal-to-noise ratio which precluded definitive coupling assignments. A triplet of doublets pattern similar to that expected was observed, but the exact peak positions could not be specified well enough to compare with the simulated spectrum based on the coupling constants ($^1J_{Y-H}$ = 29.7 Hz (3 H), 17 Hz (1 H)) derived from the ^{1}H NMR study.[7] The 3.6-Hz ^{89}Y–^{1}H (bridge methyl) coupling observed in the ^{1}H NMR spectrum of $[(CH_3C_5H_4)_2Y(\mu\text{-}CH_3)]_2$[4] was not resolved in the ^{89}Y spectrum of that sample.

Conclusion

The present study provides the first ^{89}Y NMR data on organoyttrium complexes and demonstrates the viability of ^{89}Y NMR spectroscopy as a general characterization technique for organoyttrium species. The shift range is clearly broad enough to provide information on the local environment of the metal. Hence, as more ^{89}Y NMR data are collected, it will be possible to determine more fully how ^{89}Y NMR shifts correlate with ligand environments in organoyttrium complexes. We believe it is premature to make detailed correlations at this time.[18]

Acknowledgment. For support of this research, we thank the Division of Basic Energy Sciences of the Department of Energy (W.J.E., J.H.M.), US—DOE Contract No. W31 109 ENG-38 (Argonne G.L.C., A.G.K.), and NSF Grant CHE 8218164 (Chicago, G.L.C.). We also thank the Alfred P. Sloan Foundation for a research fellowship (W.J.E.) and Dr. Timothy P. Hanusa and Timothy T. Peterson for preparing some samples.

Registry No. $(CH_3C_5H_4)_3Y(THF)$, 93895-57-9; $[C_5(CH_3)_5]_2Y(\mu\text{-}Cl)_2K(THF)_2$, 93895-59-1; $(CH_3C_5H_4)_2YCl(THF)$, 93895-60-4; $[(CH_3C_5H_4)_2YCl]_2$, 80642-81-5; $[(CH_3C_5H_4)_2Y(\mu\text{-}H)(THF)]_2$, 80658-44-2; $\{(CH_3C_5H_4)_2Y[\mu\text{-}C{\equiv}CC(CH_3)_3]\}_2$, 88181-91-3; $\{[(C_5H_5)_2Y(\mu\text{-}H)]_3(\mu_3\text{-}H)\}\{Li(THF)_4\}$, 90762-81-5; $[(CH_3C_5H_4)_2Y(\mu\text{-}CH_3)]_2$, 72556-67-3; $(CH_3C_5H_4)_2YCH_3(THF)$, 93895-61-5; YCl_3, 10361-92-9; $NaCH_3C_5H_4$, 55562-83-9.

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Diarsenic, As$_2$, as a Four-, Six-, or Eight-Electron Donor Ligand

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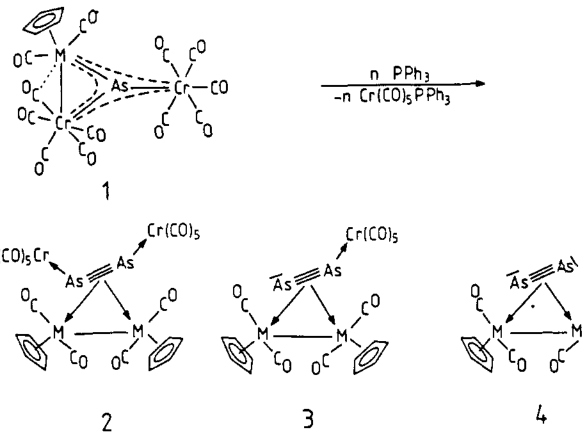
Diarsenic, As_2, is a versatile ligand. While it is side-on coordinated as a 4π ligand in $[Cp(CO)_2M]_2As_2$ (M = Mo (**4a**), W (**4b**)), it acts as a six-electron donor in $[Cp(CO)_2M]_2As_2Cr(CO)_5$ (M = Mo (**3a**) or W (**3b**)) or an eight-electron donor in $[Cp(CO)_2M]_2As_2[Cr(CO)_5]_2$ (M = Mo (**2a**) or W (**2b**)), respectively, by additional end-on coordination via its lone pairs. Another form of an eight-electron donor, As_2, is found for $[Cp(CO)_2Mn]_2As–As[Mn(CO)_2Cp]_2$ (**6a**), prepared by reductive coupling of two arsinidene complexes $[Cp(CO)_2Mn]AsCl$. In **6a** As_2 is bonded in a diarsinidene, $\overline{As}–\overline{As}$, valence state. As_2, side-on coordinated as a six-electron donor is present in the star-type compound $[(CO)_5Mo]_3As_2$ (**7a**) obtained from $Na_2Mo_2(CO)_{10}$ and $AsCl_3$. Its tungsten analogue $[(CO)_5W]_3As_2$ reacts with iodine to give $[(CO)_7W_2I](\mu\text{-}I)(\mu\text{-}\eta^2\text{-}As_2)$ (8) with a side-on coordinated four-electron donor, As_2. Syntheses and properties including structures as determined by X-ray methods are discussed.

As a higher homologue of dinitrogen, diarsenic, As_2, is a major constituent of arsenic vapor at high temperatures.[1] Even though the binding energy of this binuclear ten-electron species is quite respectable (3.93 eV),[2] it is

Scheme I



1a, **2a**, **3a**, **4a**, M = Mo; **1b**, **2b**, **3b**, **4b**, M = W

unstable in the condensed phase relative to the common elemental modifications which contain three single bonds per atom instead of the diarsenic triple bond. Inherent instability of a species may often be a real indication for pronounced ligand capabilities. Regarding diarsenic, the pioneer work in this respect was the characterization of several cobalt complexes of diarsenic such as $As_2Co_2(CO)_5PPh_3$ more than one decade ago.[3] Since that time the coordination chemistry of diarsenic and its other unstable group 5 congeners has, astonishingly enough, obviously not attracted too much attention. Until recently, only the stabilizing capabilities of $Co_2(CO)_6$ as well as its CO substitution derivatives had been explored in this respect and the diphosphorus homologues of the longer known diarsenic compounds had been isolated[4] when it had already become evident that the modes of coordination of group 5 homologues of N_2 are quite different from those of dinitrogen itself. This very fact was clearly illustrated by the recently reported characterization of most unconventionally side-on coordinated X_2 ligands within the complexes $X_2[W(CO)_5]_3$ (X = As,[5] Sb,[6] Bi[7]). Diarsenic acts as a side-on coordinated six-electron donor within these trinuclear molecules. In addition to the four π-electrons, the bonding σ-pair is also involved in coordination,[5] whereas in the dicobalt species $Co_2(CO)_5LAs_2$ diarsenic may be regarded as a four-electron π-donor, bonded like acetylenes in an extensive number of well-characterized acetylene complexes.[8]

The lack of systematic procedures for the synthesis of As_2 complexes prompted us to explore the synthetic potential of arsinidene complexes with respect to diarsenic compounds. As a first result we report here on the synthesis and reactions of compounds, which contain diarsenic as a four-, six-, or eight-electron donor ligand in different coordination geometries.

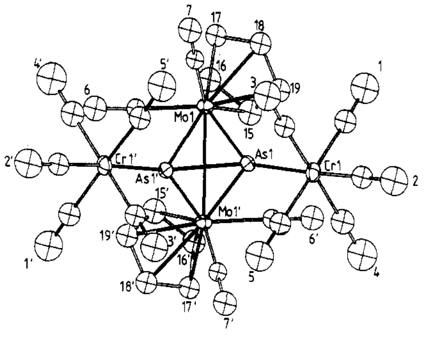


Figure 1. The structure of **2a**.

Synthesis and Ligand Capabilities of $Cp_2(CO)_4M_2As_2$ (M = Mo, W)

Starting from haloarsinidene complexes[9] via the trimetallic complexes **1**,[10] we devised a reaction sequence that leads to compounds **4**, containing a side-on coordinated bridging diarsenic entity. Compounds **4** have recently been isolated from the products of the cothermolysis of $(AsPh)_6$ and $[CpMo(CO)_3]_2$ or $CpW(CO)_3H$, respectively.[11] With regard to bonding of the diarsenic ligand, they are homologues of Dahl's long known diarsenic compounds.[3]

With the synthetic route described here in addition to **4**—depending on the amount of PPh_3 added to the reaction mixture as a $Cr(CO)_5$ scavenger—the novel complexes **2** and **3** will be formed (Scheme I). They contain a side-on coordinated bridging diarsenic that, as in the case of **4**, acts as a four-electron π-donor toward the $Cp_2(CO)_4M_2$ fragment. In addition, the diarsenic entity is end-on coordinated to two (**2**) or one (**3**) pentacarbonylchromium fragment as a σ-donor.

The properties of compounds **4** correspond to the published data in all respects where these are available.[11] The As–As distance, determined by X-ray analysis of **4a**, is 2.311 (3) Å, in even numerical correspondence to the published bond length.[11]

If, as in complexes **2**, the free electron pairs of the diarsenic ligand are involved in coordinating pentacarbonylchromium groups, the arsenic atoms might be expected to be more positively charged than in **4**. The π-donor quality of the diarsenic ligand in **2**, which is additionally end-on coordinated, should therefore be less pronounced than one As_2 ligand in **4**; at the same time, however, within this simple model the π-acceptor quality of the diarsenic ligand in **2** should be increased with respect to the one in **4**. Since the first effect would be expected to shorten the As–As bond while the second should lengthen it, the result of the X-ray analysis of **2a** implies that both effects are operative to about the same extent: The As–As distance is 2.310 (3) Å in **2a** and thus exactly corresponds to the one in **4a**.

Complexes **2a** and **4a** both have twofold rotational symmetry with the crystallographic C_2 axis passing through the midpoints of the As–As and Mo–Mo bonds.

The cyclopentadienyl groups occupy staggered positions on the side opposite the As_2 ligand (Figure 1). In complexes $Cp_2Mo_2(CO)_4(\mu\text{-}RCCR)$ which, as analogues of As_2, contain alkyne ligands as side-on coordinated bridging ligands, no such symmetrical arrangement has hitherto been observed.[12] In all those compounds the rotation of

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Table I. Selected Bond Distances (Å) and Angles (deg) with Esd's for 2a, 6a, and 8[a]

$[Cp(CO)_2Mo]_2As_2[Cr(CO)_5]_2$ (**2a**)

(a) Bond Distances

As(1)-As(1)′	2.310 (3)	Mo(1)-Mo(1)′	3.064 (3)	Cr(1)-$C_{CO(ea)}$	1.84 (1)-1.88 (1)
Cr(1)-As(1)	2.471 (3)	Mo(1)-As(1)′	2.645 (3)	Mo(1)-C_{CO}	1.98 (1)-1.96 (1)
Mo(1)-As(1)	2.531 (3)	Cr(1)-$C_{CO(ax)}$	1.81 (1)	Mo(1)-C_{Cp}	2.28 (1)-2.37 (1)

(b) Bond Angles

Mo(1)-As(1)-As(1)′	66.1 (1)	As(1)-Mo(1)-Mo(1)′	55.5 (1)	Cr(1)-As(1)-As(1)′	135.4 (1)
As(1)-Mo(1)-As(1)′	53.0 (1)	Cr(1)-As(1)-Mo(1)	147.2 (1)		

$[Cp(CO)_2Mn]_4As_2$ (**6a**)

(a) Bond Distances

As(1)-As(1)′	2.445 (4)	Mn(1)-C(11)	1.81 (2)	Mn(2)-C(22)	1.82 (1)
Mn(1)-As(1)	2.264 (4)	Mn(1)-C(12)	1.84 (1)	Mn-C_{Cp}	2.16 (1)-2.17 (1)
Mn(2)-As(1)	2.278 (3)	Mn(2)-C(21)	1.78 (2)		

(b) Bond Angles

Mn(1)-As(1)-Mn(2)	132.8 (1)	Mn(1)-As(1)-As(1)′	113.0 (1)	Mn(2)-As(1)-As(1)′	114.2 (1)

$[\mu\text{-}I][W(CO)_3I][W(CO)_4]As_2$ (**8**)

(a) Bond Distances

As(1)-As(2)	2.305 (10)	W(2)-I(2)	2.813 (11)	W(1)-C(13)	2.11 (9)
W(1)-As(1)	2.704 (9)	W(2)-As(1)	2.625 (10)	W(1)-C(14)	2.07 (5)[b]
W(1)-As(2)	2.687 (10)	W(2)-As(2)	2.619 (8)	W(2)-C(21)	2.07 (7)
W(1)-I(1)	2.807 (6)	W(1)-C(11)	2.09 (7)	W(2)-C(22)	2.05 (6)
W(1)-W(2)	3.069 (7)	W(1)-C(12)	2.02 (11)	W(2)-C(23)	2.04 (11)[c]
W(2)-I(1)	2.788 (8)				

(b) Bond Angles

W(1)-I(1)-W(2)	66.5 (1)	As(1)-W(1)-As(2)	50.6 (2)	W(2)-C(21)-O(21)	169 (10)
W(1)-As(1)-W(2)	70.3 (2)	As(1)-W(2)-As(2)	52.2 (2)	W(1)-C(12)-O(12)	171 (5)
W(1)-As(2)-W(2)	70.7 (2)	I(2)-W(2)-W(1)	145.5 (2)		

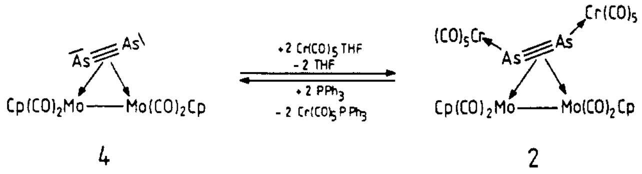
[a] Primes indicate atoms related to the original atom by the crystallographic twofold rotation. [b] Mean 2.07 (11) Å. [c] Mean 2.05 (11) Å.

the $CpMo(CO)_2$ fragments about the Mo–Mo axis relative to the central Mo_2C_2 core displays no symmetry higher than C_1.

Neither in the C_2 symmetry observed for **2a** and **4a**[11] nor in the C_1 symmetry of the acetylene complexes are four equal Mo-bridging atom distances to be expected since the individual bonds are affected differently by the cis and trans influences of the Cp and CO groups. Two significantly different Mo–As bond lengths are observed for each of the molecules in **2a** and **4a** (2.531 (3) and 2.645 (3) Å for **2a**, 2.573 (1) and 2.666 (2) Å for **4a**, and 2.571 (1) and 2.675 (2) Å for the other independent molecule within the crystal of **4a**).[11]

The observation that the As_2 ligand is not in a plane vertical to the Mo–Mo axis but is rotated from this plane by 4.9° in **2a** and by 4° in **4a**[11] cannot be attributed to steric effects alone, since the additional space that $Cr(CO)_5$ groups demand in **2a** has no obvious influence on the overall geometry of the $Cp_2(CO)_4Mo_2As_2$ core. The observed geometry must therefore correspond to the electronically most favorable arrangement.[13] As a possible electronic explanation for the twist of a side-on coordinated bridging four-electron π-ligand, a second-order Jahn–Teller effect has previously been discussed[13] for $Cp_2(CO)_2Nb_2(\mu\text{-}R_2C_2)_2$.[14,15]

Scheme II



In **2a** and **4a** the $Cp_2Mo_2(CO)_4$ fragments both have crystallographic C_2 symmetry. This means that the two $Cp(CO)_2Mo$ entities have different orientations with respect to one of the arsenic atoms of the diarsenic ligand. A conceivable C_{2v} symmetry of the compounds is already reduced to C_2 by the torsion of the $Cp(CO)_2Mo$ fragments around the Mo–Mo axis. The torsion angles Cp–Mo–Mo–Cp (Cp = center of gravity of the Cp rings) are 74.8° for **2a** and 76.6° or 78.9°, respectively, for the two independent molecules in the crystal of **4a**. The close equality of these angles is remarkable, since there is no steric demand for it. The observed torsion, therefore, is probably due to electronic reasons. It corresponds to the rotational position that allows for the optimal trans position of the Cp entities to one of the two arsenic atoms of the As_2 ligand (**2a**, CpMoAs = 166.6°, CpMoAs′ = 118.9°; **4a**, CpMoAs = 165.8°, CpMoAs′ = 118.1°).

While the end-on coordination of the As_2 ligand by $Cr(CO)_5$ groups in **2a** has no influence on the As–As distance, the Mo–As bond lengths are slightly shortened by the addition of the electron-attracting $Cr(CO)_5$ groups (Mo–As = 2.57/2.67 Å in **4a** and 2.53/2.65 Å in **2a**).

The $Cr(CO)_5$ groups in **2a** mark the direction of the free electron pairs of the coordinated As_2 ligand: The As′–As–Cr angle amounts to 135°. The hybridization of the As_2 ligand hence corresponds to the one observed for side-on bridging acetylenes (angle R–C–C = 130–150°)[12-15]

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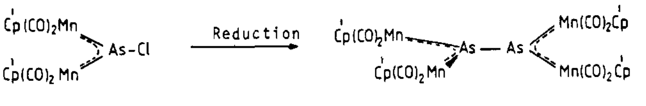
Table II. Spectral Data for $[Cp(CO)_2M]_2As_2[Cr(CO)_5]_n$ Complexes (M = Mo, W; n = 2-0)

complex	IR[a] ν(CO), cm^{-1}	^{1}H NMR[b]	mass spectra, m/e (rel int)
2a	2072 (m), 2060 (m), 1998 (m), 1989 (s), 1963 (m), 1945 (s)	5.75 (s, Cp)	776 (30 $M^+ - Cr(CO)_5$), 664 (30), 636 (30, $M^+ - Cr(CO)_5 - n(CO)$ (n = 4, 5)), 584 (50), 556 (10), 528 (70), 500 (20), 472 (100, $M^+ - 2Cr(CO)_5 - n(CO)$ (n = 0-4)
2b	2069 (m), 2058 (m), 1995 (m), 1982 (s), 1955 (m), 1939 (s)	5.75 (s, Cp)	952 (10, $M^+ - Cr(CO)_5$), 840 (10), 812 (20, $M^+ - Cr(CO)_5 - n(CO)$ (n = 4, 5)), 760 (60), 732 (5), 704 (50), 676 (80), 648 (100, $M^+ - 2Cr(CO)_5 - n(CO)$ (n = 0-4)), 150 (90, As_2^+)
3a	2060 (m), 1973 (s), 1945 (s), 1917 (sh)	5.5 (s, Cp)	584 (50), 556 (20), 528 (70), 500 (30), 472 (100, $M^+ - Cr(CO)_5 - n(CO)$ (n = 0-4))
3b	2060 (m), 1970 (s), 1945 (s), 1909 (sh)	5.5 (s, Cp)	760 (80), 704 (80), 676 (90), 648 (100, $M^+ - Cr(CO)_5 - n(CO)$ (n = 0, 2, 3, 4))
4a	1953 (s), 1900 (s)	5.3 (s, Cp)	584 (50), 556 (20), 528 (70), 500 (30), 472 (100, $M^+ - n(CO)$ (n = 0-4)
4b	1946 (s), 1891 (s)	5.3 (s, Cp)	760 (80), 704 (80), 676 (90), 648 (100, $M^+ - n(CO)$ (n = 0, 2, 3, 4))

[a] In CH_2Cl_2 solution. [b] In acetone-d_6 solution; δ.

Scheme III



5 6

5a, 6a, Cp' = C_5H_5; 5b, 6b, Cp' = $CH_3C_5H_4$

in many structurally characterized examples.

Complexes **2** and **4** undergo a stepwise transformation into each other. Addition of $Cr(CO)_5$ from $(THF)Cr(CO)_5$ to **4** leads to **2** with the spectroscopically documented intermediacy of **3** (Scheme II). Excess $(THF)Cr(CO)_5$ gives a quantitative yield of **2**. In the same way, an excess of Ph_3P will quantitatively transform **4** into **2**.

Compounds **2**–**4** yield characteristic mass spectra under EI conditions (Table II). While the molecular ions are not observed, for **2** and **3** the ions $M^+ - Cr(CO)_5$, originating from the complete loss of one $Cr(CO)_5$ entity, give rise to medium intensity signals in either case. The base peak is the one for $Cp_2M_2As_2^+$ in any case. The presence of $Cr(CO)_5$ groups in **2** and **3** is documented by $Cr(CO)_n^+$ peaks in the low mass region and by peaks for $Cp_2M_2(CO)_4AsCr(CO)_n^+$ (n = 0, 1) in the case of **2**.

The ^{1}H NMR signals of the Cp ligands in **2**–**4** clearly respond to the number of end-on coordinated $Cr(CO)_5$ groups: Increasing the number of $Cr(CO)_5$ entities corresponds to an increase in the removal of charge density and hence to a stepwise low-field shift of the Cp signals when going from **4** to **2**. The IR ν(CO) absorptions (Table II) follow this trend, with the long wavelength absorption shifting to higher wavenumbers in the sequence **4**, **3**, and **2**.

As_2 in a Diarsinidene ($\overline{As}$–$\overline{As}$) Valence State. Compounds **2**–**4** contain diarsenic as a side-on bridging four-electron π-ligand, with an additional coordination of one or two free electron pairs. In **2**, the As_2 ligand therefore acts as an eight-electron donor. A different bonding situation for an eight-electron donor diarsenic follows from reductive coupling of binuclear arsinidene complexes. $[Cp(CO)_2Mn]_2AsCl$[16] reacts with Zn or other reducing agents under reductive coupling to give **6** (Scheme III).

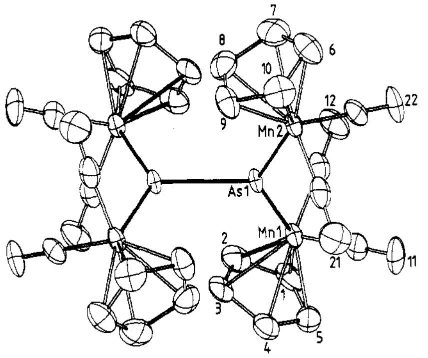
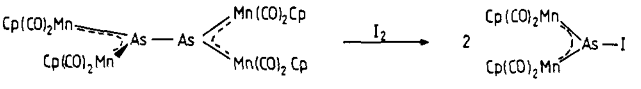


Figure 2. The structure of **6a**.

Scheme IV



6a 5c

The trigonal-planar environment of arsenic—characteristic for arsinidene complexes—is maintained in the product. The X-ray analysis of **6a** demonstrates that the coordination planes of both arsenic atoms are not far from being rotated at right angles with respect to each other (75.9°) (Figure 2). There is no conjugation between the two three-center 4π-systems Mn$\overline{\cdots}$As$\overline{\cdots}$Mn[16,20,21] of the complex. The As–As distance of 2.445 Å corresponds to a single bond.[17] The diarsenic ligand in **6a** may be thought of as being coordinated from a diarsinidene, $\overline{As}$–$\overline{As}$, valence state.

The absence of conjugation across the As–As bond in **6a** is also documented by the electronic spectrum of the highly colored complex **6b**, which shows a metallic shine in the crystalline state ($\tilde{\nu}[\mathrm{cm}^{-1}]/\epsilon[\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{cm}^{-1}] = 18020/36000$ and $25840/25000$). Position as well as intensity of the electronic bands correspond well to those of other bis(cyclopentadienyldicarbonylmanganese)arsinidene complexes.[16]

The arsenic–arsenic bond in **6a** is quantitatively split by iodine under formation of the corresponding iodoarsinidene complexes (Scheme IV). **6a** and its ring

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Table III. Crystal and Refinement Data

	2a	6a	8
formula	$C_{24}H_{10}As_2Cr_2Mo_2O_{14}$	$C_{28}H_{20}As_2O_8Mn_4$	$C_7As_2I_2O_7W_2$
cryst system	monoclinic	monoclinic	monoclinic
space group	$C2/c$ [C_{2h}^6, No. 15]	C2/c [C_{2h}^6, No. 15]	Pc [C_s^2, No. 7]
a, Å	18.36 (2)	19.19 (3)	9.606 (7)
b, Å	10.584 (8)	9.88 (1)	8.099 (3)
c, Å	16.67 (2)	16.43 (2)	17.16 (1)
β, deg	109.95 (8)	111.31 (9)	141.14 (3)
V, Å^3	3045	2902	837.7
Z	4	4	2
mol wt	968.05	854.06	967.43
ρ(calcd), g cm^{-3}	2.11	1.95	3.83
temp, °C	−50	−36	−30
cryst dimens, mm	0.38 × 0.23 × 0.17	0.30 × 0.23 × 0.09	0.32 × 0.16 × 0.05
color	red	golden	black
radiatn	graphite monochromated Mo Kα (λ = 0.710 73 Å)		
diffractometer	Syntex P3	Syntex P3	Syntex P3
abs coeff, cm^{-1}	38.6	42.2	224
scan speed, deg/min	2.0–29.3	2.2–29.3	2.5–29.3
2θ scan range, deg	$2 \leqslant 2\theta \leqslant 45$	$2 \leqslant 2\theta \leqslant 42$	$2 \leqslant 2\theta \leqslant 42$
scan technique	ω scan	ω scan	ω scan
ω scan range, deg	1.0	1.2	1.1
data collected	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$
peak measd time/bkgd measd time	2	3	3
unique data with $(F_o)^2 > 4\sigma(F_o)^2$	1885	1365	945
std reflctns	1/99	1/99	1/99
R_F, %	6.3	6.6	6.6
R_{F^2}, %	5.6	5.5	4.8

Scheme V

methylated derivative **6b** are thermally stable compounds that show the expected mass spectra under EI conditions. The IR spectra demonstrate that, as observed for binuclear arsinidene complexes,[16] the tetranuclear diarsinidene complexes **6** exist in several rotameric forms. On the ^1H NMR time scale the signals of these forms are averaged so that **6a** shows only one Cp signal and **6b** displays the signal pattern characteristic for a $CH_3C_5H_4$ group (see Experimental Section for details).

Star-Type As_2 Complexes. Complexes $X_2[W(CO)_5]_3$ (X = As, Sb, Bi), which contain the ligands As_2,[5] Sb_2,[6] or Bi_2[7] as side-on bonded six-electron donors, have only recently been characterized. In order to explain the side-on interaction of the X_2 entities with three 16-electron fragments, one has to assume a bonding interaction of the bonding X_2 σ-pair with the $W(CO)_5$ acceptor orbitals.[5] From steric considerations—the three $M(CO)_5$ moieties come into close mutual contact upon side-on coordination in the star-type molecules—as well as from electronic reasons, it may not a priori be expected that the lighter homologues such as $Mo(CO)_5$ are adequately suitable building blocks for this type of complex. It has, however, now been found that reaction of $Na_2Mo_2(CO)_{10}$ with $AsCl_3$ yields $As_2[Mo(CO)_5]_3$ (**7a**) (Scheme V).

The analytical and spectroscopic data obtained for **7a** (see Experimental Section) leave no doubt about the identity of **7a** as a lighter homologue of the structurally characterized $As_2[W(CO)_5]_3$ (**7b**).[5]

Iodine degradation of **7b** transforms the star-type coordination present in **7b** into the more common side-on bridging coordination of As_2 in **8** (Scheme VI).

Although **9** even under a wide variety of conditions is the main product and only minor amounts of the intensely violet-colored compound **8** are obtained, the formation of **8** shows the integrity of the As_2 ligand upon transformation from a six-electron donor star-type coordination to a four-electron donor side-on coordination. Compound **8** is a close analogue to the acetylene complex **10**.[18] The differing substitution at the tungsten centers leads to different As–W bond distances for **8** (Figure 3).

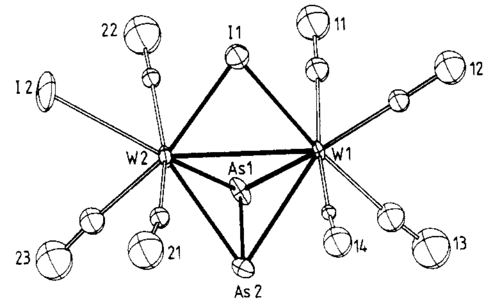
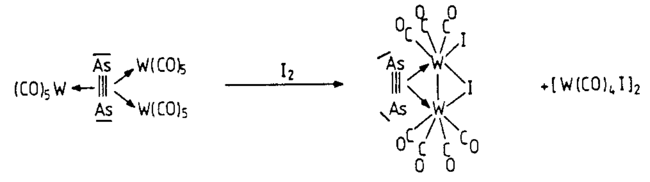
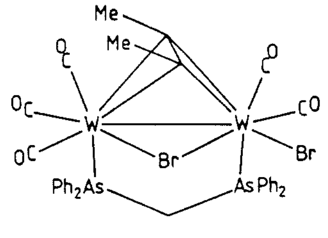


Figure 3. The structure of 8.

Scheme VI



7b 8 9



10

The bond lengths involving W(2) that bears the terminal iodine ligand are 2.62 Å in the mean and are thus shorter than the distances W(1)–As (2.69 Å) by 0.07 Å. A similarily unsymmetrical bonding situation has been observed in the case of the acetylene ligand in **10**. As one might expect, the tungsten center with the higher oxidation state forms the shorter bonds in both structural homologues. The position of the As_2 ligand is obviously affected to a greater extent by the differing electron densities at the tungsten centers than the bridging iodine ligand, which is almost symmetrically bonded (Table I).

The terminal W(2)–I(2) bond length is almost identical with the W-μ-I distances (Table I). The W–I distances correspond to those in **9**,[19] and the W–W distance (3.069 Å) is shorter than the one in $I_2W_2(CO)_8$ (3.155 Å)[19] and is in accord with the formulation of a W–W bond in the diamagnetic complex **8**. The W–As distances are similar to those in arsenido-bridged carbonyltungsten complexes;[22] they are, however, substantially shorter than the corresponding distances in the starting compound **7a** (2.83 Å).[5]

The diversified coordination behavior of As_2 described in this paper and its flexibility to act as a four- or six- or eight-electron donor ligand with different coordinative environments makes the reaction chemistry of coordinated As_2 a promising field of research, especially since rational synthetic procedures for the synthesis of As_2 complexes are now available.

Experimental Section

General Procedure and Materials. All reactions were carried out under an atmosphere of dried and purified dinitrogen. Solvents were dried by conventional methods, distilled, and stored under nitrogen. ^1H NMR spectra were measured on a Bruker Model WP 80 FT spectrometer using deuterated solvents as internal standards (acetone-d_6, δ 2.04; C_6D_6, δ 7.27). Infrared spectra were obtained on a Zeiss Model IMR 40 spectrometer. Mass spectra were measured by using a Finnigan MAT 112 or MAT 312 spectrometer, respectively, at 70 eV.

$[Cp(CO)_2Mn]_2AsCl$ (**5a**), $[MeCp(CO)_2Mn]_2AsCl$ (**5b**), $[(CO)_5Cr]_2AsMCp(CO)_2$ (M = Mo, W; **1**), and $As_2[W(CO)_5]_3$ (**7b**) were prepared as reported previously.[5,9,10,16] Melting points were obtained on a Gallenkamp melting point apparatus in sealed capillaries and are uncorrected.

Crystals suitable for X-ray structural analysis were obtained by slow cooling of CH_2Cl_2/*n*-pentane solutions to −30 °C. The crystal parameters and relevant data are provided in Table III.

The crystals were sealed in glass capillaries and mounted on a Syntex P3 diffractometer. Intensity data were collected by using the ω scan technique. An absorption correction was made by using the ψ scan technique. The structure was solved by direct methods. Solution and refinement were performed by using the SHELXTL system.[23] Final positional parameters are listed in Table IV.

Syntheses of 2–4. A solution of $[(CO)_5Cr]_2AsMCp(CO)_2$ (M = Mo, W;[10] **1**) and the appropriate amount of PPh_3 (see below) in CH_2Cl_2 (30 mL) was refluxed (time, see below) to yield a light brown solution. After addition of silica gel (5 mL) the solvent was evaporated at reduced pressure and the products were purified by chromatography. The first light brown fraction of $Cr(CO)_5PPh_3$ and **1** was eluted from a silica gel column with pentane/toluene (10:1). The fractions of **4**, **3**, and **2** were eluted in that order with pentane/toluene (1:1 and 2:3) and CH_2Cl_2. Recrystallization from CH_2Cl_2/*n*-pentane gave analytically pure crystalline compounds.

$[Cp(CO)_2Mo]_2As_2[Cr(CO)_5]_2$ (2a): $[(CO)_5Cr]_2AsMoCp(CO)_2$ (**1a**; 600 mg, 0.89 mmol); PPh_3 (220 mg, 0.84 mmol); reaction time, 3 h; yield, 95 mg (23%) of **2a**; red crystals; mp 165 °C dec. Anal. Calcd for $C_{24}H_{10}As_2Cr_2Mo_2O_{14}$: C, 29.78; H, 1.04; Cr, 10.74. Found: C, 30.01; H, 0.92; Cr, 11.10.

$[Cp(CO)_2W]_2As_2[Cr(CO)_5]_2$ (2b): $[(CO)_5Cr]_2AsWCp(CO)_2$ (**1b**; 300 mg, 0.39 mmol); PPh_3 (100 mg, 0.38 mmol); reaction time, 3 h; yield, 50 mg (22%) of **2b**; red crystals; mp 165 °C dec. Anal. Calcd for $C_{24}H_{10}As_2Cr_2O_{14}W_2$: C, 25.20; H, 0.88. Found: C, 25.09; H, 0.76.

Table IV. Atomic Coordinates with Esd's for $[Cp(CO)_2Mo]_2As_2[Cr(CO)_5]_2$ (**2a**), $[Cp(CO)_2Mn]_4As_2$ (**6a**), and (μ-I)$[W(CO)_3I][W(CO)_4]As_2$ (**8**)

atom	*x*/*a*	*y*/*b*	*z*/*c*
		2a	
Mo(1)	−0.02065 (5)	0.75148 (9)	0.33162 (6)
As(1)	0.06351 (6)	0.5875 (1)	0.29573 (7)
Cr(1)	0.1657 (1)	0.4263 (2)	0.3494 (1)
C(1)	0.1995 (7)	0.515 (1)	0.4532 (8)
O(1)	0.2193 (6)	0.570 (1)	0.5179 (7)
C(2)	0.2413 (7)	0.310 (1)	0.3930 (8)
O(2)	0.2910 (6)	0.233 (1)	0.4207 (7)
C(3)	0.1005 (7)	0.330 (1)	0.3869 (8)
O(3)	0.0603 (6)	0.265 (1)	0.4117 (7)
C(4)	0.2333 (8)	0.515 (1)	0.3103 (9)
O(4)	0.2779 (9)	0.565 (1)	0.2833 (7)
C(5)	0.1307 (7)	0.338 (1)	0.2468 (8)
O(5)	0.1091 (6)	0.281 (1)	0.1810 (7)
C(6)	−0.1281 (7)	0.790 (1)	0.2585 (7)
O(6)	−0.1919 (5)	0.8145 (9)	0.2175 (6)
C(7)	−0.0581 (6)	0.613 (1)	0.3859 (7)
O(7)	−0.0788 (5)	0.5345 (9)	0.4220 (6)
C(15)	0.0564 (8)	0.937 (1)	0.3665 (9)
C(16)	−0.0185 (8)	0.962 (1)	0.3703 (8)
C(17)	−0.0265 (7)	0.882 (1)	0.4381 (8)
C(18)	0.0447 (7)	0.809 (1)	0.4727 (8)
C(19)	0.0922 (7)	0.844 (1)	0.4272 (8)
		6a	
As(1)	0.06744 (6)	0.6787 (1)	0.26628 (8)
Mn(1)	0.1044 (1)	0.8448 (2)	0.1961 (1)
Mn(2)	0.1307 (1)	0.5123 (2)	0.3601 (1)
C(1)	0.0887 (5)	1.0406 (8)	0.1327 (6)
C(2)	0.0217 (5)	1.0017 (8)	0.1443 (6)
C(3)	−0.0044 (5)	0.8803 (8)	0.0968 (6)
C(4)	0.0466 (5)	0.8441 (8)	0.0557 (6)
C(5)	0.1041 (5)	0.9432 (8)	0.0780 (6)
C(6)	0.1677 (4)	0.389 (1)	0.4766 (6)
C(7)	0.1260 (4)	0.500 (1)	0.4893 (6)
C(8)	0.0524 (4)	0.491 (1)	0.4261 (6)
C(9)	0.0486 (4)	0.375 (1)	0.3743 (6)
C(10)	0.1199 (2)	0.311 (1)	0.4055 (6)
C(11)	0.1846 (7)	0.744 (1)	0.1996 (9)
O(11)	0.2348 (5)	0.684 (1)	0.1995 (7)
C(12)	0.1549 (7)	0.919 (1)	0.3044 (8)
O(12)	0.1841 (6)	0.969 (1)	0.3702 (7)
C(21)	0.1502 (7)	0.445 (1)	0.270 (1)
O(21)	0.1587 (6)	0.401 (1)	0.2079 (7)
C(22)	0.2154 (7)	0.614 (1)	0.3957 (9)
O(22)	0.2687 (5)	0.677 (1)	0.4192 (6)
		8	
W(1)	0.4291	0.3257 (3)	0.4684
W(2)	0.2473 (5)	0.2302 (3)	0.5500 (3)
I(1)	0.0029 (7)	0.1956 (6)	0.3065 (4)
I(2)	−0.111 (1)	0.0898 (7)	0.4757 (6)
As(1)	0.667 (1)	0.2087 (9)	0.6938 (6)
As(2)	0.527 (1)	0.4719 (8)	0.6475 (6)
C(11)	0.52 (1)	0.081 (8)	0.486 (5)
O(11)	0.551 (8)	−0.057 (6)	0.489 (4)
C(12)	0.36 (1)	0.343 (7)	0.321 (5)
O(12)	0.333 (8)	0.338 (6)	0.240 (4)
C(13)	0.73 (1)	0.438 (8)	0.567 (6)
O(13)	0.900 (9)	0.486 (7)	0.620 (5)
C(14)	0.292 (8)	0.560 (6)	0.410 (4)
O(14)	0.209 (7)	0.685 (6)	0.369 (4)
C(21)	0.09 (1)	0.453 (7)	0.497 (5)
O(21)	−0.013 (9)	0.565 (7)	0.474 (5)
C(22)	0.318 (9)	−0.017 (7)	0.573 (5)
O(22)	0.363 (9)	−0.156 (7)	0.589 (5)
C(23)	0.35 (1)	0.248 (8)	0.707 (6)
O(23)	0.417 (9)	0.262 (7)	0.800 (5)

$[Cp(CO)_2Mo]_2As_2[Cr(CO)_5]$ (3a): $[(CO)_5Cr]_2AsMoCp(CO)_2$ (**1a**; 400 mg, 0.59 mmol); PPh_3 (235 mg, 0.9 mmol); reaction time, 4 h; yield, 32 mg (14%) of **3a**; red crystals; mp 141 °C dec. Anal.

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Calcd for $C_{19}H_{10}As_2CrMo_2O_9$: C, 29.41; H, 1.30. Found: C, 29.38; H, 1.14.

$[Cp(CO)_2W]_2As_2[Cr(CO)_5]$ (3b): $[(CO)_5Cr]_2AsWCp(CO)_2$ (**1b**; 400 mg, 0.52 mmol); PPh_3 (205 mg, 0.78 mmol); reaction time, 4 h; yield, 37 mg (15%) of **3b**; red crystals; mp 139 °C dec. Anal. Calcd for $C_{19}H_{10}As_2CrO_9W_2$: C, 23.98; H, 1.06. Found: C, 23.74; H, 1.05.

$[Cp(CO)_2Mo]_2As_2$ (4a): $[(CO)_5Cr]_2AsMoCp(CO)_2$ (**1a**; 400 mg, 0.59 mmol); PPh_3 (310 mg, 1.2 mmol); reaction time, 16 h; yield, 50 mg (29%) of **4a**; orange-red crystals; mp 237 °C dec. Anal. Calcd for $C_{14}H_{10}As_2Mo_2O_4$: C, 28.50; H, 1.73. Found: C, 28.82; H, 1.63.

$[Cp(CO)_2W]_2As_2$ (4b): $[(CO)_5Cr]_2AsWCp(CO)_2$ (**1b**; 300 mg, 0.39 mmol); PPh_3 (207 mg, 0.79 mmol); reaction time, 16 h; yield, 46 mg (31%) of **4b**; orange-red crystals; mp 239 °C dec. Anal. Calcd for $C_{14}H_{10}As_2O_4W_2$: C, 22.13; H, 1.33. Found: C, 22.12; H, 1.25.

Synthesis of 4a from 2a. Complex **2a** (30 mg, 0.03 mmol) was refluxed in CH_2Cl_2 (20 mL) with 2 equiv of PPh_3 (16 mg, 0.06 mmol) for 10 h. After evaporation of the solvent, the residue is recrystallized from CH_2Cl_2/*n*-pentane to give red crystals of **4a** in a yield of 13 mg (70%). $Cr(CO)_5PPh_3$ rests in the mother liquor.

Synthesis of 2a from 4a. A THF solution of **4a** (20 mg, 0.035 mmol) was stirred for 10 h with 5 equiv of $Cr(CO)_5THF$ in THF (20 mL). After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 and the solution filtered over silica gel. Crystallization gave **2a** in a yield of 28 mg (85%).

Syntheses of $[Cp(CO)_2Mn]_4As_2$ (6a). (a) A red violet solution of $[Cp(CO)_2Mn]_2AsCl$ (**5a**; 400 mg, 0.86 mmol) in THF (20 mL) was stirred with an excess of Zn dust (200 mg, 3 mmol) for 4 h at room temperature. The color changed to blue violet. After evaporation the residue was dissolved in CH_2Cl_2 (40 mL) and the solution filtered over silica gel. Recrystallization from CH_2Cl_2 (−30 °C) gave metallic shiny crystals of **6a** in a yield of 345 mg (94%): mp 204 °C dec; ^1H NMR (C_6D_6) δ 4.50 (s, Cp); IR (toluene) ν(CO) 1990 (m), 1978 (s), 1954 (sh), 1932 (m), 1906 (m) cm^{-1}; mass spectrum, *m/e* (assignment, relative intensity) 854 (M^+, 5), 798, 770, 742, 714, 686, 658, 630 ($M^+ - n$(CO) (n = 2 − 8), 10, 20, 10, 10, 20, 10, 100), 565 (M^+ − 8CO − Cp, 10), 510 (M^+ − 8CO − Cp − Mn, 90), 445 (M^+ − 8CO − 2Cp − Mn, 10), 390 (M^+ − 8CO − 2Cp − 2Mn, 70), 205 (As_2Mn^+, 70), 150 (As_2^+, 80). Anal. Calcd for $C_{28}H_{20}As_2Mn_4O_8$: C, 39.38; H, 2.36. Found: C, 39.31; H, 2.23.

(b) $Cr(CO)_6$ (150 mg, 0.68 mmol) was irradiated in THF (100 mL) for 3 h. The resulting solution of $Cr(CO)_5THF$ was stirred with $[Cp(CO)_2Mn]_2AsCl$ (**5a**; 280 mg, 0.60 mmol) for 45 min. After evaporation, the residue was chromatographed with *n*-pentane/toluene (1:2) (R_f ~0.5). Recrystallization from CH_2Cl_2 gave pure **6a** in a yield of 80 mg (32%).

(c) A mixture of $[Cp(CO)_2Mn]_2AsCl$ (**5a**; 300 mg, 0.65 mmol) and potassium (200 mg, 5 mmol) was stirred in ethylene glycol/dimethyl ether (40 mL) for 40 h. The excess potassium was separated. The purification procedure was the same as described under (a): yield of **6a**, 250 mg (90%).

(d) Potassium (200 mg, 5 mmol) was stirred with a solution of 18-crown-6 (10 mg, 0.4 mmol) in THF (50 mL) at −80 °C until a deep blue color developed. At −80 °C a solution of $[Cp(CO)_2Mn]_2AsCl$ (**5a**; 250 mg, 0.54 mmol) in 10 mL of THF was added. The solution was allowed to warm to 20 °C, and the solvent was evaporated. The yellow residue was suspended in CH_2Cl_2 (30 mL). Upon addition of 3 g of silica gel the color changed to blue violet. Purification followed procedure b: yield of **6a**, 150 mg (65%).

Syntheses of $[MeCp(CO)_2Mn]_4As_2$ (6b). The following experiments were performed with $[CH_3C_5H_4(CO)_2Mn]_2AsCl$ (**5b**) instead of $[C_5H_5(CO)_2Mn]_2AsCl$ (**5a**). The reductive coupling with Zn followed the procedure for the Zn reduction of $[Cp(CO)_2Mn]_2AsCl$ (**5a**): $[MeCp(CO)_2Mn]_2AsCl$ (**5b**; 250 mg, 0.51 mmol); Zn (200 mg, 3 mmol); yield, 216 mg (93%); mp 178 °C dec; ^1H NMR (C_6D_6) δ 5.45–5.90 (m, 4 H, C_5H_5), 1.88 (s, 3 H, Me); IR (toluene) ν(CO) 1986 (m), 1975 (s), 1926 (s), 1898 (m) cm^{-1}; mass spectra, *m/e* (assignment, relative intensity) 910 (M^+, 2), 854, 826, 798, 770, 742, 714, 686 ($M^+ - n$(CO) (n = 2 − 8), 10, 30, 30, 20, 20, 10, 90), 552 (M^+ − 8CO − Mn − MeCp, 90), 528 (M^+ − 8CO − 2MeCp, 50), 473 (M^+ − 8CO − Mn − 2MeCp, 90), 418 ($As_2(MnMeCp)_2^+$, 90), 343 ($AsMn(MeCp)_2^+$, 50), 134 ($MnMeCp^+$, 100). Anal. Calcd for $C_{32}H_{28}As_2Mn_4O_8$: C, 42.22; H, 3.10. Found: C, 41.91; H, 3.05.

(e) $[MeCp(CO)_2Mn]_2AsCl$ (**5b**; 250 mg, 0.51 mmol) was stirred for 30 min at 40 °C with $Fe_2(CO)_9$ (190 mg, 0.52 mmol) in THF (40 mL). After evaporation of the solvent, the red residue was suspended in CH_2Cl_2 (30 mL) and adsorbed on silica gel (3 g). A first brown-red zone, eluted with *n*-pentane/toluene (2:1), was discarded. A violet zone of **6b** was then eluted with toluene. After evaporation of the solvent and recrystallization from CH_2Cl_2, **6b** was obtained as crystals exhibiting a metallic lustre: yield, 70 mg (31%).

(f) To a solution of $[MeCp(CO)_2Mn]_2AsCl$ (**5b**; 300 mg, 0.61 mmol) in THF (20 mL) was added $Et_3N{\cdot}BH_3$ (70 mg, 0.6 mmol) at 20 °C. The mixture was stirred for 5 h and then evaporated. Purification followed procedure: yield, 52 mg (19%).

Synthesis of $[Cp(CO)_2Mn]_2AsI$ (5c). Equivalent amounts of **6a** and I_2 were dissolved in CH_2Cl_2 (30 mL) and stirred for 1 h. The yield of $[Cp(CO)_2Mn]AsI$ (**5c**) was quantitative. **5c** may be crystallized from *n*-pentane/CH_2Cl_2. The identity of the product was determined by comparison with an authentic sample prepared in a different way.[16]

Synthesis of $As_2[Mo(CO)_5]_3$ (7a). To a suspension $Na_2Mo_2(CO)_{10}$ (1 g, 2 mmol) in CH_2Cl_2 (30 mL) was added $AsCl_3$ (0.18 mL, 2 mmol), and the mixture was stirred for 5 min. After evaporation of the solvent the residue was treated with CH_2Cl_2 (40 mL) and the suspension filtered over silica gel. Recrystallization from CH_2Cl_2/*n*-pentane yielded **7a** as yellow needles: yield, 17 mg (2% relative to $AsCl_3$); mp 101 °C dec; IR (*n*-pentane) ν(CO) 2067 (m), 1996 (s), 1972 (s) cm^{-1}; mass spectra, *m/e* (assignment, relative intensity) 438 (M^+ − 15CO, 1), 342 ($As_2Mo_2^+$, 10), 267 ($AsMo_2^+$, 100). Anal. Calcd for $C_{15}As_2Mo_3O_{15}$: C, 21.00. Found: C, 20.96.

Synthesis of $As_2[W(CO)_4W(CO)_3I]I$ (8). To a solution of $As_2[W(CO)_5]_3$[5] (**7b**; 125 mg, 0.11 mmol) in CH_2Cl_2 (40 mL) was added dropwise a freshly prepared I_2 solution (5 mL, 0.01 M) in CH_2Cl_2 (titrated with thiosulfate). After the mixture was stirred for 20 h at 20 °C, the solvent was evaporated and the residue suspended in CH_2Cl_2 (20 mL) and adsorbed on silica gel (5 mL). Chromatography yields an intensively yellow band of $[W(CO)_4I]_2$ (**9**) eluted with *n*-pentane. *n*-Pentane/toluene (10:1) gave a violet zone of **8**. Unreacted $As_2[W(CO)_5]_3$ (**7b**) was washed from the column with CH_2Cl_2 or toluene. The violet zones from several batches were collected and rechromatographed. Recrystallization from *n*-pentane gave **8** in the form of metallic shiny crystals: yield, 0.5 mg (1% based on I_2); mp 154 °C dec; IR (*n*-pentane) ν(CO) 2049 (s), 2015 (w), 2009 (s), 2003 (s), 1970 (s) cm^{-1}; mass spectra, *m/e* (assignment, relative intensity) 968 (M^+, 50), 940, 912, 884, 856, 828, 800, 772 ($M^+ - n$(CO) (n = 1–7), 60, 90, 30, 50, 30, 60, 100), 645 (M^+ − 7CO − I, 60), 518 (M^+ − 7CO − 2I, 20), 443 (M^+ − 7CO − 2I − As, 10). Anal. Calcd for $C_7As_2I_2O_7W_2$: C, 8.69. Found: C, 8.98.

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Supplementary Material Available: Crystallographic data including F_o/F_c tables and thermal parameters (102 pages). Ordering information is given on any current masthead page.