ORGANOMETALLICS

(Dimethylarsino)phenylchromium tricarbonyl as a source of (benzyne)chromium tricarbonyl. The novel structures of Ru3(CO)8(.mu.-H){.mu.3-.eta.2-[(.eta.6-C6H4)Cr(CO)3]}(.mu.-AsMe2) and Ru2(CO)6(.mu.-H){.mu.-.eta.2-[(.eta.6-C6H4)Cr(CO)3]}(.mu.-AsMe2)

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(Dimethylarsino)phenylchromium Tricarbonyl as a Source of (Benzyne)chromium Tricarbonyl. The Novel Structures of $Ru_3(CO)_8(\mu\text{-}H)\{\mu_3\text{-}\eta^2\text{-}[(\eta^6\text{-}C_6H_4)Cr(CO)_3]\}(\mu\text{-}AsMe_2)$ and $Ru_2(CO)_6(\mu\text{-}H)\{\mu\text{-}\eta^2\text{-}[(\eta^6\text{-}C_6H_4)Cr(CO)_3]\}(\mu\text{-}AsMe_2)$

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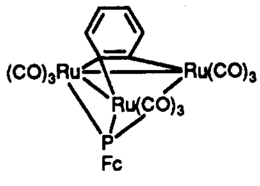
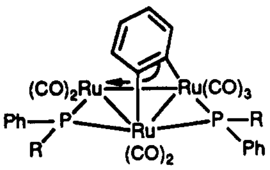
Summary: The pyrolysis of $Ru_3(CO)_{11}L$*, L =* $AsMe_2C_6H_5Cr(CO)_3$*, affords* $Ru_3(CO)_8(\mu\text{-}H)\{\mu_3\text{-}\eta^2\text{-}[(\eta^6\text{-}C_6H_4)Cr(CO)_3]\}(\mu\text{-}AsMe_2)$ *(5) and* $Ru_2(CO)_6(\mu\text{-}\eta^2\text{-}[(\eta^6\text{-}C_6H_4)Cr(CO)_3]\}(\mu\text{-}AsMe_2)$ *(6). In 5 the (benzyne)chromium tricarbonyl moiety is unsymmetrically bound to the closed* Ru_3 *triangle; in 6 the same group acts as a two-electron-donating o-phenylene derivative. A Ru–Cr bond is present in 5 but not in 6. Crystals of 5 are triclinic,* $a = 10.322(2)$ *Å,* $b = 13.290(2)$ *Å,* $c = 9.536(1)$ *Å,* $\alpha = 91.23(1)°$*,* $\beta = 95.89(1)°$*,* $\gamma = 101.89(1)°$*,* $Z = 2$*, space group* $P\bar{1}$*, and those of 6 are monoclinic,* $a = 10.862(1)$ *Å,* $b = 14.655(2)$ *Å,* $c = 14.590(3)$ *Å,* $\beta = 107.57(1)°$*,* $Z = 4$*, space group* $P2_1/c$*. The structures were solved by heavy-atom methods and were refined by full-matrix least-squares procedures to* $R = 0.027$ *for 6446 and 4577 reflections with* $I \geq 3\sigma(I)$*, respectively.*

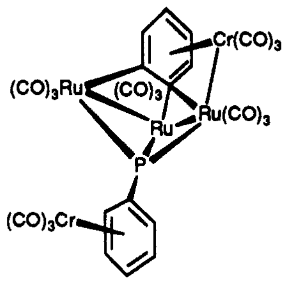
The pyrolysis of tertiary phosphine derivatives of $Ru_3(CO)_{12}$ has been a fruitful method for the preparation of Ru_n clusters (n = 3–6) such as 1 and 2 that contain benzyne moieties.[1] We have utilized this same approach in the synthesis of Ru_3 derivatives of (benzyne)chromium tricarbonyl and have successfully prepared and characterized 3 and 4, products respectively of heating $Ru_3(CO)_{12}$ with $PPh[C_6H_5Cr(CO)_3]_2$ or $PBu^t[C_6H_5Cr(CO)_3]_2$.[1g,2] One notable feature of both structures 3 and 4 is the presence of a Cr–Ru bond. If the C_6 ring in 3 is regarded as being a two-electron donor to the open Ru_3 core, which is likely on the basis of the Ru–C distances, the Cr–Ru bond can be regarded as being formed in the sense Cr→Ru.[1g] The reverse sense Ru→Cr seems to apply to the bonding in 4 where the C_6 ring acts as a four-electron donor to the closed Ru_3 core.[2] The symmetrical bonding of the aryne moiety in 4 and 2 is the usual orientation found in benzyne derivatives of Ru_n clusters, and complexes 3 and 1 are the only known examples of unsymmetrical bonding of the aryne moiety to an open Ru_3 cluster. Osmium analogues of 2 are very well-known;[3] less so are analogues of 1.[4]



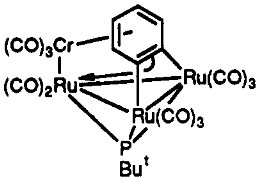
1



2a: R = Ph
b: R = Fc



3



4

We now describe an unprecedented derivative of (benzyne)chromium tricarbonyl 5 in which the C_6 ring is unsymmetrically bound to a closed Ru_3 cluster. The same reaction also afforded the first example of a dinuclear o-phenylenechromium tricarbonyl derivative 6.

Experimental Section

Unless otherwise stated, all reactions were conducted in an argon atmosphere by using standard Schlenk and vacuum line techniques. Literature procedures were used for the preparation of $(CH_3)_2AsI$[5] and $Ru_3(CO)_{12}$.[6] Solvents were freshly distilled from the appropriate drying agents prior to use. Preparative flash chromatography was performed on silica gel (230–400 mesh) from BDH.

^1H NMR spectra were recorded by using Varian XL300 and Bruker WH400 spectrometers. Low resolution mass spectra, in both electron ionization (EI) and fast atom bombardment (FAB) modes, were obtained by using Kratos MS-50 and AEI MS-9 spectrometers, and infrared spectra by using Perkin-Elmer 598 and 783 infrared spectrophotometers.

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Preparation of (η^6-Phenyl)tricarbonylchromium Dimethylarsine. *n*-Butyllithium (1.9 mL, 1.6 M solution in hexane, 3 mmol) was added to a cold, stirred solution of (benzene)chromium tricarbonyl (534 mg, 2.5 mmol) in 30 mL of tetrahydrofuran at −78 °C. The solution was stirred at this temperature for 60 min, then 0.3 mL (3 mmol) of $(CH_3)_2AsI$ in 5 mL of THF was added. The resulting solution was stirred for 60 min at −78 °C and allowed to warm to room temperature slowly. The solution was filtered through a short column of silica gel (230–400 mesh). Removal of the solvent under reduced pressure gave a red oil which yielded crystals from CH_2Cl_2/hexanes. The yield was 550 mg (70%). Mass spectrum (EI): *m/e* 318 (P^+). ^1H NMR ($CDCl_3$, 300 MHz), δ: 1.4 (s, 6H), 5.3 (m, 2H), 5.5 (m, 3H). IR (KBr): 1950 (s), 1870 (s) cm^{-1}. Anal. Calcd for $C_{11}H_{11}O_3CrAs$: C, 41.53; H, 3.49. Found: C, 41.63; H, 3.49.

Preparation of $Ru_3(CO)_{11}[AsMe_2C_6H_5Cr(CO)_3]$. To a rapidly stirred solution of $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol) and $(CH_3)_2AsC_6H_5Cr(CO)_3$ (99.5 mg, 0.31 mmol) in 25 mL of THF was added dropwise freshly prepared $Na(Ph_2CO)$ solution until the solution darkened (typically 5–10 drops). When TLC examination of the reaction mixture showed that no starting material remained, the solvent was removed under vacuum. The residual dark red oil was chromatographed on silica gel with CH_2Cl_2/hexanes as eluant to give $Ru_3(CO)_{11}[Me_2AsC_6H_5Cr(CO)_3]$ (245 mg, 85% yield) as a red powder. Mass spectrum (FAB): *m/e* 931 (P^+). ^1H NMR ($CDCl_3$, 300 MHz), δ: 1.9 (s, 6H), 5.3 (t, 2H), 5.4 (d, 2H), 5.6 (t, 1H). IR (KBr): 2100 (m), 2040 (s), 2020 (s), 1970 (s), 1900 (s), 1890 (sh) cm^{-1}. Anal. Calcd for $C_{22}H_{11}O_{14}AsRu_3Cr$: C, 28.43; H, 1.20. Found: C, 28.14; H, 1.23.

Pyrolysis of $Ru_3(CO)_{11}[AsMe_2C_6H_5Cr(CO)_3]$. A sample of the complex (400 mg, 0.43 mmol) was heated in refluxing octane (40 mL) for 5 h. The reaction was monitored by TLC. Evaporation of the solvent followed by chromatography of the residue (silica gel; CH_2Cl_2/hexanes 1:1.8) gave six bands. Bands 2, 3, and 5 contained small amounts of unidentified complexes. Band 1 was $Ru_3(CO)_{12}$ of known IR spectrum. Band 4 (red) gave $HRu_3(CO)_8[C_6H_4Cr(CO)_3](AsMe_2)$ (120 mg) (**5**). Crystals suitable for X-ray analysis were grown from CH_2Cl_2/hexanes by the layering technique. FAB mass spectrum: *m/e* 846 $(M)^+$. ^1H NMR (CD_2Cl_2, 400 MHz), δ: −18.2 (s, 1H) 2.3 (s, 3H), 2.5 (s, 3H), 4.7 (d, 1H), 4.8 (t, 1H), 5.0 (d, 1H), 6.05 (t, 1H). Anal. Calcd for $C_{19}H_{11}O_{11}AsCrRu_3$: C, 26.99; H, 1.31. Found: C, 26.95; H, 1.32.

Band 5 (yellow) contained $HRu_2(CO)_6\{C_6H_4Cr(CO)_3\}(AsMe_2)$ (**6**) (170 mg), recrystallized as above from CH_2Cl_2/hexanes, as yellow crystals suitable for X-ray analysis. FAB mass spectrum: *m/e* 689 $(M)^+$. ^1H NMR (CD_2Cl_2, 400 MHz), δ: −12 (s, 1H), 1.4 (s, 3H), 1.8 (s, 3H), 5.0 (t, 2H), 5.2 (t, 2H). Anal. Calcd for $C_{17}H_{11}O_9AsRu_2Cr$: C, 29.66; H, 1.61. Found: C, 29.72; H, 1.70.

X-ray Crystallographic Analyses. Crystallographic data for $\{\mu_3\text{-}\eta^2\text{-}[(\eta^6\text{-}C_6H_4)Cr(CO)_3)]\text{-}Cr,C^1,C^1,C^2\}(\mu\text{-}AsMe_2)(\mu\text{-}H)Ru_3(CO)_8$ (**5**) and $[\mu\text{-}\eta^2\text{-}(\eta^6\text{-}C_6H_4)Cr(CO)_3)](\mu\text{-}H)Ru_2(CO)_6$ (**6**) appear in Table I. The final unit-cell parameters were obtained by least squares on the setting angles for 25 reflections with $2\theta = 52.0$–54.8° for **5** and 46.4–52.5° for **6**. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, remained constant for both complexes. The data were processed[7] and corrected for Lorentz–polarization effects and absorption (empirical, based on azimuthal scans for three reflections).

Both structures were solved by heavy atom methods, the coordinates of the Ru, Cr, and As atoms being determined from the Patterson functions and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. The structure analysis of **5** was initiated in the centrosymmetric space group $P\bar{1}$, this choice being confirmed by the subsequent successful solution and refinement of the structure. All non-hydrogen atoms of both complexes were refined with anisotropic thermal parameters. The metal hydride atoms in both complexes were refined with isotropic thermal parameters. All other hydrogen atoms were fixed in idealized positions (methyl groups staggered, C–H = 0.98 Å, $B_H = 1.2B_{\text{bonded atom}}$). Corrections for secondary extinction were applied for both structures,[7d] the final values of the extinction coefficient being 3.05×10^{-7} for **5** and 1.79×10^{-6} for **6**. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 7a. Final atomic coordinates and equivalent isotropic thermal parameters, selected bond lengths, and selected bond angles appear in Tables II–V, respectively. Hydrogen atom parameters, anisotropic thermal parameters, complete tables of bond lengths and bond angles, torsion angles, and least-squares planes are included as supplementary material.

Table I. Crystallographic Data[a]

compd	**5**	**6**
formula	$C_{19}H_{11}AsCrO_{11}Ru_3$	$C_{17}H_{11}AsCrO_9Ru_2$
fw	845.42	688.33
color, habit	orange, irregular	yellow, prism
cryst size, mm	0.25 × 0.35 × 0.40	0.17 × 0.35 × 0.40
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	10.322(2)	10.862(1)
b, Å	13.290(2)	14.655(2)
c, Å	9.356(1)	14.590(3)
α, deg	91.23(1)	90
β, deg	95.89(1)	107.57(1)
γ, deg	101.89(1)	90
V, Å^3	1248.2(3)	2214.1(5)
Z	2	4
ρ_{calc}, g/cm^3	2.249	2.065
F(000)	804	1320
μ(Mo Kα), cm^{-1}	35.28	33.16
trans factors (relative)	0.68–1.00	0.53–1.00
scan type	ω–2θ	ω–2θ
scan range, deg in ω	$1.52 + 0.35 \tan\theta$	$1.31 + 0.35 \tan\theta$
scan rate, deg/min	32	32
data collected	$+h,\pm k,\pm l$	$+h,+k,\pm l$
$2\theta_{\max}$, deg	70	65
cryst decay	negligible	negligible
total no. of reflns	11 466	8665
no. of unique reflns	10 955	8296
R_{merge}	0.034	0.039
no. of reflns with $I \geq 3\sigma(I)$	6446	4577
no. of variables	321	276
R	0.027	0.027
R_w	0.024	0.025
gof	1.75	1.54
max Δ/σ (final cycle)	0.06	0.001
residual density, e/Å^3	−0.59 to +0.58	−0.56 to +0.43

[a] Temperature 294 K, Rigaku AFC6S diffractometer, Mo Kα radiation (λ = 0.710 69 Å), graphite monochromator, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan:background time ratio 2:1, up to eight rescans), $\sigma^2(F^2) = [S^2(C + 4B)]/Lp^2$ (S = scan rate, C = scan count, B = normalized background count), function minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and gof $= [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$. Values given for R, R_w, and gof are based on those reflections with $I \geq 3\sigma(I)$.

Results and Discussion

The pyrolysis of $Ru_3(CO)_9(PPh_3)_3$ in refluxing decalin yielded **2a** in ~20% yield. Significant amounts of

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Table II. Final Atomic Coordinates (Fractional) and B_{eq} (Å^2)^a for 5

atom	x	y	z	B_{eq}
Ru(1)	0.13696(2)	0.16794(2)	0.28475(2)	2.513(7)
Ru(2)	0.42480(2)	0.24464(2)	0.33347(3)	3.026(9)
Ru(3)	0.30123(2)	0.25649(2)	0.05198(2)	2.932(8)
As(1)	0.29925(3)	0.06673(2)	0.33178(4)	3.29(1)
Cr(1)	0.04096(5)	0.36375(3)	0.27006(5)	2.94(2)
O(1)	–0.0888(3)	0.0006(2)	0.1499(3)	6.4(1)
O(2)	0.0506(3)	0.1233(2)	0.5788(3)	5.5(1)
O(3)	0.6485(3)	0.1705(2)	0.2063(3)	6.6(1)
O(4)	0.5132(4)	0.2465(3)	0.6562(3)	8.7(2)
O(5)	0.5506(3)	0.4744(2)	0.3256(3)	5.7(1)
O(6)	0.5450(3)	0.4025(2)	–0.0345(3)	7.6(1)
O(7)	0.1169(3)	0.2961(2)	–0.2048(3)	7.2(2)
O(8)	0.3988(3)	0.0809(2)	–0.0974(3)	6.5(1)
O(9)	–0.1845(3)	0.4710(2)	0.2082(3)	6.6(1)
O(10)	–0.1065(3)	0.2348(2)	0.0132(3)	6.5(1)
O(11)	–0.1400(3)	0.2697(2)	0.4854(3)	5.3(1)
C(1)	0.2449(3)	0.3272(2)	0.3254(3)	2.7(1)
C(2)	0.2407(3)	0.3638(2)	0.1816(3)	2.8(1)
C(3)	0.2020(3)	0.4584(2)	0.1544(3)	3.5(1)
C(4)	0.1721(3)	0.5175(2)	0.2677(4)	3.9(1)
C(5)	0.1817(3)	0.4853(2)	0.4095(3)	3.7(1)
C(6)	0.2143(3)	0.3902(2)	0.4376(3)	3.3(1)
C(7)	0.3023(4)	–0.0467(3)	0.1998(4)	5.4(2)
C(8)	0.3003(4)	–0.0040(3)	0.5120(4)	4.9(2)
C(9)	–0.0039(3)	0.0622(2)	0.2034(3)	3.7(1)
C(10)	0.0836(3)	0.1452(2)	0.4695(3)	3.5(1)
C(11)	0.5655(3)	0.1979(3)	0.2551(4)	4.4(1)
C(12)	0.4758(4)	0.2441(3)	0.5373(4)	4.8(2)
C(13)	0.5044(3)	0.3891(2)	0.3247(3)	3.9(1)
C(14)	0.4546(4)	0.3509(3)	0.0009(4)	4.5(1)
C(15)	0.1854(4)	0.2800(3)	–0.1104(3)	4.2(1)
C(16)	0.3625(3)	0.1425(3)	–0.0395(4)	4.3(1)
C(17)	–0.0950(4)	0.4318(3)	0.2302(4)	4.2(1)
C(18)	–0.0471(3)	0.2795(3)	0.1140(4)	4.3(1)
C(19)	–0.0684(3)	0.3015(2)	0.4015(4)	3.6(1)

[a] $B_{eq} = (8/3)\pi^2\sum\sum U_{ij}a_i^*a_j^*(\mathbf{a}_i\cdot\mathbf{a}_j)$.

Table III. Final Atomic Coordinates (Fractional) and B_{eq} (Å^2)^a for 6

atom	x	y	z	B_{eq}
Ru(1)	0.25424(2)	0.37898(2)	0.16130(2)	2.57(1)
Ru(2)	0.25587(2)	0.58064(2)	0.18744(2)	2.60(1)
As(1)	0.44037(3)	0.47714(2)	0.23341(3)	2.89(1)
Cr(1)	0.01748(5)	0.46055(4)	0.31544(4)	2.78(2)
O(1)	–0.0081(2)	0.2842(2)	0.0816(2)	5.6(1)
O(2)	0.3988(3)	0.2171(2)	0.2716(2)	6.1(1)
O(3)	0.3351(3)	0.3509(2)	–0.0225(2)	6.8(2)
O(4)	0.3846(3)	0.7269(2)	0.3309(2)	6.3(2)
O(5)	–0.0132(3)	0.6679(2)	0.1274(2)	5.6(1)
O(6)	0.3409(3)	0.6649(2)	0.0212(2)	6.9(2)
O(7)	–0.1302(3)	0.4669(2)	0.1067(2)	5.6(1)
O(8)	–0.1853(3)	0.3389(2)	0.3482(2)	6.0(2)
O(9)	–0.1544(3)	0.6143(2)	0.3295(2)	5.6(1)
C(1)	0.2058(3)	0.4153(2)	0.2861(2)	2.6(1)
C(2)	0.2087(3)	0.5118(2)	0.2996(2)	2.6(1)
C(3)	0.1879(3)	0.5473(2)	0.3836(2)	3.3(1)
C(4)	0.1650(3)	0.4889(3)	0.4541(3)	4.1(2)
C(5)	0.1605(3)	0.3952(3)	0.4389(3)	4.2(2)
C(6)	0.1790(3)	0.3686(2)	0.3553(2)	3.3(1)
C(7)	0.3423(3)	0.2755(2)	0.2267(3)	3.9(2)
C(8)	0.0873(3)	0.3213(2)	0.1101(3)	3.6(1)
C(9)	0.3061(3)	0.3616(3)	0.0441(3)	4.0(2)
C(10)	0.3363(3)	0.6737(2)	0.2746(3)	3.9(2)
C(11)	0.0854(3)	0.6343(2)	0.1483(3)	3.5(1)
C(12)	0.3079(3)	0.6329(3)	0.0795(3)	4.0(2)
C(13)	0.5766(3)	0.4838(3)	0.1732(3)	4.6(2)
C(14)	0.5329(4)	0.4609(3)	0.3685(3)	5.2(2)
C(15)	–0.0713(3)	0.4628(2)	0.1868(3)	3.6(1)
C(16)	–0.1067(3)	0.3839(2)	0.3335(3)	3.8(1)
C(17)	–0.0864(3)	0.5555(3)	0.3249(3)	3.6(1)

[a] $B_{eq} = (8/3)\pi^2\sum\sum U_{ij}a_i^*a_j^*(\mathbf{a}_i\cdot\mathbf{a}_j)$.

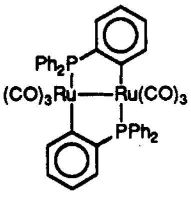
Table IV. Selected Bond Lengths (Å) for 5 and 6

Compound 5			
Ru(1)–Ru(2)	2.9203(6)	Ru(3)–C(2)	2.084(3)
Ru(1)–Ru(3)	3.0082(5)	Ru(3)–H(1)	1.75(2)
Ru(1)–As(1)	2.3689(5)	Cr(1)–R^a	1.746(2)
Ru(1)–Cr(1)	2.9704(6)	C(1)–C(2)	1.441(4)
Ru(1)–C(1)	2.185(3)	C(1)–C(6)	1.429(4)
Ru(1)–H(1)	1.74(2)	C(2)–C(3)	1.416(4)
Ru(2)–Ru(3)	2.8282(5)	C(3)–C(4)	1.402(4)
Ru(2)–As(1)	2.4499(5)	C(4)–C(5)	1.403(4)
Ru(2)–C(1)	2.339(3)	C(5)–C(6)	1.396(4)
Compound 6			
Ru(1)–Ru(2)	2.9791(5)	Cr(1)–R^a	1.750
Ru(1)–As(1)	2.4453(5)	C(1)–C(2)	1.427(4)
Ru(1)–C(1)	2.111(3)	C(1)–C(6)	1.404(4)
Ru(1)–H(1)	1.79(3)	C(2)–C(3)	1.411(4)
Ru(2)–As(1)	2.4403(5)	C(3)–C(4)	1.417(5)
Ru(2)–C(2)	2.113(3)	C(4)–C(5)	1.390(5)
Ru(2)–H(1)	1.79(3)	C(5)–C(6)	1.401(50)

[a] Here and elsewhere, R refers to the unweighted centroid of the C(1–6) aromatic ring.

Table V. Selected Bond Angles (deg) for 5 and 6

Compound 5			
Ru(2)–Ru(1)–Ru(3)	56.96(1)	Ru(1)–Cr(1)–R	85.4
Ru(2)–Ru(1)–As(1)	53.97(1)	C(17)–Cr(1)–C(18)	82.8(2)
Ru(2)–Ru(1)–Cr(1)	101.12(2)	C(17)–Cr(1)–C(19)	82.3(1)
Ru(2)–Ru(1)–C(1)	52.14(8)	Ru(1)–Ru(2)–Ru(3)	63.08(1)
Ru(2)–Ru(1)–H(1)	83.8(8)	Ru(1)–Ru(2)–As(1)	51.44(1)
Ru(3)–Ru(1)–As(1)	85.27(2)	Ru(1)–Ru(2)–C(1)	47.51(6)
Ru(3)–Ru(1)–Cr(1)	83.96(2)	Ru(3)–Ru(2)–As(1)	87.87(2)
Ru(3)–Ru(1)–C(1)	64.64(7)	Ru(1)–Ru(3)–Ru(2)	59.95(1)
Ru(3)–Ru(1)–H(1)	30.5(8)	Ru(1)–Ru(3)–H(1)	30.4(8)
Cr(1)–Ru(1)–C(1)	49.38(8)	C(18)–Cr(1)–C(19)	95.2(1)
Ru(2)–Ru(3)–H(1)	86.6(8)	Ru(1)–C(1)–Ru(2)	80.35(9)
Ru(1)–As(1)–Ru(2)	74.58(2)	Ru(1)–H(1)–Ru(3)	119(1)
Compound 6			
Ru(2)–Ru(1)–As(1)	52.35(1)	Ru(2)–H(1)–Ru(1)	113(2)
Ru(2)–Ru(1)–C(1)	68.47(8)	Ru(1)–Ru(2)–H(1)	34(1)
Ru(2)–Ru(1)–H(1)	34(1)	As(1)–Ru(2)–C(2)	82.03(8)
As(1)–Ru(1)–C(1)	82.50(8)	As(1)–Ru(2)–H(1)	83(1)
As(1)–Ru(1)–H(1)	82(1)	Ru(1)–As(1)–Ru(2)	75.15(2)
Ru(1)–Ru(2)–As(1)	52.50(1)	C(15)–Cr(1)–C(16)	88.6(2)
Ru(1)–Ru(2)–C(2)	68.41(9)	C(15)–Cr(1)–C(17)	85.2(2)
Ru(1)–C(1)–C(2)	111.6(2)	C(16)–Cr(1)–C(17)	87.6(1)



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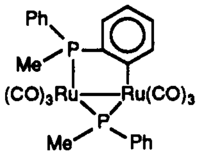

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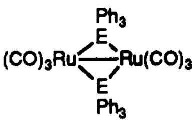


9a: E = P
b: E = As

dinuclear complexes, which were formulated as in **7**–**9**, were also formed in this and related reactions.[1a] The benzyne complex **2a** is also a product of the pyrolysis of $Ru_3(CO)_{11}PPh_3$ (33% yield) although $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}PPh)(\mu_4\text{-}\eta^4\text{-}C_6H_4)$ (50%) and $Ru_5(CO)_{13}(\mu_4\text{-}PPh)(\mu_4\text{-}PPh)(\mu_5\text{-}\eta^6\text{-}C_6H_4)$ (7%) can be isolated.[1e] Apparently, no dinuclear species are formed. In like manner $Ru_3(CO)_{11}AsPh_3$ affords Ru_4– and Ru_5–benzyne complexes analogous to the phosphorus derivatives, but the major product, 65% yield, is **9b**.[1e]

Phosphine and arsine derivatives of $Os_3(CO)_{12}$ undergo similar thermal reactions although only Os_3–benzyne derivatives are isolated.[3,4] Thus $Os_3(CO)_{11}PPh_3$ yields an osmium analogue of **1** with PPh replacing the PFc group,[4] $Os_3(CO)_{11}PMe_2Ph$ yields a benzyne derivative **10a**.[3e] Complex **10b** is a product of the thermolysis of $Os_3(CO)_{11}AsMe_2Ph$; in addition **11**, which was not well characterized, is produced in very low yield.

The nature of the ligand is clearly important in determining product distribution in these pyrolytic de-

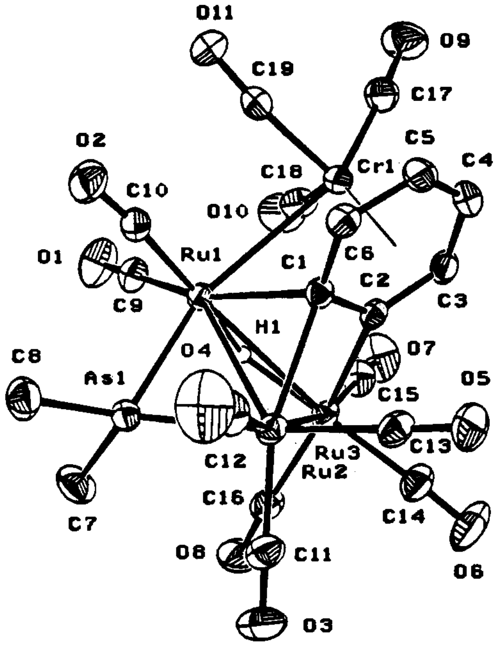
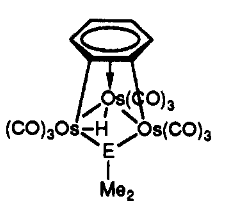
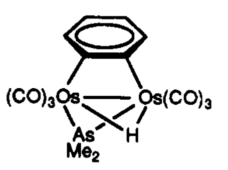


Figure 1. Perspective view of 5. Probability thermal ellipsoids (33%) are shown for the non-hydrogen atoms.



10a: E = P
b: E = As



11

composition reactions, so it was of interest to establish if an arsine would act as a source of benzynechromium tricarbonyl and if it would afford an aryne complex substantially different from **3** and **4**.

The new ligand $AsMe_2[C_6H_5Cr(CO)_3]$ proved to be easily prepared from $AsMe_2I$ and $LiC_6H_5Cr(CO)_3$ and it reacts readily with $Ru_3(CO)_{12}$ to afford $Ru_3(CO)_{11}AsMe_2[C_6H_5Cr(CO)_3]$, when benzophenone ketyl is used as catalyst.[8] The spectroscopic and analytical data support the formulation of the ligand and its complex. After the latter is heated in refluxing octane, two main products can be isolated; these are $Ru_3(CO)_8(H)(AsMe_2)(C_6H_4Cr(CO)_3)$ (**5**) and $Ru_2(CO)_6(H)(AsMe_2)[C_6H_4Cr(CO)_3]$ (**6**). It seemed that **6** was a ruthenium analogue of the tentatively characterized compound **11** and that **5** was of a different structure from the previously known structural types **3** and **4**; consequently the structure of both compounds was determined, and ORTEP plots are shown in Figures 1 and 2.

The (benzyne)chromium tricarbonyl moiety in **5**, Figure 1, is unsymmetrically bound to a closed Ru_3 cluster. One long metal–metal bond (Ru(1)–Ru(2) = 2.9203(6) Å) is bridged unsymmetrically by an $AsMe_2$ group; another (Ru(1)–Ru(3) = 3.0082(5) Å) is bridged by a hydride that was located in the refinement. The third Ru–Ru bond is normal at 2.8285(2) Å. A Cr→Ru bond (2.9704(6) Å) is present, and if the aryne C_6 ring is regarded as being a two-electron donor to the cluster, the chromium atom supplies the necessary electrons for an electron-precise structure. Thus the bonding of the aryne moiety in **5** is similar to that in **3**.[1g] (The reverse flow of electrons Ru→Cr in **4** is indicated by a distinct folding of the aromatic ring.[2]) The pattern of C–C bond lengths in the aryne rings of both structures **3** and **5** is remarkably similar, as are the Cr–ring centroid distances, 1.746(2) Å for **5** and 1.751(3) Å for **3**.

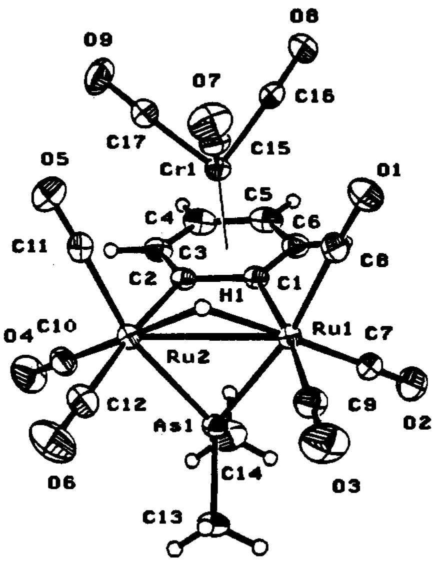
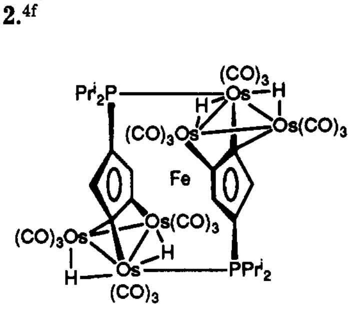


Figure 2. Perspective view of **6**. Probability thermal ellipsoids (33%) are shown for the non-hydrogen atoms.

The unsymmetrical bonding of the C_6 ring in **5** is evident from the following data: the Ru(2)–C(1)–C(2)–Ru(3) conformational angle is 33.2(2)°; Ru(2) is 1.323 Å from the C_6 plane, and Ru(3) is at a 0.118-Å distance but on the opposite side; Ru(1)–C(1) = 2.185(3) Å, Ru(2)–C(1) = 2.339(3) Å, Ru(3)–C(2) = 2.084(3) Å, but Ru(1)–C(2) = 2.833(3) Å, longer than any reasonable bonding interaction. The only previously known example of an aryne bound unsymmetrically to a *closed* M_3 cluster is the ferrodicyne derivative, **12**.[4f]



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The *o*-phenylene moiety in the Ru_2 complex **6**, Figure 2, is required to be a two-electron donor.[9] The molecule appears to have mirror symmetry, but minor distortions are present, e.g. As(1)–Ru(1) = 2.4453(5) Å and As(1)–

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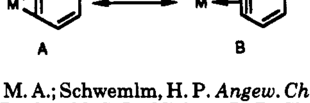
(8) Bruce, M. I. *Coord. Chem. Rev.* 1987, *76*, 1.

(9) The bonding of benzyne in a mononuclear metal complex represented by the canonical form A where M lies in the plane of the ring, can be described in terms of an *o*-phenylene/metal interaction; however, the phrase "delocalized benzometallacyclopropene" seems more appropriate.[10] We suggest that the use of *o*-phenylene be confined to descriptions of derivatives such as **6**, **13**, **14**, and **15** where the structure is analogous to that of 1,2-diiodobenzene.



(10) (a) Bennett, M. A.; Schwemlm, H. P. *Angew. Chem., Int. Ed. Eng.* 1989, *28*, 1296. (b) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* 1988, *88*, 1047.

Ru(2) = 2.4403(5) Å and the conformational angle Ru(1)–C(1)–C(2)–Ru(2) is 1.4(2)°. The Cr–ring centroid distance is 1.750 Å, the same as in **5**, and the average Cr–C(ring) distances are the same, 2.247 Å. The C–C distances in **6** may be on average (1.408 Å) slightly shorter than in **5**, and the two equal Ru–C(ring) distances in **6** (2.112 Å) are within the range 2.084(3)–2.339(3) Å found in **5**.

Structures have been determined for two dinuclear *o*-phenylene complexes $Ir_2(CO)_2Cp_2(\mu\text{-}\eta^2\text{-}C_6H_4)$[11] (**13**) and $Fe_2(CO)_8(\mu\text{-}\eta^2\text{-}C_6F_4)$[12] (**14**) and one trinuclear derivative $Os_3(CO)_8(H)_3(\mu\text{-}\eta^2\text{-}C_6H_4)(\mu\text{-}\eta^2\text{-}HC{=}NC_6H_5)$[13] (**15**). Complex **15** is the only known trinuclear *o*-phenylene derivative.[14] As for **6** the metal–metal-bonded atoms in **13**–**15** do not quite lie in the plane of the aromatic moiety. The C–C distances average 1.379 Å for **13**, 1.375 Å for **14**, and 1.37 Å for **15**, and with no significant variation around the rings. As mentioned above, the average C—C lengths for **5** and **6** are longer than these values. However, it should be noted that the C—C bond lengths of $C_6H_6Cr(CO)_3$ range from 1.406 to 1.423 Å and are longer than those of free benzene, 1.397 Å, so the trends noted above may be a simple extension of this fundamental observation.[16]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Supplementary Material Available: Tables of hydrogen atom parameters, anisotropic thermal parameters, complete bond lengths and bond angles, torsion angles, and least-squares planes and stereo ORTEP diagrams for **5** and **6** (24 pages). Ordering information is given on any current masthead page.

OM920627T

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[12] Bennett, M. J.; Graham, W. A. G.; Stewart, R. P.; Tuggle, R. M. *Inorg. Chem.* **1973**, *12*, 2944.

[13] Adams, R. D.; Golembeski, N. M. *J. Organomet. Chem.* **1979**, *172*, 239.

[14] The anion $[Pt_4(C_6H_4)_2Cl_{14}]^{2-}$ consists of two $[Pt_2Cl_4(\mu\text{-}C_6H_4)(\mu\text{-}Cl)_2]$ moieties linked by two bridging chlorine atoms. Unfortunately, few details of the structure are available.[15]

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[16] Rees, B.; Coppens, P. *Acta Crystallogr., Sect. B* **1973**, *29*, 2516.