What was most surprising about this reaction was that we isolated some biphenyl (32%) (the product of an S_2O-complex-induced oxidative carbon–carbon coupling?) as well as complex **5** (49%). When **1** was treated with Ph_2CuLi followed by iodomethane, we saw no **6**, **7**, or **8**, and instead, we isolated only biphenyl (71%) along with **5** (45%). Oxidative coupling of carbanions by Cu(II)[15] and Fe(III)[16] has been reported previously. The formal oxidation state of the molybdenum in **1** is +4; thus, this oxidative-coupling reactivity may not be surprising here. The recovery of **5** from these reactions poses interesting questions about the mechanism of this oxidative coupling. We do not know the fate of the oxygen lost from **1**. Oxygen labeling studies will be required to determine whether the sulfur-bound oxygen or the molybdenum-bound oxygen is lost. Future work will involve investigation of **1**'s ability to effect S or O transfer to alkenes and the possible use of **1** to effect oxidative coupling of enolates as well as the synthesis of other S_2O complexes in lower formal oxidation states.

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Supplementary Material Available: Tables of all bond lengths and angles, thermal parameters, and calculated hydrogen positions (4 pages); a table of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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Synthesis and Thermolysis of Di- and Triarsenic Complexes of Chromium. Crystal Structure of $[CpCr(CO)_2]_2As_2$

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The cothermolysis of $[CpCr(CO)_3]_2$ (Cp = η^5-C_5H_5) with excess gray arsenic in refluxing toluene for 1–1.5 h resulted in the isolation of $Cp_2Cr_2(CO)_4(\mu$-η^2-$As_2)$ (**2**), $CpCr(CO)_2(\eta^3$-$As_3)$ (**3**), $Cp_2Cr_2(CO)_4(Cr{\equiv}Cr)$ (**4**), and $Cp_2Cr_2AsO_5$ (**6**) in 20.4, 14.2, 5.3, and 13.6% yields, respectively. The reaction when extended to 16 h gave **3**, $Cp_2Cr_2As_5$ (**5**), **6**, and $Cp_5Cr_5As_4O_8$ (**7**) in 5, 22, 39, and 8% yields, respectively. In refluxing xylene for 6 h, the reaction produced **3** (3%) and **7** (15%). **4** likewise reacted with excess elemental arsenic in refluxing toluene, yield **2** (18.5%), **3** (31.9%), and **6** (38.3%) after 1 h but only **2** (18.6%) and **6** (44.2%) after 5 h. Thermal degradation of **2** at 110 °C for 16 h yielded **6** (46.5%) and **7** (28%). **3** also degrades to **5**, but at a much slower rate. **2** crystallizes as dark purple needles. Crystal data: space group $C2/c$ (No. 15), $Z = 4$, $a = 15.551$ (3) Å, $b = 7.453$ (1) Å, $c = 13.446$ (2) Å.

Introduction

Since the first synthesis of the arsenic complexes $Co_2(CO)_6As_2$ and $Co(CO)_3As_3$ from the reaction of $Co_2(CO)_8$ with $AsCl_3$ and *cyclo*-$(MeAs)_5$, respectively,[1] and again later from the reaction of $Na[Co(CO)_4]$ with AsX_3 (X = Cl, Br, I),[2] there has been a gradual development in the role of these As_2 and As_3 units as ligands in complexes of other transition metals. Thus, diarsenic complexes have been derived from the reactions of the M—M-bonded $[CpM(CO)_3]_2$ dimers with *cyclo*-$(PhAs)_6$ (for M = Mo, Cp = C_5H_5),[3] with *cyclo*-$(MeAs)_5$ (for M = Mo, Cp = MeC_5H_4),[4] and with metallic As (for M = Mo, W, Cp = C_5H_5),[5] M≡M-bonded $[(C_5Me_5)Mo(CO)_2]_2$ with As_4S_4[6] and yellow As_4,[7] $CpW(CO)_3H$ with *cyclo*-$(PhAs)_6$,[3] $Na_2W_2(CO)_{10}$ or $W(CO)_5(THF)$ with $AsCl_3$,[8] $[(C_5Me_5)Mn(CO)_2(THF)]$ with AsH_3,[9] metal carbonyl fragment abstraction of $Cp(CO)_2MAs[Cr(CO)_5]_2$ (M = Mo, W), and reductive coupling of $Cp(CO)_2Mn_2AsCl$.[10] *cyclo*-As_3 complexes are less common. Only two other examples are known, viz. $(C_5Me_5)Mo(CO)_2As_3$[6] and the triple-decker $[(triphos)(Co)(As_3)Co(triphos)](PPh_4)_2$ complexes formed from the reaction

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of Co^{2+} with yellow As_4 in the presence of the triphos $(CH_3C(CH_2PPh_2)_3)$ ligand.[11]

Having successfully developed in depth the reactivity of the highly reactive $[CpCr(CO)_3]_2$ dimer with elemental P_4,[12-14] we have extended the study to elemental gray arsenic and herein describe the results.

Experimental Section

General Procedures and Physical Measurements. Inert-atmosphere manipulation techniques and sources and preparation of reagents and solvents were as described previously.[12] Arsenic was obtained as the Fluka AG powder and was finely ground up before use. IR spectra were measured on a Perkin-Elmer 1330 instrument. ^1H NMR spectra were measured on a JEOL FX100 100-MHz spectrometer, and chemical shifts are relative to residual C_6H_6 in benzene-d_6 or to $(CH_3)_4Si$. ^{13}C NMR and mass spectra were measured at the Research School of Chemistry, Australian National University, which also carried out the elemental analyses, except for Cr, which we analyzed as CrO_4^{2-}.[15]

Cothermolysis Reactions with Elemental Arsenic. Reaction of $[CpCr(CO)_3]_2$ (1). A suspension of finely ground gray arsenic (1.23 g, 16.4 mmol) in a deep green solution of $[CpCr(CO)_3]_2$ (400 mg, 0.995 mmol) in toluene (ca. 20 mL) was stirred under gentle reflux for ca. 1 h. The reaction mixture had changed to purplish black. The mixture was concentrated to ca. 2 mL absorbed onto silica gel (ca. 1.5 g), and evacuated to dryness. It was then loaded onto a silica gel column (1.5 cm × 10 cm) prepared in *n*-hexane. Elution with *n*-hexane (5 mL) followed by a 9:1 *n*-hexane–toluene mixture (5 mL) gave a yellow fraction, which on concentration to dryness yielded fine yellow flakes of $CpCr(CO)_2As_3$ (**3**); 112 mg, 0.28 mmol, 14.2% yield). Anal. Calcd for $(C_5H_5)Cr(CO)_2As_3$: C, 21.13; H, 1.27; Cr, 13.06; As, 56.49. Found: C, 21.23; H, 1.28; Cr, 13.29; As, 56.49. IR: ν(CO) 1960 vs, 1905 vs cm^{-1} (toluene). ^1H NMR (C_6D_6): δ(Cp) 3.94. ^{13}C NMR (C_6D_6): δ(Cp) 83.04, δ(CO) 233.93. Further elution with a 1:1 *n*-hexane–toluene mixture (ca. 10 mL (gave a dirty green fraction (21 mg, dried residue), the ^1H NMR spectrum of which showed the presence of a 6:1 molar mixture of $[CpCr(CO)_2]_2(\mathit{Cr}{\equiv}\mathit{Cr})$ (**4**; δ 4.23, 5.3% yield) and **3** (δ 3.94, 0.4% yield), respectively. Continued elution with toluene (40 mL) gave a purple fraction, which when dried yielded fine dark purple crystalline solids of $[CpCr(CO)_2]_2As_2$ (**2**; 100 mg, 0.20 mmol, 20.4% yield). Anal. Calcd for $(C_5H_5)_2Cr_2(CO)_4As_2$: C, 33.90; H, 2.03; Cr, 20.97; As, 30.21. Found: C, 33.92; H, 1.92; Cr, 20.75; As, 30.36. IR: ν(CO) 1932 vs, 1875 vs cm^{-1} (toluene). ^1H NMR (C_6D_6): δ(Cp) 4.12. ^{13}C NMR: δ(Cp) 85.23, δ(CO) 239.31. MS: *m/z* 609 ($Cp_2Cr_2As_5$), 5.34 ($Cp_2Cr_2As_4$), 496 ($Cp_2Cr_2(CO)_4As_2$), 468 ($Cp_2Cr_2(CO)_3As_2$), 459 ($Cp_2Cr_2As_3$), 440 ($Cp_2Cr_2(CO)_2As_2$), 412 ($Cp_2Cr_2(CO)As$, 384 ($Cp_2Cr_2As_2$), 319 ($CpCr_2As_2$), 267 ($CpCrAs_2$), 192 (CpCrAs), 182 (Cp_2Cr), 117 (CpCr). The next fractions were a brown solution in ether (5 mL) and THF (5 mL) and a light green solution in CH_3CN (20 mL), each giving ca. 10 mg of mixtures of Cp-containing species that could not be separated for identification. The final fraction was a Prussian blue solution eluted with methanol (20 mL), which on concentration yielded a paramagnetic dark blue crystalline solid (53 mg; 13.6% yield based on its Cr content). Its elemental analysis indicated the empirical formula $(C_5H_5)_2Cr_2AsO_5$ (**6**). Attempts to grow a single crystal for a structural analysis have not proved successful so far.

A similar reaction for 16 h gave **3**, **5**, **6**, and **7** (described below) in yields of 5, 22, 39, and 8%, respectively.

Prolonged Reaction of $[CpCr(CO)_3]_2$ (1) at 140 °C. A suspension of finely ground gray arsenic (600 mg, 8.0 mmol) in a deep green solution of $[CpCr(CO)_3]_2$ (200 mg, 0.453 mmol) in xylene (10 mL) was refluxed with stirring for ca. 6 h. The resultant brown mixture was concentrated to ca. 1 mL and loaded onto a silica gel column (1 × 10 cm) prepared in *n*-hexane. Elution with *n*-hexane (5 mL) followed by a 1:1 *n*-hexane–toluene mixture (5 mL) gave a yellow fraction, from which $CpCr(CO)_2As_3$ (**3**) (12 mg, 0.03 mmol, 3% yield) was obtained. Elution with toluene (5 mL) followed by ether (5 mL) and finally a 1:1 ether–THF mixture (5 mL) gave a brown fraction, which on concentration to dryness yielded fine dark brown crystalline solids (50 mg). The ^1H NMR spectrum of these solids showed two broad peaks centered at δ 15.5 and 14.8. Chromatography of this brown product on a silica gel column (1 × 6 cm) prepared in *n*-hexane gave (i) a light brown fraction (11 mg residue, δ 14.8 and 11.3) eluted with 1:1 *n*-hexane–toluene (10 mL) (ii) a brown fraction eluted with toluene and ether (15 mL), which gave 29 mg of a dark solid (**7**; 15% yield based on Cr content, δ 14.8) (elemental analyses indicated the approximate molecular formula $(C_5H_5)_5Cr_5As_4O_8$, but this could not be structurally confirmed due to lack of a single diffraction-quality crystal), and (iii) a yellowish brown fraction (12-mg residue, δ 15.5 and 14.8) on further elution with a 1:1 ether–THF mixture (10 mL).

Reaction of $[CpCr(CO)_2]_2$ (4). A suspension of finely ground arsenic (215 mg, 2.87 mmol) in a deep green solution of $[CpCr(CO)_2]_2$ (60 mg, 0.173 mmol) in toluene (4 mL) was stirred under reflux for 1 h to give a dark purplish blue mixture.

A 2-mL aliquot of the supernatant solution was removed via a syringe, filtered through a 1-cm disk of Celite, and eluted with THF (ca. 3 mL). The filtrate/eluate was concentrated to dryness and the residue (33 mg) redissolved in toluene (ca. 1 mL) and loaded onto a column (1.5 × 2.5 cm) of silica gel prepared in *n*-hexane. Elution gave (1) a yellow fraction with *n*-hexane (15 mL), which yielded yellowish brown flakes of $CpCr(CO)_2As_3$ (**3**; 11 mg, 0.028 mmol, 31.9% yield), (ii) a purple fraction with 1:1 *n*-hexane–toluene (10 mL) followed by toluene (5 mL), from which was obtained fine purplish black crystalline solids of $[CpCr(CO)_2]_2As_2$ (**2**; 8 mg, 0.016 mmol, 18.5% yield), and finally (iii) a Prussian blue fraction with THF (20 mL), which yielded dark blue crystalline solids (**6**; 13 mg, 38.3% yield based on its Cr content).

The remaining aliquot in the flask was refluxed for a further 4 h, after which the resultant dark blue mixture was worked up via similar column chromatography. Elution gave (i) a purple fraction with 1:1 *n*-hexane–toluene (10 mL) followed by toluene (5 mL), which yielded **2** (8 mg, 0.02 mmol, 18.6% yield), (ii) a greenish brown fraction with 1:1 toluene–ether, which when dried gave an unidentified brown residue (2 mg), and (iii) a Prussian blue fraction with ether (5 mL) followed by THF (10 mL), which yielded fine dark blue crystalline solids of **6** (15 mg, 44.2% yield). A blue immovable band remained at the top of the column.

Thermolysis of $[CpCr(CO)_2]_2As_2$ (2). NMR Study. A purple solution of $[CpCr(CO)_2]_2As_2$ (**2**; 10 mg, 0.020 mmol) in toluene-d_8 (ca. 0.5 mL) in a 5-mm NMR tube vented via a syringe needle into a nitrogen line was maintained at ca. 110–115 °C, and its degradation was monitored by ^1H NMR spectroscopy at 0.5-h intervals. After 0.5 h, the spectrum showed three peaks corresponding to the presence of **2** (δ 4.12), **4** (δ 4.23), and $Cp_2Cr_2As_5$ (**5**; δ 23.5, $\nu_{1/2}$ 176 Hz) in the molar ratio of 3.5:2.8:1, respectively. After 5 h, **2** completely converted to a 1:1 molar mixture of **4** and **5**. After 18 h, **4** was no longer detected in the resultant brown solution but only **5** and two new broad peaks centered at δ 15.5 and 14.8 in the ratio of 2.5:1:1, with a substantial amount of a dark brown precipitate of $Cp_2Cr_2As_5$ (δ 23.5) at the bottom of the tube.

Product Isolation. A deep purple solution of $[CpCr(CO)_2]_2As_2$ (70 mg, 0.14 mmol) in toluene (10 mL) was stirred under nitrogen at reflux temperature for ca. 16 h. Filtration of the resultant brown solution gave ca. 25 mg (0.04 mmol, 29% yield) of dark brown amorphous solids of $Cp_2Cr_2As_5$ (δ 23.5). The filtrate, concentrated to ca. 1 mL, was loaded onto a silica gel column (1.5 × 7 cm) prepared in *n*-hexane. Elution with *n*-hexane (25 mL) followed by a 1:1 *n*-hexane–toluene mixture (10 mL) gave a golden yellow fraction, which on concentration yielded fine black crystalline solids of $Cp_2Cr_2As_5$ (15 mg, 0.025 mmol, 17.5% yield). Anal. Calcd for $(C_5H_5)_2Cr_2As_5$: C, 19.73; H, 1.66; Cr, 17.08. Found: C, 20.13; H, 1.67; Cr, 17.31. Further elution with a 1:1 toluene–ether mixture gave a brown fraction, which yielded 15 mg (28% yield) of a dark solid (**7**; δ14.8), described above. An immovable greenish

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Table I. Data Collection and Processing Parameters

mol formula	$[C_5H_5Cr(CO)_2]_2As_2$
mol wt	496.07
color and habit	dark-purple flat needles with (100) well developed
unit-cell params	a = 15.551 (3) Å b = 7.453 (1) Å c = 13.446 (2) Å β = 96.21 (2)° V = 1549.4 (4) $Å^3$ Z = 4 $F(000)$ = 960
density (calcd)	2.127 g/cm^3
space group	$C2/c$ (No. 15)
radiation	graphite-monochromatized Mo Kα, λ = 0.71073 Å
std rflns	(222), (422)
intens variation	±1%
R_{int} (from merging of equiv rflns)	0.022
abs coeff	56.13 cm^{-1}
cryst size	0.40 × 0.32 × 0.04 mm^3
mean μr	0.025
transmissn factors	0.347–0.839
scan type and rate	ω–2θ; 2.93–14.65 deg min^{-1}
scan range	0.65° below Kα_1 to 0.65° above Kα_2
bkgd counting	stationary counts for 1/5 of scan time at each end of scan range
hkl collecn range	0–18, 0–8, −17 to +17; $2\theta_{max}$ = 50°
no. of unique data measured	1201
no. of obsd data with $\lvert F_o\rvert \geq 6\sigma(\lvert F_o\rvert)$, n	893
no. of variables, p	100
$R_F = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$	0.034
weighting scheme	$w = [\sigma^2(F_o) + 0.0006\lvert F_o\rvert^2]^{-1}$
$R_G =]\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.040
$S = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(n - p)]^{1/2}$	1.141
resid extrema in final diff map	+0.34 to −0.42 e $Å^{-3}$

blue rim remained at the top of the column.

Thermolysis of $CpCr(CO)_2As_3$. A yellow solution of $CpCr(CO)_2As_3$ (**3**; 40 mg, 0.10 mmol) in toluene (4 mL) was thermolyzed with stirring under reflux. No color change was observed up to 7 h. After 21 h, the solution had turned slightly brownish with some dark precipitate. Filtration removed fine black crystalline solids of $Cp_2Cr_2As_5$ (**5**; 3 mg 0.005 mmol, 5% yield). The concentrated filtrate (ca. 1 mL) was loaded onto a column (1.5 × 3.5 cm) of silica gel prepared in *n*-hexane. Elution with *n*-hexane (15 mL) gave a yellow fraction, which yielded yellowish brown flakes on unreacted **3** (27 mg, 0.068 mmol, 68% yield). Further elution with toluene (10 mL) gave a golden yellow fraction, which yielded more fine black crystalline solids of **5** (8 mg, 0.013 mmol, 13% yield). A dark layer remained immovable at the top of the column.

Crystal Structure Analysis of 2. Single crystals of **2** were obtained as dark purple flat trapezoidal-shaped needles from toluene layered with *n*-hexane after 6 days at −30 °C.

Details of crystal parameters, data collection, and structure refinement are given in Table I. Raw intensities collected on a Nicolet R3m/V four-circle diffractometer at room temperature (294 K) were processed with the profile-fitting procedure of Diamond[16] and corrected for absorption with use of the ψ-scan data of eight selected reflections over the range $6 < 2\theta < 23°$.[17] Patterson superposition yielded the positions of all non-hydrogen atoms except those of the cyclopentadienyl group, which were derived from successive difference Fourier syntheses. All non-hydrogen atoms were subjected to anisotropic refinement, and the H atoms were generated geometrically (C–H bonds fixed at 0.96 Å) and assigned the same isotropic temperature factor of U = 0.12 $Å^2$. No extinction correction was applied. Computations were performed with use of the SHELTXL-PLUS program package[18] on a DEC MicroVAX-II computer. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated.[19]

Table II. Atomic Coordinates (×10⁵ for Cr and As; ×10⁴ for Other Atoms) and Equivalent Isotropic Temperature Factors[a] (×10⁴ Å² for Cr and As; ×10³ Å² for Other Atoms)

atom	x	y	z	U_{eq}
Cr(1)	41514 (6)	28153 (11)	18336 (6)	452 (3)
As(1)	54323 (4)	50593 (7)	18693 (4)	510 (2)
C(1)	4742 (5)	2347 (7)	758 (4)	64 (3)
O(1)	5074 (5)	1981 (8)	53 (3)	111 (3)
C(2)	3622 (5)	4711 (8)	1107 (5)	66 (2)
O(2)	3274 (4)	5839 (7)	636 (4)	91 (2)
C(3)	2810 (5)	2090 (11)	2034 (10)	115 (5)
C(4)	3322 (6)	1695 (9)	2927 (7)	92 (4)
C(5)	3917 (5)	365 (8)	2734 (5)	65 (2)
C(6)	3772 (6)	−35 (8)	1706 (6)	74 (3)
C(7)	3109 (6)	1019 (11)	1287 (8)	106 (4)

[a] U_{eq} defined as one-third of the trace of the orthogonalized **U** tensor.

Results and Discussion

Products and Reaction Pathways. A deep green solution of $[CpCr(CO)_3]_2$ (**1**) underwent complete reaction under rigorous stirring with excess gray arsenic powder in refluxing toluene after 1–1.5 h. Column chromatography of the resultant purplish black solution led to the isolation of a μ-η^2-As_2 complex (**2**) as dark purple crystals (20.4% yield), a η^3-As_3 complex (**3**) as yellow crystalline flakes (14.2% yield), the known Cr≡Cr-bonded complex **4** (5.3% yield), and a Prussian blue complex of empirical formula $Cp_2Cr_2AsO_5$ (**6**); 13.6% yield), as shown in eq i, as well as

$$[CpCr(CO)_3]_2 \xrightarrow[1.5\ h/110\ °C]{As} \underset{2,\ 21.4\%}{[CpCr(CO)_2]_2As_2} + \underset{3,\ 14.2\%}{[CpCr(CO)_2(\eta^3\text{-}As_3)]} + \underset{4,\ 5.3\%}{[CpCr(CO)_2]_2(Cr{\equiv}Cr)} + \underset{6,\ 13.6\%}{[Cp_2Cr_2AsO_5]} + \text{others (very low yields)} \qquad \text{(i)}$$

minor amounts of two as yet uncharacterizable Cp-containing species, showing bonds at δ 14.8 and 15.5 in the ^1H NMR spectrum. This facile reaction with elemental gray As under heterogeneous conditions is unusual. Only a few reactions of organotransition-metal complexes with elemental arsenic have been reported hitherto, and all but one of these invariably involved the use of the reactive yellow As_4 vapor dissolved in solution. Ziegler's reaction of the analogous Mo and W complexes with metallic As required more drastic conditions (24 h in refluxing xylene) to produce the respective μ-η^2-As_2 and $Cp_3M_3(CO)_6As$ complexes.[5] It is conceivable that the ease of reaction in this case derives from the high propensity of **1** to dissociate into its monomer radicals (eq ii).[20,21]

$$[CpCr(CO)_3]_2 \rightleftharpoons 2[CpCr(CO)_3{}^\bullet] \qquad \text{(ii)}$$

Indeed, ample evidence has accumulated to indicate that all reactions of **1** occur via its monomeric form.[21] The subsequent radical attack of $CpCr(CO)_3{}^\bullet$ on elemental

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arsenic would generate the Cr–As complexes 2 and 3, as postulated for the analogous reaction with P_4.[12] However, as in all reactions of 1 under thermolytic conditions, the intermediatory role of $[CpCr(CO)_2]_2$(*Cr*≡*Cr*) (4) arising from the decarbonylation of 1[12,14,22] always provides an alternative pathway. In this reaction, 4 was indeed isolated (5.3% yield) from the product mixture. Subsequently, it is herein demonstrated that the reaction of a suspension of 4 with a 16–17-fold molar excess of pulverized elemental arsenic reaches completion within 1 h in refluxing toluene, giving 2 (18.5), 3 (31.9%), and 6 (38.3%). An extended reaction period of 5 h gave 2 (18.6%) and 6 (44.2%).

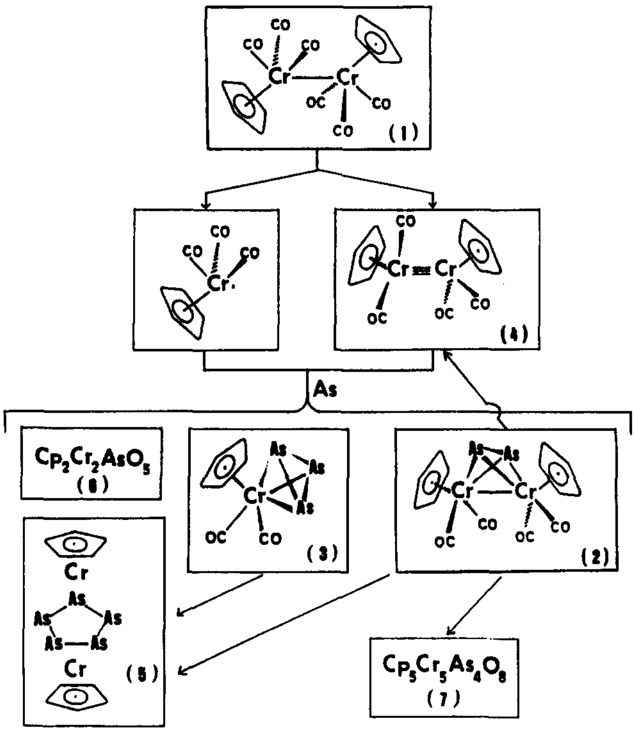
This finding indicates the route via 4 could contribute substantially to the reaction. However, as in the reaction with P_4,[12,14] this contribution can only be subsidiary, judging from the short reaction time versus the longer time required for complete decarbonylation, which has been reported to exceed 2.5 h in refluxing toluene.[22] It is appropriate to note here that Scherer's reaction of the analogous $[Cp^*Mo(CO)_2]_2$(*Mo*≡*Mo*) complex ($Cp^* = \eta^5\text{-}C_5Me_5$) with yellow As_4 in refluxing xylene (140 °C) gave, after 30 h, $[Cp^*Mo(CO)_2]_2(\mu\text{-}\eta^2\text{-}As_2)$ (1.2%), $Cp^*Cr(CO)_2(\eta^3\text{-}As_3)$ (15%), $[Cp^*Mo(CO)(\mu\text{-}\eta^2\text{-}As_2)]_2$ (1.7%), and *cis*-$[Cp^*_2Mo_2(\mu\text{-}O)_2O_2]$ (2%).[7]

Thermolytic Degradation of 2 and 3. Compared to the isolation of 2, 3, and 6 in 20.4%, 14.2%, and 13.6% yields, respectively, from 1 to 1.5 h reaction time in refluxing toluene, the reaction when extended to 16 h gave 3, 5, 6, and 7 in 5, 22, 39, and 8% yields, respectively. Prolonged cothermolysis of 1 with As in refluxing xylene (ca. 140 °C) for 6 h led to the isolation of 3 (3% yield) and a mixture of two Cp-containing species possessing δ(Cp) 14.8 and 15.5 in the ^1H NMR spectrum. These could be separated to give the former species in 15% yield (δ 14.8, approximate empirical formula $Cp_5Cr_5As_4O_8$ (7)). Indeed, an NMR study of the thermolytic degradation of 2 in toluene-d_8 at ca. 110 °C indicated a fairly rapid transformation to 4 and $Cp_2Cr_2As_5$ (5), which is spectrally detected at 30 min and is complete in 5 h to give a 1:1 millimolar mixture of 4 and 5. Further thermolysis to 18 h gave only 5 and the species possessing broad resonances at δ 14.8 and 15.5 mentioned above. A product isolation from the thermolysis of 2 after 16 h in refluxing toluene yielded 5 (46.5%) and 7 (δ 14.8, 28%).

Likewise, 3 also thermally degrades to 5, though at a much slower rate (ca. 30% after 21 h in refluxing toluene). The thermolytic degradation of 2 and 3 to 5 is consistent with Scherer's isolation of only $Cp_2Cr_2As_5$ (5) in 37.7% yield from the reaction of 1 with yellow As_4 at 150 °C for 2.5-3 h.[23] Similarly, the forcing conditions employed (30 h, 150 °C) may be the cause of the low yield of the $\mu\text{-}\eta^2\text{-}As_2$ complex (1.2%) from the reaction of the $[Cp^*Cr(CO)_2]_2$(*Mo*≡*Mo*) complex with yellow As_4.[7]

The observations described above are best presented schematically as in Scheme I. The findings are reminiscent of similar reaction and degradation pathways for the analogous P complexes[13,14] and indicate that, as in the case of the $\eta^5\text{-}P_5$ complex,[13] the formation of $Cp_2Cr_2As_5$ proceeds via thermal degradation of the $\mu\text{-}\eta^2\text{-}As_2$ and $\eta^3\text{-}As_3$ complexes.

Scheme I



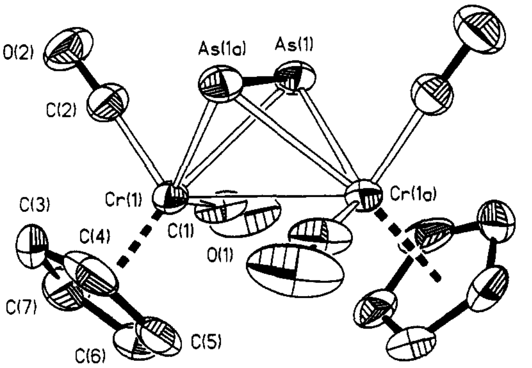


Figure 1. ORTEP drawing of the molecular structure of 2. The thermal ellipsoids are shown at the 35% probability level.

Properties and Spectral Characteristics. Deep purple crystals of the complex 2 are air-stable for extended periods at ambient temperature, whereas the yellow crystals of 3 are much less stable and definitely incapable of lasting several days in transit for an X-ray structural analysis. Both of these compounds dissolve readily in most organic solvents, giving purple and yellow solutions, respectively. A toluene solution of 2 exhibits ν(CO) at 1932 vs and 1875 vs cm^{-1}. The CO stretching frequencies of 3 in toluene at 1960 vs and 1905 vs cm^{-1} are strikingly similar to those of its analogous cyclo $\eta^3\text{-}P_3$ complexes (1975 vs and 1920 vs cm^{-1})[12] and point to a similarity in symmetry and structure. Both 2 and 3 are diamagnetic, and the Cp rings and CO ligands appear as singlets in both the ^1H and ^{13}C NMR spectra. These resonances of 2 (δ(Cp) 4.12 for ^1H and 85.23 for ^{13}C and δ(CO) 239.31) and of 3 (δ(Cp) 3.94 for ^1H and 83.04 for ^{13}C and δ(CO) 233.93) are very close to values obtained for their analogous $\mu\text{-}\eta^2\text{-}P_2$ (δ(Cp) 4.15 and 86.4 and δ(CO) 238.60) and $\eta^3\text{-}P_3$ (δ(Cp) 3.92 and 84.91 and δ(CO) 233.74) complexes.[12] The Cp resonance of the complex 5 as reported before shows a paramagnetic downfield shift to δ 23.5 ($\nu_{1/2}$ 176 Hz).

The mass spectrum of 2 shows the parent ion and its fragmentation ions, as well as those of $Cp_2Cr_2As_5$ (5), which is consistent with its facile degradation to 5, which is consistent with its facile degradation to 5 observed under thermolytic conditions. Similar observations have been made for the analogous $\mu\text{-}\eta^2\text{-}P_2$ complexes.[12]

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Table III. Bond Lengths (Å) and Bond Angles (deg)

Cr(1)–Cr(1a)[a]	3.026 (1)	Cr(1)–As(1)	2.597 (1)
Cr(1)–As(1a)	2.452 (1)	As(1)–As(1a)	2.276 (1)
Cr(1)–C(1)	1.829 (7)	Cr(1)–C(2)	1.859 (6)
Cr(1)–X(1a)[b]	1.862 (6)	C(1)–O(1)	1.160 (9)
C(2)–O(2)	1.152 (8)	C(3)–C(4)	1.40 (1)
C(3)–C(7)	1.40 (2)	C(4)–C(5)	1.40 (1)
C(5)–C(6)	1.41 (1)	C(6)–C(7)	1.37 (1)
Cr(1a)–Cr(1)–As(1)	51.0 (1)	Cr(1a)–Cr(1)–As(1a)	55.4 (1)
As(1)–Cr(1)–As(1a)	53.5 (1)	Cr(1a)–Cr(1)–C(1)	89.3 (2)
As(1)–Cr(1)–C(1)	71.8 (2)	As(1a)–Cr(1)–C(1)	125.2 (2)
Cr(1a)–Cr(1)–C(2)	128.3 (2)	As(1)–Cr(1)–C(2)	79.4 (2)
As(1a)–Cr(1)–C(2)	85.6 (2)	C(1)–Cr(1)–C(2)	87.8 (3)
Cr(1a)–Cr(1)–X(1a)	114.0 (2)	AS(1)–Cr(1)–X(1a)	164.6 (2)
As(1a)–Cr(1)–X(1a)	117.3 (2)	C(1)–Cr(1)–X(1a)	115.1 (3)
C(2)–Cr(1)–X(1a)	113.7 (3)	Cr(1)–As(1)–Cr(1a)	73.6 (1)
Cr(1)–As(1)–As(1a)	60.0 (1)	Cr(1a)–As(1)–As(1a)	66.5 (1)
Cr(1)–C(1)–O(1)	175.7 (6)	CR(1)–C(2)–O(2)	177.4 (5)
C(4)–C(3)–C(7)	107.0 (7)	C(3)–C(4)–C(5)	108.5 (8)
C(4)–C(5)–C(6)	107.0 (6)	C(5)–C(6)–C(7)	108.5 (7)
C(3)–C(7)–C(6)	109.0 (8)		

[a] Symmetry transformation for a: $1 - x, y, {}^1/_2 - z$. [b] X(1a) is the center of the ring composed of carbon atoms C(3)–C(7).

Table IV. Comparison of Selected Bond Distances (Å) and Angles (deg) for $[CpM(CO)_2]_2As_2$

	M = Cr[a]	M = Mo[3]	M = W[3]	$Co_2(CO)_5(PPh_3)As_2$[1]	$[(MeC_5H_4)Mo(CO)]_2(As_2)_2$[4]
M–M′	3.026 (1)	3.038 (2) 3.039 (2)	3.026 (2) 3.013 (2)	2.594[b]	2.950 (1)
As–As′	2.276 (1)	2.311 (3) 2.312 (3)	2.326 (5) 2.319 (5)	2.273 (3)	2.300 (2) 2.279 (2)
M–As	2.597 (1)	2.676 (2) 2.663 (2)	2.682 (3) 2.663 (3)	2.386 (av)	2.626 (1)
M–As′	2.452 (1)	2.569 (2) 2.567 (2)	2.573 (3) 2.571 (3)		
M–M′–As	55.4 (1)	53.0 (1) 53.0 (1)	53.2 (1) 53.4 (1)		
M′–M–As	51.0 (1)	56.3 (1) 56.0 (1)	56.5 (1) 56.3 (1)	57.1 (av)	
M–As–M′	73.6 (1)	70.8 (1) 71.0 (1)	70.3 (1) 70.3 (1)	65.8 (av)	
M–As–As′	66.5 (1) 60.0 (1)	61.5 (1) 61.6 (1)	61.3 (1) 61.7 (1)		
M′–As–As′	73.6 (1)	66.3 (1) 65.9 (1)	66.2 (1) 65.8 (1)	61.5 (av)	
As–M–As′	53.5 (1)	52.2 (1) 52.4 (1)	52.5 (1) 52.6 (1)	56.9 (av)	

[a] This work. [b] No esd was given in ref 3.

Molecular Structure of 2. A perspective view of the molecular structure with atom numbering is shown in Figure 1. The molecule is isostructural with the isomorphous Mo and W analogues,[3] having a μ-η^2-As_2 ligand bridging two Cr atoms, and also with the analogous μ-η^2-P_2 complex,[12] although the compounds crystallize in different space groups. The unit-cell dimensions of 2 are in fact consistent with those of the Mo and W analogues[3] with interchange of the *a* and *c* axes. Some selected bond lengths and bond angles are presented in Table III and compared in Table IX with those of the Mo and W analgues and two other structurally determined μ-η^2-As_2 complexes.

The As–As distance (2.276 Å) almost matches the shortest ever observed As–As bond (2.273 Å) in $Co_2(CO)_5(PPh_3)As_2$[1] and is significantly shorter than that in gaseous As_4 (2.44 Å)[24] and in the *cyclo*-polyarsines $[AsCH_3]_5$ (2.428 (8) Å)[25] and $[As(C_6H_5)]_6$ (2.456 (5) Å).[26] Dahl et al. had attributed this bond shortening to a partial charge transfer from the As_2 moiety to the metal fragment "electron sink", thereby decreasing electron-pair repulsion between the As atoms.[1] The Cr–Cr distance of 3.026 Å is close to that expected of a single bond.[20]

In the presence of a single metal–metal bond and on the assumption that the μ-η^2-As_2 ligand serves as a 4e donor, the noble-gas configuration at each Cr atom is achieved. The marginally shorter M–As and M–As′ distances in 2 could result from the smaller size of Cr when compared to those of Mo and W.

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Registry No. 1, 12194-12-6; 2, 132344-58-2; 3, 132344-59-3; 4, 54667-87-7; 5, 124273-44-5; As, 7440-38-2.

Supplementary Material Available: Listings of anisotropic thermal parameters and hydrogen atom coordinates for 2 (1 page); a listing of observed and calculated structure factor amplitudes for 2 (5 pages). Ordering information is given on any current masthead page.

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