Ferrocyne and Ferrodicyne. Preparation and Structures of $Os_3(CO)_9[\mu_3\text{-}(C_5H_3)Fe(C_5H_5)][\mu_3\text{-}P(C_5H_4)Fe(C_5H_5)]$, $Os_3(H)_2(CO)_8(PPr^i_2C_5H_2)Fe(C_5H_2PPr^i_2)Os_3(H)_2(CO)_8$, and $Os_3(CO)_9[\mu_3\text{-}C_6H_4][\mu_3\text{-}P(C_5H_4)Fe(C_5H_5)]$

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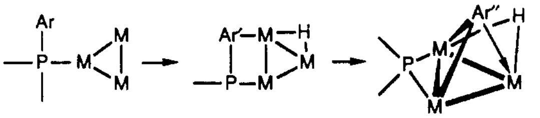
The thermolysis of $Os_3(CO)_{11}PPhFc_2$ affords $Os_3(CO)_9[\mu_3\text{-aryne}][\mu_3\text{-}P(C_5H_4)Fe(C_5H_5)]$ (aryne = ferrocyne, $(C_5H_3)Fe(C_5H_5)$ (2), benzyne, C_6H_4 (6)). Likewise the ferrodicyne $Fe(C_5H_3)_2$ derivative $Os_3(H)_2(CO)_8(PPr^i_2C_5H_2)Fe(C_5H_2PPr^i_2)Os_3(H)_2(CO)_8$ (3) is obtained from $Os_3(CO)_{11}(PPr^i_2C_5H_4)Fe(C_5H_4PPr^i_2)Os_3(CO)_{11}$. In 2 the ferrocyne moiety is a symmetrical four-electron donor to an open Os_3P cluster; in 6 the benzyne is an unsymmetrical donor of two to four electrons to the open Os_3P cluster. In 3 each aryne ring acts as an unsymmetrical four-electron donor to a closed Os_3 cluster that is also coordinated to the PPr^i_2 group of the other aryne ring. Crystal data for $2\cdot0.5CH_2Cl_2$: triclinic, $P\bar{1}$, a = 12.638 (4) Å, b = 15.244 (5) Å, c = 9.867 (3) Å, α = 100.85 (2)°, β = 105.56 (2)°, γ = 69.80 (2)°, Z = 2; final R = 0.028 (R_w = 0.030) from 6180 observed reflections. Crystal data for 3: monoclinic, $P2_1/c$, a = 13.607 (2) Å, b = 22.925 (6) Å, c = 16.649 (3) Å, β = 113.00 (2)°, Z = 4; final R = 0.031 (R_w = 0.026) from 7034 observed reflections. Crystal data for 6: triclinic, $P\bar{1}$, a = 10.858 (3) Å, b = 13.960 (3) Å, c = 10.383 (3) Å, α = 95.54 (3)°, β = 110.98 (3)°, γ = 106.34 (2)°, Z = 2; final R = 0.035 (R_w = 0.040) from 6251 observed reflections.

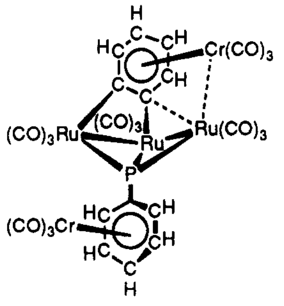
Although the analogy between benzene and ferrocene is well established, the literature is silent on the parallel association between the very reactive molecule benzyne, C_6H_4, and ferrocyne, $Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_3)$.[1-4] In fact, references to ferrocyne are limited to reports which suggest that the species might be involved as a reaction intermediate.[2] Benzyne has been trapped on transition-metal centers in η^2, $\mu_3\text{-}\eta^2$, and $\mu_4\text{-}\eta^2$ bonding modes,[3] and this success has prompted us to attempt the same with ferrocyne.[4]

Our approach has been to heat arylphosphine derivatives of ruthenium and osmium carbonyls in order to activate an aryl C–H bond and form a metal–carbon bond. Phosphorus–carbon bond cleavage then leads to aryne capture by the metal cluster. A typical sequence is shown in eq 1.



(1)

We have recently achieved some success in this general area with the characterization of the (benzyne)chromium tricarbonyl complex 1, which was prepared by heating $Ru_3(CO)_{12}$ with $PhP[C_6H_5Cr(CO)_3]_2$.[5] There is good evidence that the aryne moiety acts as a four-electron donor in this molecule, with two electrons coming from the chromium atom in the form of a Cr→Ru bond of length 3.098 (3) Å.



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We now describe the ferrocyne complex $Os_3(CO)_9[\mu_3\text{-}(C_5H_3)Fe(C_5H_5)][\mu_3\text{-}P(C_5H_4)Fe(C_5H_5)]$ (2) and the ferrodicyne[6] complex $Os_3(H)_2(CO)_8(PPr^i_2C_5H_2)Fe(C_5H_2PPr^i_2)Os_3(H)_2(CO)_8$ (3), respectively products of the thermal decomposition of $Os_3(CO)_{11}PPhFc_2$ (4) and $[Os_3(CO)_{11}]_2[Fe(C_5H_4PPr^i_2)_2]$ (5).

The structures of 2 and 3 are shown in Figures 1 and 2. Figure 3 shows the structure of the benzyne derivative $Os_3(CO)_9[\mu_3\text{-}C_6H_4][\mu_3\text{-}P(C_5H_4)Fe(C_5H_5)]$ (6), isolated from the same reaction that afforded 2.

Experimental Section

Standard Schlenk and Vacuum-line techniques were used for the manipulation of air-sensitive substances. Argon was usually used as the inert atmosphere. ^{31}P chemical shifts are reported relative to 85% H_3PO_4.

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(6) Buchwald and co-workers[7] have described the structure of the zirconocene–benzdiyne complex $[(Me_3P)Cp_2Zr]_2C_6(OMe)_2$. On this basis a suitable name for $Fe(\eta\text{-}C_5H_3)_2$ would be ferrodiyne; however, we prefer the more euphonious ferrodicyne.

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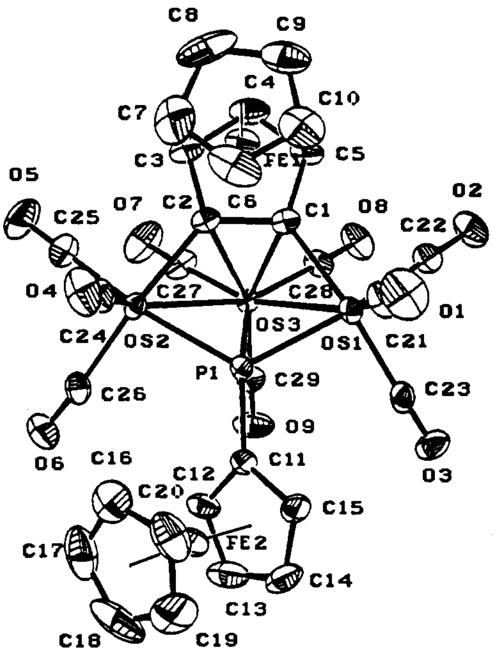

Figure 1. ORTEP diagram for 2.

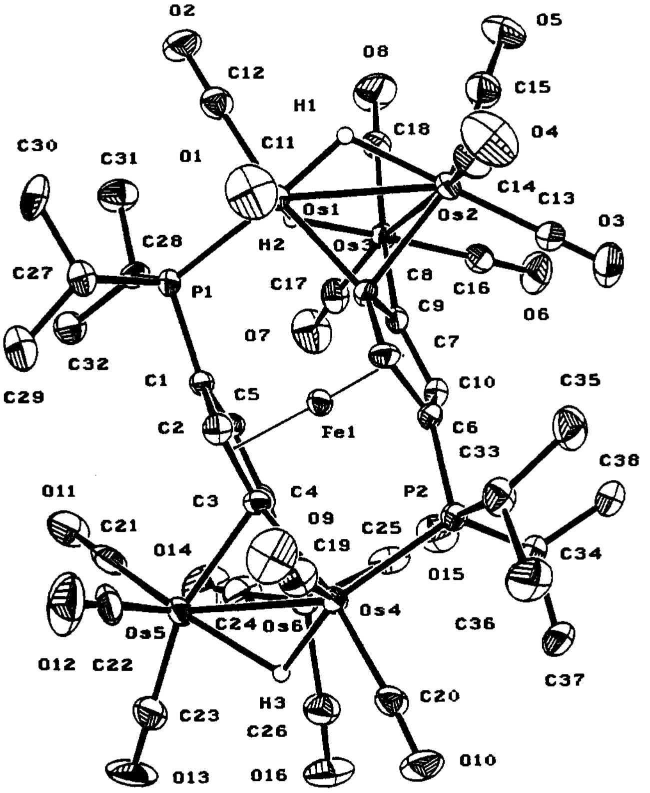

Figure 2. ORTEP diagram for 3.

Preparation of 2 and 6. $Os_3(CO)_{11}PPhFc_2$[8] (100 mg, 0.074 mmol) in octane (80 mL) was heated to reflux under an Ar atmosphere for 3 h. Six compounds were produced in moderate yield, as judged by TLC, and they were separated by column chromatography on silica by using 4:1 petroleum ether/CH_2Cl_2 as eluant. The first band (orange) was identified as 6 (20% yield) and the second band (green) proved to be 2 (25% yield). Suitable crystals of 2 and 6 were grown from ~1:1 mixtures of CH_2Cl_2/diethyl ether and CH_2Cl_2/petroleum ether, respectively. 6: ^1H NMR ($CDCl_3$, 400 MHz) δ 4.26 (s, 5 H), 4.55 (m, 2 H), 4.62 (m, 2 H), 7.11 (m, 2 H), 7.62 (m, 2 H); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.4 MHz) δ 207.2; mass spectrum (FAB) *m/e* 1116 (M^+) with successive loss of 9 CO's. Anal. Calcd for $C_{25}H_{13}FeO_9Os_3P$: C, 26.94; H, 1.18. Found: C, 27.01, H, 1.20. 2: ^1H NMR ($CDCl_3$, 400 MHz) δ 3.98 (m, 1 H), 4.20 (s, 5 H), 4.36 (s, 5 H), 4.52 (m, 4 H), 5.04 (dm, 2 H); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.4 MHz) δ 189.8; mass spectrum (FAB) *m/e* 1224 (M^+) with successive loss of 9 CO's. Anal. Calcd for $C_{29}H_{17}Fe_2O_9Os_3P$: C, 28.48; H, 1.39. Found: C, 28.21; H, 1.27.

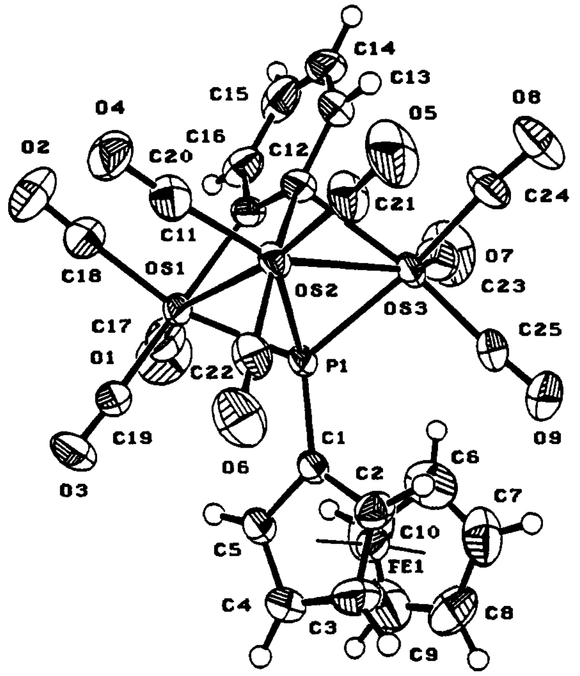

Figure 3. ORTEP diagram for 6.

Preparation of 5. A solution of $Os_3(CO)_{12}$ (453 mg, 0.5 mmol) and $Fe(C_5H_4PPr^i_2)_2$ (209 mg, 0.5 mmol) in toluene (100 mL) was refluxed (4 h). The solvent was removed under reduced pressure, and the solid residue was chromatographed on a silica column with 3:1 petroleum ether/CH_2Cl_2 as eluant. The first band was identified as 5 (20% yield): ^1H NMR ($CDCl_3$, 200 MHz) δ 4.62 (s, 4 H), 4.35 (s, 4 H), 2.36 (m, 4 H), 1.20 (dd, 12 H), 1.02 (dd, 12 H); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.4 MHz) δ 14.8; mass spectrum (FAB) *m/e* 2176 (P^+), 2148, 1182, 1061, 1003, 975, 947, 919. Anal. Calcd for $C_{44}H_{36}FeO_{22}Os_6P_2$: C, 24.29; H, 1.67. Found C, 24.08; H, 1.59.

The second major band was identified as $Os_3(CO)_{10}[Fe(C_5H_4PPr^i_2)_2]$ (70% yield): ^1H NMR ($CDCl_3$, 200 MHz) δ 4.3 (2 × s, 8 H), 2.42 (m, 4 H), 1.08 (dd, 24 H); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.4 MHz) δ 7.3; mass spectrum (FAB) *m/e* 1270 (M^+) with successive loss of 10 CO's and 2 isopropyl groups. Anal. Calcd for $C_{32}H_{36}FeO_{10}Os_3P_2$: C, 30.88; H, 2.86. Found: C, 30.49; H, 2.84.

Preparation of 3. Compound 5 (50 mg, 0.023 mmol) was refluxed in octane (20 mL) for 2.5 h. The solvent was removed under reduced pressure and the residue chromatographed on silica as above. Compound 3 eluted as the third band (15% yield), and suitable crystals for X-ray diffraction studies were obtained by slow evaporation of the eluant: ^1H NMR ($CDCl_3$, 200 MHz) δ −19.54 (d, *J* = 14.6 Hz, 2 H), −17.36 (d, *J* = 32.0 Hz, 2 H), 1.21 (m, 24 H), 2.40 (bm, 4 H), 4.58 (s, 2 H), 5.24 (s, 2 H); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.4 MHz) δ −5.3. Anal. Calcd for $C_{38}H_{36}FeO_{16}Os_6P_2$: C, 22.73; H, 1.81. Found C, 22.87; H, 1.89.

X-ray Crystallographic Analyses. Crystallographic data for $Os_3(CO)_9[\mu_3\text{-}(C_5H_3)Fe(C_5H_3)][\mu_3\text{-}P(C_5H_4)Fe(C_5H_5)]\cdot 0.5CH_2Cl_2$ ($2\cdot 0.5CH_2Cl_2$), $Os_3(H)_2(CO)_8(PPr^i_2C_5H_2)Fe(C_5H_2PPr^i_2)Os_3(H)_2(CO)_8$ (3), and $Os_3(CO)_9[\mu_3\text{-}C_6H_4][\mu_3\text{-}P(C_5H_4)Fe(C_5H_5)]$ (6) appear in Table I. The final unit-cell parameters were obtained by least squares on the setting angles for 25 reflections with 2θ = 30.7–46.6° for 2, 32.7–40.6° for 3, and 44.7–49.6° for 6. The intensities of 3 standard reflections, measured every 200 reflections throughout the data collections, showed only small random variations for all

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[8] 4 was prepared by the reaction of $Os_3(CO)_{11}(MeCN)$ in CH_2Cl_2 at room temperature with $PPhFe_2$. The compound was isolated in 75% yield by column chromatography (silica, 3:1 petroleum ether/CH_2Cl_2 eluant) and characterized by using spectroscopic and microanalytical techniques.

Table I. Crystallographic Data[a]

compd	$\mathbf{2}\cdot 0.5CH_2Cl_2$	**3**	**6**
formula	$C_{29.5}H_{18}ClFe_2O_9Os_3P$	$C_{38}H_{36}FeO_{16}Os_6P_2$	$C_{25}H_{13}FeO_9Os_3P$
fw	1265.18	2007.70	1114.79
color, habit	green, prism	orange, prism	red, irregular
cryst size, mm	0.25 × 0.30 × 0.32	0.08 × 0.22 × 0.25	0.40 × 0.40 × 0.45
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a, Å	12.638 (4)	13.607 (2)	10.858 (3)
b, Å	15.244 (5)	22.925 (6)	13.960 (3)
c, Å	9.867 (3)	16.649 (3)	10.383 (3)
α, deg	100.85 (2)	90	95.54 (3)
β, deg	105.56 (2)	113.00 (2)	110.98 (2)
γ, deg	69.80 (2)	90	106.34 (2)
V, Å^3	1708.9 (9)	4781 (2)	1375.5 (7)
Z	2	4	2
ρ_{calc}, g/cm^3	2.458	2.789	2.691
$F(000)$	1158	3616	1008
μ(Mo Kα), cm^{-1}	121.3	163.2	144.5
transmission factors	0.45–1.00	0.43–1.00	0.69–1.00
scan type	ω–2θ	ω–2θ	ω–2θ
scan range in ω, deg	1.31 + 0.35 tan θ	1.00 + 0.35 tan θ	1.21 + 0.35 tan θ
scan rate, deg/min	32	16	32
data collected	$h\pm k\pm l$	$+h,+k,\pm l$	$+h,\pm k,\pm l$
$2\theta_{max}$, deg	60	65	65
cryst decay, %	negligible	5.1	negligible
total no. of rflns	10383	18273	10360
no. of unique rflns	9966	17649	9908
R_{merge}	0.040	0.057	0.045
no. of rflns with $I > 3\sigma(I)$	6180	7034	6251
no. of variables	425	568	353
R	0.028	0.031	0.035
R_w	0.030	0.026	0.040
GOF	1.22	1.26	1.54
max Δ/σ (final cycle)	0.10	0.01	0.01
residual density, e/Å^3	−1.00 to +0.87	−1.12 to +1.07	−1.77 to +1.82

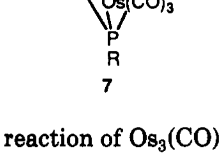
[a] Additional details: temperature 294 K, Rigaku AFC6S diffractometer, Mo Kα radiation (λ = 0.71069 Å), graphite monochromator, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1, up to 8 rescans), $\sigma^2(F^2) = [S^2(C + 4B) + (PF^2)^2]/(Lp)^2$ (S = scan rate, C = scan count, B = normalized background count, P = 0.03 for **2**, 0.01 for **3**, and 0.03 for **6**), 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 $I \geq 3\sigma(I)$.

three compounds. The data were processed[9] and corrected for Lorentz and polarization effects and absorption (empirical, based on azimuthal scans for 4 reflections).

For compounds **2** and **6**, the structure analyses were initiated in the centrosymmetric space group $P\bar{1}$ on the basis of the E statistics and the Patterson functions, these choices being confirmed by the subsequent successful solutions and refinements of the structures. The three structures were solved by heavy-atom methods, the coordinates of the Os atoms being determined from the Patterson functions and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. The asymmetric unit of **2** contains $^1/_2$ of a dichloromethane solvate molecule which is (1:1) disordered about a center of symmetry. The atoms of the dichloromethane were assigned site occupancy factors of 0.50. All non-hydrogen atoms of the three complexes were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in idealized positions (C–H = 0.98 Å, $B_H = 1.2B_{\text{bonded atom}}$). Three of the metal hydride atoms in **3** were located. Secondary extinction corrections were applied for all three complexes, the final values of the extinction coefficient being 1.72 × 10^{-6} for **2** and 9.55 × 10^{-6} for **6**. Neutral atom scattering factors and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 10. Final atomic coordinates and equivalent isotropic thermal parameters, bond lengths, and bond angles appear in Tables II–X. Stereoscopic ORTEP diagrams and tables of hydrogen atom parameters, torsion angles, least-squares planes, and measured and calculated structure factor amplitudes are included as supplementary material.

Results and Discussion

The thermal decomposition of $Os_3(CO)_{11}PPhFc_2$ (**4**) affords the unprecedented ferrocyne complex **2** and the benzyne complex **6** (Figures 1 and 3). In both cases one aryl moiety is probably lost as arene in a reaction sequence similar to that outlined by Deeming and co-workers[3g] for the formation of $Os_3(CO)_9(\mu_3\text{-}C_6H_4)(\mu_3\text{-}PR)$ from $Os_3(CO)_{11}PPh_2R$ (R = Me, Et, Ph; **7**).[3e] This scheme has been further elaborated to account for the products of the thermolysis of $Ru_3(CO)_{10}Fe(C_5H_4PPh_2)_2$.[4b]



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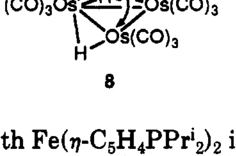

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The reaction of $Os_3(CO)_{12}$ with $Fe(\eta\text{-}C_5H_4PPr^i{}_2)_2$ in refluxing toluene affords as the major product the disubstituted derivative $Os_3(CO)_{10}Fe(\eta\text{-}C_5H_4PPr^i{}_2)_2$. In addition, the bis-monosubstituted complex **5** ($(Os_3(CO)_{11}PPr^i{}_2C_5H_4)Fe(C_5H_4PPr^i{}_2Os_3(CO)_{11})$) is also formed in lower yield. When **5** is refluxed in octane, the novel

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[9] TEXSAN/TEXRAY structure analysis package (Molecular Structure Co., 1985), which includes versions of the following: DIRDIF, direct methods for difference structures, by P. T. Beurskens; ORFLS, full-matrix least-squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; ORTEP II, illustrations, by C. K. Johnson.

[10] *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K. (present distributor Kluwer Academic Publishers: Dordrecht, The Netherlands), 1974; Vol. IV, pp 99–102, 149.

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

atom	x	y	z	B_{eq}[a]
Os(1)	0.34999 (2)	0.12545 (2)	0.22825 (3)	2.64 (1)
Os(2)	0.18155 (2)	0.40609 (2)	0.29064 (3)	2.72 (1)
Os(3)	0.31598 (2)	0.28707 (2)	0.10055 (2)	2.45 (1)
Fe(1)	0.46874 (8)	0.28634 (8)	0.5408 (1)	3.73 (5)
Fe(2)	−0.10938 (8)	0.26214 (8)	0.1351 (1)	4.17 (5)
P(1)	0.1805 (1)	0.2532 (1)	0.2051 (2)	2.47 (7)
O(1)	0.3495 (6)	0.0401 (5)	0.4802 (7)	7.3 (4)
O(2)	0.5882 (4)	−0.0040 (4)	0.1883 (6)	5.7 (3)
O(3)	0.2405 (5)	−0.0045 (4)	−0.0001 (7)	6.4 (3)
O(4)	0.1145 (5)	0.4201 (4)	0.5679 (6)	6.1 (3)
O(5)	0.2305 (6)	0.5946 (4)	0.3309 (8)	7.7 (5)
O(6)	−0.0616 (5)	0.5074 (4)	0.1291 (6)	5.5 (3)
O(7)	0.3456 (7)	0.4710 (5)	0.0613 (7)	7.3 (5)
O(8)	0.5355 (5)	0.1643 (4)	0.0031 (6)	5.5 (3)
O(9)	0.1631 (5)	0.2689 (5)	−0.1888 (5)	5.8 (4)
C(1)	0.4253 (5)	0.2314 (5)	0.3296 (6)	2.9 (3)
C(2)	0.3624 (5)	0.3359 (5)	0.3516 (6)	2.9 (3)
C(3)	0.4533 (6)	0.3806 (6)	0.4103 (7)	4.1 (4)
C(4)	0.5636 (6)	0.3105 (7)	0.4226 (8)	4.7 (4)
C(5)	0.5470 (5)	0.2223 (6)	0.3772 (7)	4.0 (4)
C(6)	0.3829 (8)	0.2631 (1)	0.6721 (9)	6.6 (6)
C(7)	0.403 (1)	0.3469 (8)	0.714 (1)	7.4 (7)
C(8)	0.529 (1)	0.330 (1)	0.7464 (9)	9 (1)
C(9)	0.5743 (8)	0.233 (1)	0.721 (1)	6.8 (7)
C(10)	0.486 (1)	0.1940 (8)	0.6780 (8)	6.2 (6)
C(11)	0.0525 (5)	0.2303 (5)	0.0964 (7)	3.2 (3)
C(12)	−0.0339 (6)	0.2823 (6)	−0.0104 (7)	4.1 (4)
C(13)	−0.1118 (7)	0.2332 (9)	−0.076 (1)	6.2 (6)
C(14)	−0.0781 (8)	0.1503 (7)	−0.013 (1)	6.2 (6)
C(15)	0.0224 (6)	0.1463 (5)	0.096 (1)	4.7 (4)
C(16)	−0.128 (1)	0.3481 (9)	0.318 (1)	6.5 (6)
C(17)	−0.214 (1)	0.3873 (8)	0.208 (2)	7.8 (7)
C(18)	−0.2756 (8)	0.325 (1)	0.150 (1)	9.2 (9)
C(19)	−0.227 (1)	0.2469 (9)	0.226 (2)	7.8 (8)
C(20)	−0.134 (1)	0.2621 (8)	0.330 (1)	6.8 (6)
C(21)	0.3523 (6)	0.0716 (6)	0.3854 (8)	4.3 (4)
C(22)	0.5001 (6)	0.0436 (5)	0.2035 (7)	3.5 (3)
C(23)	0.2781 (6)	0.0435 (5)	0.0862 (9)	4.0 (4)
C(24)	0.1407 (6)	0.4176 (5)	0.4660 (7)	3.9 (3)
C(25)	0.2128 (7)	0.5242 (6)	0.3155 (8)	4.6 (4)
C(26)	0.0255 (6)	0.4671 (5)	0.1896 (7)	3.6 (3)
C(27)	0.3316 (7)	0.4025 (6)	0.0770 (7)	4.2 (4)
C(28)	0.4534 (6)	0.2078 (5)	0.0393 (7)	3.6 (3)
C(29)	0.2210 (6)	0.2768 (5)	−0.0800 (7)	3.6 (3)
Cl(1)	−0.104 (3)	0.054 (2)	0.565 (3)	32 (4)
Cl(2)	0.087 (2)	0.056 (2)	0.628 (3)	36 (3)
C(30)	0.021 (4)	0.015 (4)	0.55 (1)	24 (6)

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

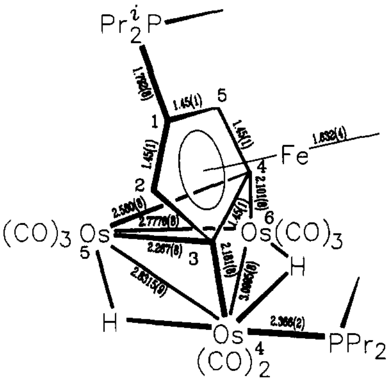
ferrodicyne cluster **3** (Figure 3) is produced in moderate yield.

The molecule of **3** can be regarded as the product of the oxidative addition of two adjacent C–H bonds in each C_5 ring to Os_3 clusters. The P–C(sp^2) bonds, which would normally be expected to be cleaved, remain intact. A close analogy to this result is found in the work of Deeming,[11] who reports the formation of **8** by heating indene with $Os_3(CO)_{12}$.[12] Benzene reacts similarly to afford the benzyne complex $Os_3(CO)_9(H)_2(\mu_3\text{-}C_6H_4)$ (**9**)[14] of known structure (Figure 4).[14c] Apparently **5** is set up so that the Os_3 fragment on each Cp ring can be brought close enough to the other Cp ring to allow C–H bond activation to take place.

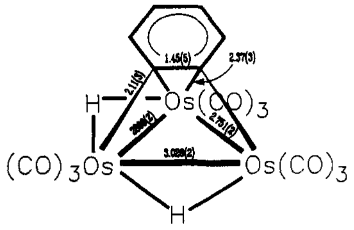
Table III. Bond Lengths (Å) with Estimated Standard Deviations for 2[a]

Os(1)–Os(3)	2.827 (1)	Fe(2)–C(17)	2.04 (1)
Os(1)–P(1)	2.336 (2)	Fe(2)–C(18)	2.018 (9)
Os(1)–C(1)	2.110 (6)	Fe(2)–C(19)	2.023 (9)
Os(1)–C(21)	1.876 (8)	Fe(2)–C(20)	2.03 (1)
Os(1)–C(22)	1.927 (7)	Fe(2)–Cp(3)	1.644 (4)
Os(1)–C(23)	1.947 (8)	Fe(2)–Cp(4)	1.654 (6)
Os(2)–Os(3)	2.828 (1)	P(1)–C(11)	1.792 (7)
Os(2)–P(1)	2.328 (2)	O(1)–C(21)	1.142 (9)
Os(2)–C(2)	2.132 (6)	O(2)–C(22)	1.131 (7)
Os(2)–C(24)	1.896 (7)	O(3)–C(23)	1.129 (8)
Os(2)–C(25)	1.931 (9)	O(4)–C(24)	1.130 (8)
Os(2)–C(26)	1.944 (7)	O(5)–C(25)	1.15 (1)
Os(3)–P(1)	2.454 (2)	O(6)–C(26)	1.124 (8)
Os(3)–C(1)	2.445 (6)	O(7)–C(27)	1.162 (9)
Os(3)–C(2)	2.421 (6)	O(8)–C(28)	1.131 (8)
Os(3)–C(27)	1.900 (8)	O(9)–C(29)	1.137 (8)
Os(3)–C(28)	1.918 (7)	C(1)–C(2)	1.519 (9)
Os(3)–C(29)	1.875 (7)	C(1)–C(5)	1.449 (9)
Fe(1)–C(1)	2.096 (6)	C(2)–C(3)	1.468 (9)
Fe(1)–C(2)	2.085 (6)	C(3)–C(4)	1.42 (1)
Fe(1)–C(3)	2.033 (8)	C(4)–C(5)	1.40 (1)
Fe(1)–C(4)	2.037 (7)	C(6)–C(7)	1.35 (2)
Fe(1)–C(5)	2.033 (6)	C(6)–C(10)	1.36 (1)
Fe(1)–C(6)	2.040 (8)	C(7)–C(8)	1.47 (2)
Fe(1)–C(7)	2.025 (9)	C(8)–C(9)	1.39 (2)
Fe(1)–C(8)	2.036 (8)	C(9)–C(10)	1.37 (1)
Fe(1)–C(9)	2.032 (9)	C(11)–C(12)	1.42 (1)
Fe(1)–C(10)	2.05 (1)	C(11)–C(15)	1.45 (1)
Fe(1)–Cp(1)	1.645 (3)	C(12)–C(13)	1.39 (1)
Fe(1)–Cp(2)	1.571 (4)	C(13)–C(14)	1.40 (1)
Fe(2)–C(11)	2.057 (6)	C(14)–C(15)	1.42 (1)
Fe(2)–C(12)	2.042 (7)	C(16)–C(17)	1.37 (2)
Fe(2)–C(13)	2.04 (1)	C(16)–C(20)	1.37 (1)
Fe(2)–C(14)	2.024 (9)	C(17)–C(18)	1.38 (2)
Fe(2)–C(15)	2.025 (7)	C(18)–C(19)	1.40 (2)
Fe(2)–C(16)	2.04 (1)	C(19)–C(20)	1.39 92)

[a] In this table and Table IV, Cp(1–4) refer to the centroids of the C(1–5), C(6–10), C(11–15), and C(16–20) cyclopentadienyl rings, respectively.



3



9

Figure 4. Some metrical details for **3** and **9**.

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[11] Deeming, A. J. *J. Organomet. Chem.* **1978**, *150*, 123.

[12] The related reactions of cyclopentadiene and pyrrole with $Os_3(CO)_{12}$ have been described.[13]

[13] (a) Yin, C. C.; Deeming, A. J. *J. Chem. Soc., Dalton Trans*, **1982**, 2563. (b) Humphries, A. P.; Knox, S. A. R. *J. Chem. Soc., Dalton Trans.* **1975**, 1710.

[14] (a) Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1974**, 1415. (b) Kneuper, H.-J.; Shapley, J. R. *Organometallics* **1987**, *6*, 2455. (c) Goudsmit, R. J.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Rosales, M. F. *J. Chem. Soc., Dalton Trans.* **1983**, 2257.

Table IV. Bond Angles (deg) with Estimated Standard Deviations for 2

Os(3)–Os(1)–P(1)	55.78 (4)	C(2)–Os(3)–C(29)	156.8 (2)
Os(3)–Os(1)–C(1)	57.2 (2)	C(27)–Os(3)–C(28)	96.0 (3)
Os(3)–Os(1)–C(21)	149.5 (2)	C(27)–Os(3)–C(29)	93.8 (3)
Os(3)–Os(1)–C(22)	104.4 (2)	C(28)–Os(3)–C(29)	93.2 (3)
Os(3)–Os(1)–C(23)	107.2 (2)	Cp(1)–Fe(1)–Cp(2)	176.6 (3)
P(1)–Os(1)–C(1)	82.3 (2)	Cp(3)–Fe(2)–Cp(4)	176.6 (3)
P(1)–Os(1)–C(21)	104.5 (2)	Os(1)–P(1)–Os(2)	121.98 (7)
P(1)–Os(1)–C(22)	159.8 (2)	Os(1)–P(1)–Os(3)	72.29 (5)
P(1)–Os(1)–C(23)	93.2 (2)	Os(1)–P(1)–C(11)	116.4 (2)
C(1)–Os(1)–C(21)	100.5 (3)	Os(2)–P(1)–Os(3)	72.46 (5)
C(1)–Os(1)–C(22)	89.2 (3)	Os(2)–P(1)–C(11)	121.0 (2)
C(1)–Os(1)–C(23)	163.4 (3)	Os(3)–P(1)–C(11)	120.9 (2)
C(21)–Os(1)–C(22)	95.0 (3)	Os(1)–C(1)–Os(3)	76.3 (2)
C(21)–Os(1)–C(23)	96.2 (3)	Os(1)–C(1)–C(2)	126.5 (4)
C(22)–Os(1)–C(23)	89.7 (3)	Os(1)–C(1)–C(5)	127.8 (5)
Os(3)–Os(2)–P(1)	55.83 (4)	Os(3)–C(1)–C(2)	71.0 (3)
Os(3)–Os(2)–C(2)	56.4 (2)	Os(3)–C(1)–C(5)	120.8 (4)
Os(3)–Os(2)–C(24)	145.3 (2)	C(2)–C(1)–C(5)	105.3 (6)
Os(3)–Os(2)–C(25)	105.3 (2)	Os(2)–C(2)–Os(3)	76.5 (2)
Os(3)–Os(2)–C(26)	110.7 (2)	Os(2)–C(2)–C(1)	127.7 (4)
P(1)–Os(2)–C(2)	81.5 (2)	Os(2)–C(2)–C(3)	126.4 (5)
P(1)–Os(2)–C(24)	100.0 (2)	Os(3)–C(2)–C(1)	72.7 (3)
P(1)–Os(2)–C(25)	161.0 (2)	Os(3)–C(2)–C(3)	120.4 (4)
P(1)–Os(2)–C(26)	95.8 (2)	C(1)–C(2)–C(3)	105.6 (6)
C(2)–Os(2)–C(24)	99.2 (3)	C(2)–C(3)–C(4)	109.4 (7)
C(2)–Os(2)–C(25)	89.6 (3)	C(3)–C(4)–C(5)	108.6 (6)
C(2)–Os(2)–C(26)	165.8 (2)	C(1)–C(5)–C(4)	111.1 (6)
C(24)–Os(2)–C(25)	97.9 (3)	C(7)–C(6)–C(10)	109 (1)
C(24)–Os(2)–C(26)	95.0 (3)	C(6)–C(7)–C(8)	108 (1)
C(25)–Os(2)–C(26)	88.7 (3)	C(7)–C(8)–C(9)	104 (1)
Os(1)–Os(3)–Os(2)	92.33 (3)	C(8)–C(9)–C(10)	109 (1)
Os(1)–Os(3)–P(1)	51.93 (4)	C(6)–C(10)–C(9)	110 (1)
Os(1)–Os(3)–C(1)	46.5 (2)	P(1)–C(11)–C(12)	129.6 (5)
Os(1)–Os(3)–C(2)	76.1 (2)	P(1)–C(11)–C(15)	124.1 (6)
Os(1)–Os(3)–C(27)	159.1 (2)	C(12)–C(11)–C(15)	106.2 (6)
Os(1)–Os(3)–C(28)	81.6 (2)	C(11)–C(12)–C(13)	109.4 (8)
Os(1)–Os(3)–C(29)	107.0 (2)	C(12)–C(13)–C(14)	108.3 (8)
Os(2)–Os(3)–P(1)	51.71 (4)	C(13)–C(14)–C(15)	109.2 (8)
Os(2)–Os(3)–C(1)	76.8 (1)	C(11)–C(15)–C(14)	106.8 (8)
Os(2)–Os(3)–C(2)	47.1 (1)	C(17)–C(16)–C(20)	109 (1)
Os(2)–Os(3)–C(27)	81.8 (2)	C(16)–C(17)–C(18)	108 (1)
Os(2)–Os(3)–C(28)	157.0 (2)	C(17)–C(18)–C(19)	108 (1)
Os(2)–Os(3)–C(29)	109.7 (2)	C(18)–C(19)–C(20)	107 (1)
P(1)–Os(3)–C(1)	73.5 (1)	C(16)–C(20)–C(19)	108 (1)
P(1)–Os(3)–C(2)	73.4 (1)	Os(1)–C(21)–O(1)	177.6 (7)
P(1)–Os(3)–C(27)	131.5 (2)	Os(1)–C(22)–O(2)	179.5 (6)
P(1)–Os(3)–C(28)	132.0 (2)	Os(1)–C(23)–O(3)	176.4 (6)
P(1)–Os(3)–C(29)	90.3 (2)	Os(2)–C(24)–O(4)	176.3 (7)
C(1)–Os(3)–C(2)	36.4 (2)	Os(2)–C(25)–O(5)	179.4 (8)
C(1)–Os(3)–C(27)	112.6 (3)	Os(2)–C(26)–O(6)	174.7 (7)
C(1)–Os(3)–C(28)	83.1 (2)	Os(3)–C(27)–O(7)	177.2 (8)
C(1)–Os(3)–C(29)	153.5 (3)	Os(3)–C(28)–O(8)	177.2 (7)
C(2)–Os(3)–C(27)	85.3 (3)	Os(3)–C(29)–O(9)	178.6 (7)
C(2)–Os(3)–C(28)	110.0 (2)		

Table V. Final Atomic Coordinates (Fractional) and B_{eq} Values (Å^2) for 3

atom	*x*	*y*	*z*	$B_{eq}{}^{a}$
Os(1)	−0.01289 (3)	0.09298 (2)	0.19664 (2)	2.54 (1)
Os(2)	0.03270 (3)	−0.02172 (2)	0.26535 (3)	3.02 (1)
Os(3)	0.11826 (3)	0.06389 (2)	0.39219 (2)	2.70 (1)
Os(4)	0.47038 (3)	0.08050 (1)	0.16115 (2)	2.67 (1)
Os(5)	0.46493 (3)	0.20375 (2)	0.16963 (3)	3.54 (2)
Os(6)	0.55102 (3)	0.15166 (2)	0.33311 (3)	3.10 (1)
Fe(1)	0.2624 (1)	0.09296 (5)	0.23867 (8)	2.65 (5)
P(1)	0.0631 (2)	0.1833 (1)	0.1825 (2)	2.60 (8)
P(2)	0.4108 (2)	−0.0065 91)	0.2040 (1)	2.60 (9)
O(1)	−0.0769 (7)	0.0590 (4)	0.0076 (5)	6.8 (4)
O(2)	−0.2299 (5)	0.1452 (3)	0.1696 (5)	5.8 (4)
O(3)	0.1961 (7)	−0.1143 (4)	0.3602 (6)	7.3 (4)
O(4)	−0.0594 (7)	−0.0927 (4)	0.0965 (5)	7.7 (5)
O(5)	−0.1230 (6)	−0.0632 (4)	0.3432 (5)	6.4 (4)
O(6)	0.2464 (6)	−0.0257 (4)	0.5276 (5)	6.3 (4)
O(7)	0.2617 (7)	0.1617 (4)	0.4955 (5)	6.8 (4)
O(8)	−0.0535 (7)	0.0735 (4)	0.4687 (6)	8.6 (5)
O(9)	0.3223 (7)	0.0682 (4)	−0.0280 (5)	6.6 (4)
O(10)	0.6671 (6)	0.0268 (3)	0.1440 (5)	6.2 (4)
O(11)	0.3708 (7)	0.3072 (3)	0.2295 (7)	7.7 (5)
O(12)	0.3466 (8)	0.2239 (4)	−0.0261 (6)	9.0 (6)
O(13)	0.6705 (6)	0.2671 (4)	0.1931 (7)	8.9 (5)
O(14)	0.5628 (7)	0.2637 (4)	0.4321 (6)	8.4 (5)
O(15)	0.5557 (6)	0.0747 (4)	0.4838 (5)	6.1 (4)
O(16)	0.7895 (6)	0.1591 (4)	0.3634 (6)	7.7 (5)
C(1)	0.2001 (6)	0.1725 (3)	0.1990 (5)	2.5 (3)
C(2)	0.2360 (7)	0.1456 (4)	0.1364 (5)	2.9 (3)
C(3)	0.3501 (6)	0.1353 (4)	0.1799 (6)	2.8 (3)
C(4)	0.3840 (6)	0.1549 (3)	0.2694 (5)	2.5 (3)
C(5)	0.2914 (6)	0.1782 (4)	0.2813 (6)	3.0 (4)
C(6)	0.2984 (6)	0.0081 (4)	0.2347 (6)	2.7 (3)
C(7)	0.1938 (6)	0.0216 (4)	0.1740 (5)	2.7 (3)
C(8)	0.1316 (6)	0.0415 (3)	0.2220 (5)	2.5 (3)
C(9)	0.2035 (6)	0.0434 (4)	0.3149 (5)	2.6 (3)
C(10)	0.3052 (6)	0.0217 (4)	0.3215 (5)	2.7 (3)
C(11)	−0.0574 (7)	0.0739 (4)	0.0782 (7)	3.9 (4)
C(12)	−0.1474 (8)	0.1272 (4)	0.1823 (6)	3.7 (4)
C(13)	0.1362 (7)	−0.0807 (4)	0.3248 (7)	4.2 (4)
C(14)	−0.0226 (9)	−0.0660 (5)	0.1578 (7)	4.8 (5)
C(15)	−0.0635 (8)	−0.0478 (5)	0.3136 (7)	4.7 (5)
C(16)	0.1976 (7)	0.0081 (4)	0.4769 (6)	3.3 (4)
C(17)	0.2054 (9)	0.1269 (4)	0.4555 (6)	4.0 (5)
C(18)	0.0095 (7)	0.0711 (4)	0.4396 (6)	4.0 (4)
C(19)	0.3824 (9)	0.0719 (5)	0.0429 (7)	4.3 (5)
C(20)	0.5934 (8)	0.0452 (4)	0.1526 (6)	3.6 (4)
C(21)	0.4072 (9)	0.2685 (5)	0.2065 (8)	5.2 (5)
C(22)	0.387 (1)	0.2169 (5)	0.0457 (9)	5.5 (6)
C(23)	0.593 (1)	0.2431 (5)	0.1841 (9)	5.8 (6)
C(24)	0.5596 (9)	0.2216 (5)	0.3949 (8)	5.7 (6)
C(25)	0.5572 (7)	0.1038 (5)	0.4288 (7)	4.5 (5)
C(26)	0.7018 (8)	0.1557 (5)	0.3536 (7)	4.7 (5)
C(27)	0.0046 (8)	0.2154 (4)	0.0723 (6)	4.0 (4)
C(28)	0.0711 (7)	0.2375 (4)	0.2661 (6)	3.4 (4)
C(29)	0.069 (1)	0.2624 (5)	0.0499 (8)	6.3 (6)
C(30)	−0.111 (1)	0.2351 (6)	0.0458 (8)	6.6 (6)
C(31)	−0.0334 (8)	0.2474 (5)	0.2795 (7)	5.1 (5)
C(32)	0.1219 (8)	0.2957 (4)	0.2602 (7)	4.8 (5)
C(33)	0.3553 (8)	−0.0611 (4)	0.1147 (6)	3.8 (4)
C(34)	0.5089 (7)	−0.0401 (4)	0.3028 (6)	3.1 (4)
C(35)	0.2966 (9)	−0.1126 (5)	0.1339 (7)	5.2 (5)
C(36)	0.435 (1)	−0.0818 (5)	0.0783 (8)	5.8 (6)
C(37)	0.6182 (7)	−0.0499 (4)	0.2997 (6)	4.2 (4)
C(38)	0.4733 (8)	−0.0957 (5)	0.3342 (7)	4.6 (5)

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

The three new aryne derivatives **2**, **3**, and **6** are well characterized by the microanalytical and spectroscopic results. However, in view of the unprecedented formulations of **2** and **3** it was necessary to establish their structures by using X-ray methods.

The structure of **2** (Figure 1) shows the ferrocyne moiety bonded essentially symmetrically to the Os_3P butterfly assembly: the Os(1)C(1)C(2)Os(2) torsion angle is 1.1 (8)°. The ferrocyne fragment donates four electrons to the cluster, two via σ bonds from C(1) and C(2) and two via η^2 bonding from the same carbon atoms to Os(3) (Os(1)–C(1) = 2.110 (6) Å, Os(3)–C(1) = 2.445 (6) Å). These interactions lengthen the C(1)–C(2) bond to 1.519 (9) Å. The lengths of C–C bonds in benzyne moieties η^2-bound to osmium and ruthenium closed clusters are lengthened in a similar way. For example, in the closed metal cluster $Ru_3(CO)_7(\mu_3\text{-}\eta^2\text{-}C_6H_4)(\mu\text{-}PPhFc)_2$[4a] the η^2-bound carbon atoms are 1.417 (9) Å apart. The analogous C–C bond in the benzyne complex **6** (Figure 3) reflects this trend (C(11)–C(12) = 1.43 (1) Å), although here the benzyne moiety is bound in an unsymmetrical mode.[15] In the ferrodicyne complex **3** (Figure 2) the corresponding bonds C(8)–C(9) and C(3)–C(4) are lengthened to 1.47 (1) and 1.45 (1) Å, respectively.

In addition to C(2)–C(1) the other C–C distances in the aryne ring of **2** are generally longer than in the other C_5 rings in the molecule, ranging from 1.468 (9) Å for C(2)–

Table VI. Bond Lengths (Å) with Estimated Standard Deviations for 3[a]

Os(1)–Os(2)	2.8379 (8)	Os(5)–C(3)	2.267 (8)	P(1)–C(28)	1.838 (9)	C(2)–C(3)	1.45 (1)
Os(1)–Os(3)	3.1127 (9)	Os(5)–C(21)	1.89 (1)	P(2)–C(6)	1.823 (8)	C(3)–C(4)	1.45 (1)
Os(1)–P(1)	2.366 (2)	Os(5)–C(22)	1.91 (1)	P(2)–C(33)	1.86 (1)	C(4)–C(5)	1.45 (1)
Os(1)–P(1)	2.366 (2)	Os(5)–C(23)	1.90 (1)	P(2)–C(34)	1.84 (1)	C(6)–C(7)	1.42 (1)
Os(1)–C(8)	2.189 (8)	Os(6)–C(4)	2.101 (8)	O(1)–C(11)	1.15 (1)	C(6)–C(10)	1.45 (1)
Os(1)–C(11)	1.87 (1)	Os(6)–C(24)	1.88 (1)	O(2)–C(12)	1.13 (1)	C(7)–C(8)	1.45 (1)
Os(1)–C(12)	1.92 (1)	Os(6)–C(25)	1.91 (1)	O(3)–C(13)	1.11 (1)	C(8)–C(9)	1.47 (1)
Os(2)–Os(3)	2.7831 (7)	Os(6)–C(26)	1.95 (1)	O(4)–C(14)	1.13 (1)	C(9)–C(10)	1.43 (1)
Os(2)–C(8)	2.279 (8)	Fe(1)–C(1)	2.011 (8)	O(5)–C(15)	1.15 (1)	C(27)–C(29)	1.52 (1)
Os(2)–C(13)	1.92 (1)	Fe(1)–C(2)	2.002 (9)	O(6)–C(16)	1.15 (1)	C(27)–C(30)	1.53 (1)
Os(2)–C(14)	1.94 (1)	Fe(1)–C(3)	2.058 (8)	O(7)–C(17)	1.13 (1)	C(28)–C(31)	1.54 (1)
Os(2)–C(15)	1.88 (1)	Fe(1)–C(4)	2.086 (8)	O(8)–C(18)	1.14 (1)	C(28)–C(32)	1.52 (1)
Os(3)–C(9)	2.095 (8)	Fe(1)–C(5)	2.063 (9)	O(9)–C(19)	1.15 (1)	C(33)–C(35)	1.53 (1)
Os(3)–C(16)	1.90 (1)	Fe(1)–C(6)	2.014 (8)	O(10)–C(20)	1.15 (1)	C(33)–C(36)	1.51 (1)
Os(3)–C(17)	1.91 (1)	Fe(1)–C(7)	1.981 (8)	O(11)–C(21)	1.15 (1)	C(34)–C(37)	1.52 (1)
Os(3)–C(18)	1.937 (9)	Fe(1)–C(8)	2.062 (8)	O(12)–C(22)	1.12 (1)	C(34)–C(38)	1.53 (1)
Os(4)–Os(5)	2.8315 (9)	Fe(1)–C(9)	2.084 (8)	O(13)–C(23)	1.14 (1)	Os(1)–H(1)	1.53
Os(4)–Os(6)	3.0995 (8)	Fe(1)–C(10)	2.069 (8)	O(14)–C(24)	1.14 (1)	Os(1)–H(2)	1.75
Os(4)–P(2)	2.366 (2)	Fe(1)–Cp(1)	1.630 (4)	O(15)–C(25)	1.14 (1)	Os(2)–H(1)	1.91
Os(4)–C(3)	2.181 (8)	Fe(1)–Cp(2)	1.632 (4)	O(16)–C(26)	1.14 (1)		
Os(4)–C(19)	1.87 (1)	P(1)–C(1)	1.792 (8)	C(1)–C(2)	1.45 (1)	Os(3)–H(2)	1.80
Os(4)–C(20)	1.91 (1)	P(1)–C(27)	1.85 (1)	C(1)–C(5)	1.45 (1)	Os(4)–H(3)	1.82
Os(5)–Os(6)	2.776 (8)					Os(5)–H(3)	1.98

[a] In this table and in Table VII, Cp(1) and Cp(2) refer to the unweighted centroids of the C(1–5) and C(6–10) rings, respectively.

Table VII. Bond Angles (deg) with Estimated Standard Deviations for 3

Os(2)–Os(1)–Os(3)	55.54 (1)	C(9)–Os(3)–C(17)	97.8 (4)	Os(5)–Os(6)–C(4)	62.0 (2)	C(6)–C(7)–C(8)	108.4 (7)
Os(2)–Os(1)–P(1)	144.63 (6)	C(9)–Os(3)–C(18)	164.5 (4)	Os(5)–Os(6)–C(24)	94.7 (4)	Os(1)–C(8)–Os(2)	78.8 (2)
Os(2)–Os(1)–C(8)	52.0 (2)	C(16)–Os(3)–C(17)	92.9 (4)	Os(5)–Os(6)–C(25)	158.3 (3)	Os(1)–C(8)–C(7)	137.7 (6)
Os(2)–Os(1)–C(11)	97.9 (3)	C(16)–Os(3)–C(18)	93.3 (4)	Os(5)–Os(6)–C(26)	99.4 (3)	Os(1)–C(8)–C(9)	111.3 (5)
Os(2)–Os(1)–C(12)	118.5 (3)	C(17)–Os(3)–C(18)	96.8 (4)	C(4)–Os(6)–C(24)	94.0 (4)	Os(2)–C(8)–C(7)	121.4 (6)
Os(3)–Os(1)–P(1)	101.37 (6)	Os(5)–Os(4)–Os(6)	55.63 (2)	C(4)–Os(6)–C(25)	97.4 (3)	Os(2)–C(8)–C(9)	85.3 (5)
Os(3)–Os(1)–C(8)	65.0 (2)	Os(5)–Os(4)–P(2)	143.88 (5)	C(4)–Os(6)–C(26)	161.0 (4)	C(7)–C(8)–C(9)	107.4 (7)
Os(3)–Os(1)–C(11)	150.2 (3)	Os(5)–Os(4)–C(3)	51.8 (2)	C(24)–Os(6)–C(25)	93.4 (5)	Os(3)–C(9)–C(8)	110.7 (5)
Os(3)–Os(1)–C(12)	110.3 (3)	Os(5)–Os(4)–C(19)	98.0 (3)	C(24)–Os(6)–C(26)	91.6 (5)	Os(3)–C(9)–C(10)	141.2 (6)
P(1)–Os(1)–C(8)	95.5 (2)	Os(5)–Os(4)–C(20)	117.8 (3)	C(25)–Os(6)–C(26)	100.4 (4)	C(8)–C(9)–C(10)	107.2 (7)
P(1)–Os(1)–C(11)	94.2 (3)	Os(6)–Os(4)–P(2)	101.82 (6)	Cp(1)–Fe(1)–Cp(2)	174.1 (2)	C(6)–C(10)–C(9)	108.4 (7)
P(1)–Os(1)–C(12)	93.6 (3)	Os(6)–Os(4)–C(3)	65.1 (2)	Os(1)–P(1)–C(1)	109.5 (3)	Os(1)–C(11)–O(1)	173.9 (9)
C(8)–Os(1)–C(11)	88.5 (3)	Os(6)–Os(4)–C(19)	151.3 (3)	Os(1)–P(1)–C(27)	114.4 (3)	Os(1)–C(12)–O(2)	175.8 (9)
C(8)–Os(1)–C(12)	170.5 (4)	Os(6)–Os(4)–C(20)	106.7 (3)	Os(1)–P(1)–C(28)	114.5 (3)	Os(2)–C(13)–O(3)	179 (1)
C(11)–Os(1)–C(12)	93.7 (4)	P(2)–Os(4)–C(3)	94.5 (2)	C(1)–P(1)–C(27)	103.1 (4)	Os(2)–C(14)–O(4)	176 (1)
Os(1)–Os(2)–Os(3)	67.24 (2)	P(2)–Os(4)–C(19)	94.2 (3)	C(1)–P(1)–C(28)	103.1 (4)	Os(2)–C(15)–O(5)	179 (1)
Os(1)–Os(2)–C(8)	49.2 (2)	P(2)–Os(4)–C(20)	94.5 (3)	C(27)–P(1)–C(28)	111.0 (5)	Os(3)–C(16)–O(6)	179.1 (8)
Os(1)–Os(2)–C(13)	149.2 (3)	C(3)–Os(4)–C(19)	90.3 (4)	Os(4)–P(2)–C(6)	110.7 (3)	Os(3)–C(17)–O(7)	176 (1)
Os(1)–Os(2)–C(14)	99.7 (3)	C(3)–Os(4)–C(20)	168.9 (3)	Os(4)–P(2)–C(33)	113.9 (3)	Os(3)–C(18)–O(8)	178 (1)
Os(1)–Os(2)–C(15)	112.8 (3)	C(19)–Os(4)–C(20)	95.5 (4)	Os(4)–P(2)–C(34)	114.1 (3)	Os(4)–C(19)–O(9)	174.8 (9)
Os(3)–Os(2)–C(8)	70.6 (2)	Os(4)–Os(5)–Os(6)	67.08 (2)	C(6)–P(2)–C(33)	103.0 (4)	Os(4)–C(20)–O(10)	175.8 (9)
Os(3)–Os(2)–C(13)	95.7 (3)	Os(4)–Os(5)–C(3)	49.1 (2)	C(6)–P(2)–C(34)	102.8 (4)	Os(5)–C(21)–O(11)	178.6 (9)
Os(3)–Os(2)–C(14)	165.3 (3)	Os(4)–Os(5)–C(21)	145.3 (3)	C(33)–P(2)–C(34)	111.1 (4)	Os(5)–C(22)–O(12)	177 (1)
Os(3)–Os(2)–C(15)	93.1 (3)	Os(4)–Os(5)–C(22)	96.6 (3)	P(1)–C(1)–C(2)	124.8 (6)	Os(5)–C(23)–O(13)	180 (1)
C(8)–Os(2)–C(13)	101.9 (3)	Os(4)–Os(5)–C(23)	116.1 (3)	P(1)–C(1)–C(5)	126.0 (6)	Os(6)–C(24)–O(14)	179 (1)
C(8)–Os(2)–C(14)	96.0 (4)	Os(6)–Os(5)–C(3)	70.6 (2)	C(2)–C(1)–C(5)	108.2 (7)	Os(6)–C(25)–O(15)	177 (1)
C(8)–Os(2)–C(15)	159.0 (4)	Os(6)–Os(5)–C(21)	95.1 (4)	C(1)–C(2)–C(3)	107.8 (7)	Os(6)–C(26)–O(16)	178 (1)
C(13)–Os(2)–C(14)	92.8 (4)	Os(6)–Os(5)–C(22)	162.8 (3)	Os(4)–C(3)–Os(5)	79.0 (2)	P(1)–C(27)–C(29)	117.4 (8)
C(13)–Os(2)–C(15)	92.8 (4)	Os(6)–Os(5)–C(23)	93.8 (4)	Os(4)–C(3)–C(2)	137.5 (6)	P(1)–C(27)–C(30)	113.6 (7)
C(14)–Os(2)–C(15)	98.3 (4)	C(3)–Os(5)–C(21)	97.6 (3)	Os(4)–C(3)–C(4)	111.8 (6)	C(29)–C(27)–C(30)	110.2 (9)
Os(1)–Os(3)–Os(2)	57.22 (2)	C(3)–Os(5)–C(22)	94.7 (4)	Os(5)–C(3)–C(2)	118.9 (6)	P(1)–C(28)–C(31)	115.2 (7)
Os(1)–Os(3)–C(9)	68.5 (2)	C(3)–Os(5)–C(23)	161.4 (4)	Os(5)–C(3)–C(4)	84.9 (5)	P(1)–C(28)–C(32)	115.9 (7)
Os(1)–Os(3)–C(16)	148.1 (3)	C(21)–Os(5)–C(22)	95.8 (5)	C(2)–C(3)–C(4)	108.1 (7)	C(31)–C(28)–C(32)	110.4 (8)
Os(1)–Os(3)–C(17)	113.2 (3)	C(21)–Os(5)–C(23)	93.7 (4)	Os(6)–C(4)–C(3)	110.8 (5)	P(2)–C(33)–C(35)	115.8 (7)
Os(1)–Os(3)–C(18)	101.0 (3)	C(22)–Os(5)–C(23)	98.8 (5)	Os(6)–C(4)–C(5)	140.3 (6)	P(2)–C(33)–C(36)	113.7 (7)
Os(2)–Os(3)–C(9)	62.8 (2)	Os(4)–Os(6)–Os(5)	57.29 (2)	C(3)–C(4)–C(5)	108.0 (7)	C(35)–C(33)–C(36)	110.8 (9)
Os(2)–Os(3)–C(16)	92.1 (3)	Os(4)–Os(6)–C(4)	68.2 (2)	C(1)–C(5)–C(4)	107.9 (7)	P(2)–C(34)–C(37)	114.2 (6)
Os(2)–Os(3)–C(17)	160.1 (3)	Os(4)–Os(6)–C(24)	151.2 (4)	P(2)–C(6)–C(7)	123.8 (6)	P(2)–C(34)–C(38)	116.1 (7)
Os(2)–Os(3)–C(18)	102.1 (3)	Os(4)–Os(6)–C(25)	110.7 (3)	P(2)–C(6)–C(10)	126.0 (6)	C(37)–C(34)–C(38)	109.5 (7)
C(9)–Os(3)–C(16)	90.8 (3)	Os(4)–Os(6)–C(26)	98.9 (3)	C(7)–C(6)–C(10)	108.6 (7)		

C(3) to 1.40 (1) Å for C(4)–C(5); in the C_5H_5 ring of the ferrocyne moiety the C–C bond lengths range from 1.35 (2) Å for C(6)–C(7) to 1.47 (2) Å for C(7)–C(8). This latter range is similar to that found in the phosphorus-bound ferrocene fragments in **2** and **6**, although in both these molecules the C–C bonds adjacent to the phosphorus atom are longer than usual: for **2** C(11)–C(12) = 1.42 (1) Å and C(11)–C(15) = 1.45 (1) Å; for **6** C(1)–C(2) = 1.43 (1) Å and C(1)–C(5) = 1.43 (1) Å.

The iron atom in the ferrocyne fragment is 1.645 (3) Å from the centroid of the C_5H_3 ring but is closer to the C_5H_5 ring (Fe(1)–Cp(2) = 1.571 (4) Å). In **3**, both Fe–ring centroid distances are lengthened, being 1.630 (4) and 1.632 (4) Å. This shift of the metal away from the bound aryne ring is also seen in the (benzyne)chromium tricarbonyl moiety of **1**.[5] Here Cr(2) is 1.751 (3) Å from the aryne ring centroid, whereas Cr(1) is 1.694 (2) Å from the centroid of the arene ring.

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

atom	x	y	z	B_{eq}[a]
Os(1)	0.46802 (3)	0.28010 (2)	0.08737 (3)	2.340 (8)
Os(2)	0.33464 (3)	0.08848 (2)	0.14983 (3)	2.458 (8)
Os(3)	0.36464 (3)	0.20038 (2)	0.40232 (3)	2.640 (9)
Fe(1)	0.8586 (1)	0.31747 (9)	0.5697 (1)	3.15 (3)
P(1)	0.5316 (2)	0.2371 (1)	0.3054 (2)	2.23 (5)
O(1)	0.6133 (8)	0.5087 (5)	0.1574 (9)	6.8 (3)
O(2)	0.2794 (8)	0.2524 (6)	−0.2242 (7)	6.0 (3)
O(3)	0.6900 (7)	0.2226 (7)	0.0088 (7)	6.6 (3)
O(4)	0.1721 (7)	0.0338 (6)	−0.1697 (6)	5.5 (2)
O(5)	0.1285 (8)	−0.0904 (5)	0.1958 (8)	6.4 (3)
O(6)	0.5494 (8)	−0.0155 (5)	0.1641 (8)	5.5 (3)
O(7)	0.377 (1)	0.4077 (6)	0.533 (1)	7.6 (4)
O(8)	0.1214 (7)	0.0678 (6)	0.4629 (8)	6.1 (3)
O(9)	0.5517 (8)	0.1678 (7)	0.6751 (8)	7.0 (3)
C(1)	0.7016 (7)	0.2259 (5)	0.3872 (7)	2.5 (2)
C(2)	0.7458 (8)	0.1656 (6)	0.4864 (8)	3.2 (2)
C(3)	0.8887 (9)	0.1826 (7)	0.518 (1)	4.0 (3)
C(4)	0.9347 (8)	0.2519 (8)	0.444 (1)	4.1 (3)
C(5)	0.8209 (8)	0.2804 (6)	0.3620 (8)	3.1 (2)
C(6)	0.790 (1)	0.4136 (9)	0.668 (1)	5.8 (4)
C(7)	0.856 (1)	0.3594 (9)	0.762 (1)	6.0 (4)
C(8)	0.992 (1)	0.384 (1)	0.775 (1)	7.2 (5)
C(9)	1.015 (1)	0.450 (1)	0.691 (1)	6.4 (4)
C(10)	0.892 (2)	0.4688 (8)	0.622 (1)	6.6 (4)
C(11)	0.2970 (7)	0.2897 (6)	0.1346 (7)	2.8 (2)
C(12)	0.2320 (8)	0.1976 (6)	0.1696 (8)	3.1 (2)
C(13)	0.0972 (8)	0.1835 (8)	0.1715 (9)	4.2 (3)
C(14)	0.038 (1)	0.259 (1)	0.150 (1)	5.5 (4)
C(15)	0.106 (1)	0.349 (1)	0.1230 (9)	5.1 (4)
C(16)	0.232 (1)	0.3635 (7)	0.1131 (9)	4.0 (3)
C(17)	0.557 (1)	0.4221 (6)	0.124 (1)	4.1 (3)
C(18)	0.3509 (9)	0.2645 (6)	−0.1112 (9)	3.6 (3)
C(19)	0.6088 (8)	0.2430 (7)	0.0388 (8)	3.5 (2)
C(20)	0.2378 (9)	0.0556 (6)	−0.0513 (9)	3.7 (3)
C(21)	0.208 (1)	−0.0234 (6)	0.182 (1)	3.9 (3)
C(22)	0.4674 (8)	0.0206 (6)	0.1561 (8)	3.2 (2)
C(23)	0.372 (1)	0.3300 (8)	0.489 (1)	4.6 (3)
C(24)	0.2057 (9)	0.1165 (7)	0.436 (1)	4.2 (3)
C(25)	0.485 (1)	0.1814 (8)	0.573 (1)	4.4 (3)

[a] $B_{eq} = {}^8/_3\pi^2\sum\sum U_{ij}a_ia_j(\mathbf{a}_i\cdot\mathbf{a}_j)$.

Table IX. Bond Lengths (Å) with Estimated Standard Deviations for 6[a]

Os(1)–Os(2)	2.9156 (9)	Fe(1)–Cp(2)	1.661 (5)
Os(1)–P(1)	2.310 (2)	P(1)–C(1)	1.794 (7)
Os(1)–C(11)	2.118 (7)	O(1)–C(17)	1.14 (1)
Os(1)–C(17)	1.876 (8)	O(2)–C(18)	1.12 (1)
Os(1)–C(18)	1.948 (8)	O(3)–C(19)	1.13 (1)
Os(1)–C(19)	1.951 (8)	O(4)–C(20)	1.14 (1)
Os(2)–Os(3)	2.780 (1)	O(5)–C(21)	1.14 (1)
Os(2)–P(1)	2.423 (2)	O(6)–C(22)	1.12 (1)
Os(2)–C(12)	2.160 (8)	O(7)–C(23)	1.12 (1)
Os(2)–C(20)	1.911 (8)	O(8)–C(24)	1.12 (1)
Os(2)–C(21)	1.916 (8)	O(9)–C(25)	1.12 (1)
Os(2)–C(22)	1.922 (8)	C(1)–C(2)	1.43 (1)
Os(3)–P(1)	2.333 (2)	C(1)–C(5)	1.43 (1)
Os(3)–C(12)	2.318 (7)	C(2)–C(3)	1.41 (1)
Os(3)–C(23)	1.91 (1)	C(3)–C(4)	1.39 (1)
Os(3)–C(24)	1.959 (8)	C(4)–C(5)	1.41 (1)
Os(3)–C(25)	1.885 (9)	C(6)–C(7)	1.41 (2)
Fe(1)–C(1)	2.030 (7)	C(6)–C(10)	1.41 (2)
Fe(1)–C(2)	2.042 (8)	C(7)–C(8)	1.37 (2)
Fe(1)–C(3)	2.052 (9)	C(8)–C(9)	1.36 (2)
Fe(1)–C(4)	2.048 (9)	C(9)–C(10)	1.39 (2)
Fe(1)–C(5)	2.030 (7)	C(11)–C(12)	1.43 (1)
Fe(1)–C(6)	2.05 (1)	C(11)–C(16)	1.40 (1)
Fe(1)–C(7)	2.04 (1)	C(12)–C(13)	1.43 (1)
Fe(1)–C(8)	2.03 (1)	C(13)–C(14)	1.37 (1)
Fe(1)–C(9)	2.04 (1)	C(14)–C(15)	1.38 (2)
Fe(1)–C(10)	2.02 (1)	C(15)–C(16)	1.37 (1)
Fe(1)–Cp(1)	1.648 (4)		

[a] In this table and in Table X Cp(1) and Cp(2) refer to the unweighted centroids of the C(1–5) and C(6–10) cyclopentadienyl rings, respectively.

The iron atom in the ferrocyne fragment is displaced away from the η^2-bound carbon atoms (Fe(1)–C(1) = 2.096 (6) Å, Fe(1)–C(2) = 2.085 (6) Å), whereas other Fe(1)–C distances in the same ring are shorter; e.g., Fe(1)–C(3) = 2.033 (8) Å. In the C_5H_5 ring of the ferrocyne fragment, the longest Fe(1)–C bond (2.040 (8) Å) involves C(6). It should be noted that the ferrocyne fragment has staggered carbon atoms; the more usual eclipsed conformation is seen in the PFc group.

The Os(3)–Os(1) and Os(3)–Os(2) distances, 2.827 (1) and 2.828 (1) Å, respectively, are unexceptional[17] and equal.

The structure of 6 (Figure 3) shows the aryne moiety, in this case benzyne, in a different orientation relative to the Os_3P butterfly assembly. The structure is very similar to that described for $Os_3(CO)_9(C_6H_4)(PEt)$ (7; R = Et),[15] but the present results are more accurate: $R_F = 0.028$ for 6 and 0.079 for 7 (R = Et).[3c] The structure of the analogous osmium–arsenic compound $Os_3(CO)_9(\mu_3\text{-}C_6H_3CH_3)(\mu_3\text{-}AsC_6H_4CH_3)$ (10) has been recently reported.[15,16] In 6 the benzyne binds to the open cluster via three bonds, one from C(11) (C(11)–Os(1) = 2.118 (7) Å) and two from C(12), one shorter (C(12)–Os(2) = 2.160 (8) Å) than the other (C(12)–Os(3) = 2.318 (7) Å). The corresponding lengths in 7 (R = Et) are, in the same sequence, 2.13 (3), 2.17 (3), and 2.31 (3) Å and in 10 2.113 (8), 2.191 (8), and 2.323 (8) Å.

The benzyne plane is tilted 65.10° from the plane of the Os_3 plane, which is similar to the angle of tilt found in closed Os_3– and Ru_3–benzyne complexes.[3,4] The tilt angle in 1, another open cluster, is 76.4°.[5] Os(1) and Os(2) lie close to the benzyne plane, respectively 0.424 and 0.437 Å away, accounting for the small value of the torsion angle Os(1)C(11)C(12)Os(2) (2.2 (6)°). The bond lengths in the aryne ring seems to support 7a as the major contributor (four electrons) with longer bonds between C(16), C(11), C(12), and C(13) and shorter bonds in the rest of the ring.

The change in orientation of the aryne fragment in 6 results in significant changes in the dimensions of the Os_3P moiety relative to those in 2. The Os–Os bonds are no longer the same length (Os(1)–Os(2) = 2.9156 (9) Å, Os(2)–Os(3) = 2.780 (1) Å), and this change is accompanied by appropriate modifications in the P(1)–Os lengths (Os(1)–P(1) = 2.310 (2) Å, Os(3)–P(1) = 2.333 (2) Å): the angle Os(1)–Os(3)–Os(2) is 88.54 (3)°. The Os(1)–P(1) and Os(2)–P(1) bond lengths in 2 are 2.336 (2) and 2.328 (2) Å, respectively, and the Os(1)–Os(3)–Os(2) angle is 92.33 (3)°.

The crystal structure of 3 is shown in Figure 2. Each aryne ring acts as a four-electron donor to a closed Os_3 cluster that is also coordinated by a PPr^i_2 group attached to the other C_5 ring. Three of the four hydride ligands that

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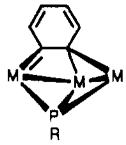
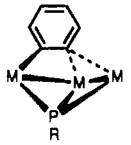
[15] The bonding in these unsymmetrical benzyne complexes can be described in terms of an *o*-phenylene ligand with some carbenoid character, i.e. contributions from **7a** and **7b**:[3e]



7a



7b

Others[16] have advanced an alternative view of the bonding in terms of two σ-interactions (*o*-phenylene) and a π-interaction between the third osmium atom and a molecular orbital of appropriate symmetry on the benzyne moiety.

[16] Johnson, B. F. G.; Lewis, J.; Massey, A. D.; Braga, D.; Grepioni, F. *J. Organomet. Chem.* **1989**, *369*, C43.

[17] Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1.

Table X. Bond Angles (deg) with Estimated Standard Deviations for 6

Os(2)–Os(1)–P(1)	53.75 (5)	C(12)–Os(3)–C(24)	94.9 (3)
Os(2)–Os(1)–C(11)	70.0 (2)	C(12)–Os(3)–C(25)	167.2 (4)
Os(2)–Os(1)–C(17)	155.2 (3)	C(23)–Os(3)–C(24)	97.1 (4)
Os(2)–Os(1)–C(18)	102.7 (2)	C(23)–Os(3)–C(25)	93.3 (4)
Os(2)–Os(1)–C(19)	99.4 (3)	C(24)–Os(3)–C(25)	88.4 (4)
P(1)–Os(1)–C(11)	80.7 (2)	Cp(1)–Fe(1)–Cp(2)	176.6 (3)
P(1)–Os(1)–C(17)	105.6 (3)	Os(1)–P(1)–Os(2)	76.00 (6)
P(1)–Os(1)–C(18)	156.2 (2)	Os(1)–P(1)–Os(3)	117.86 (8)
P(1)–Os(1)–C(19)	95.7 (2)	Os(1)–P(1)–C(1)	119.0 (2)
C(11)–Os(1)–C(17)	95.1 (4)	Os(2)–P(1)–Os(3)	71.52 (5)
C(11)–Os(1)–C(18)	88.0 (3)	Os(2)–P(1)–C(1)	119.6 (2)
C(11)–Os(1)–C(19)	169.0 (3)	Os(3)–P(1)–C(1)	123.0 (2)
C(17)–Os(1)–C(18)	96.2 (3)	P(1)–C(1)–C(2)	128.9 (5)
C(17)–Os(1)–C(19)	95.9 (4)	P(1)–C(1)–C(5)	123.6 (6)
C(18)–Os(1)–C(19)	91.5 (3)	C(2)–C(1)–C(5)	107.5 (6)
Os(1)–Os(2)–Os(3)	88.54 (3)	C(1)–C(2)–C(3)	107.2 (7)
Os(1)–Os(2)–P(1)	50.25 (5)	C(2)–C(3)–C(4)	109.5 (7)
Os(1)–Os(2)–C(12)	69.3 (2)	C(3)–C(4)–C(5)	108.5 (7)
Os(1)–Os(2)–C(20)	80.4 (2)	C(1)–C(5)–C(4)	107.3 (7)
Os(1)–Os(2)–C(21)	165.0 (3)	C(7)–C(6)–C(10)	106 (1)
Os(1)–Os(2)–C(22)	99.9 (2)	C(6)–C(7)–C(8)	108 (1)
Os(3)–Os(2)–P(1)	52.74 (5)	C(7)–C(8)–C(9)	110 (1)
Os(3)–Os(2)–C(12)	54.2 (2)	C(8)–C(9)–C(10)	108 (1)
Os(3)–Os(2)–C(20)	145.4 (3)	C(6)–C(10)–C(9)	108 (1)
Os(3)–Os(2)–C(21)	86.3 (3)	Os(1)–C(11)–C(12)	111.2 (5)
Os(3)–Os(2)–C(22)	118.1 (2)	Os(1)–C(11)–C(16)	128.4 (6)
P(1)–Os(2)–C(12)	78.4 (2)	C(12)–C(11)–C(16)	119.6 (7)
P(1)–Os(2)–C(20)	130.2 (2)	Os(2)–C(12)–Os(3)	76.7 (2)
P(1)–Os(2)–C(21)	133.3 (3)	Os(2)–C(12)–C(11)	109.5 (5)
P(1)–Os(2)–C(22)	87.5 (2)	Os(2)–C(12)–C(13)	130.8 (7)
C(12)–Os(2)–C(20)	91.2 (3)	Os(3)–C(12)–C(11)	108.7 (5)
C(12)–Os(2)–C(21)	96.4 (4)	Os(3)–C(12)–C(13)	101.7 (5)
C(12)–Os(2)–C(22)	165.7 (3)	C(11)–C(12)–C(13)	117.1 (7)
C(20)–Os(2)–C(21)	96.0 (4)	C(12)–C(13)–C(14)	121.1 (9)
C(20)–Os(2)–C(22)	96.2 (4)	C(13)–C(14)–C(15)	120.5 (8)
C(21)–Os(2)–C(22)	94.9 (4)	C(14)–C(15)–C(16)	120.3 (9)
Os(2)–Os(3)–P(1)	55.75 (5)	C(11)–C(16)–C(15)	121 (1)
Os(2)–Os(3)–C(12)	49.1 (2)	Os(1)–C(17)–O(1)	174.8 (8)
Os(2)–Os(3)–C(23)	142.8 (3)	Os(1)–C(18)–O(2)	177.0 (8)
Os(2)–Os(3)–C(24)	102.8 (3)	Os(1)–C(19)–O(3)	178.7 (8)
Os(2)–Os(3)–C(25)	118.1 (3)	Os(2)–C(20)–O(4)	175.4 (7)
P(1)–Os(3)–C(12)	77.3 (2)	Os(2)–C(21)–O(5)	177.0 (8)
P(1)–Os(3)–C(23)	105.4 (3)	Os(2)–C(22)–O(6)	177.0 (7)
P(1)–Os(3)–C(24)	157.0 (3)	Os(3)–C(23)–O(7)	176 (1)
P(1)–Os(3)–C(25)	95.0 (2)	Os(3)–C(24)–O(8)	175 (1)
C(12)–Os(3)–C(23)	98.6 (4)	Os(3)–C(25)–O(9)	176.8 (8)

are indicated by the stoichiometry and the ^{1}H NMR spectrum (δ −19.54, J(PH) = 14.6; δ −17.36, J(PH) = 32.0 Hz) were located in the refinement; the hydrides bridge the two longer Os–Os bonds in each Os$_3$ unit, namely those that are centered on Os(4) and Os(1) (Os(5)–Os(6) = 2.7776 (9) Å, Os(4)–Os(5) = 2.8315 (9) Å, Os(4)–Os(6) = 3.0995 (8) Å). These distances are similar to those found in **9**, namely 2.751 (2), 2.866 (2), and 3.026 (2) Å (Figure 4). The hydride atoms were not located during the X-ray analysis of **9**, and they were placed along the longer Os–Os bonds.[14c]

The halves of the molecule of **3** are very similar in the solid-state structure; therefore, discussion of metrical details is focused on the Os(4)Os(5)Os(6) moiety. The halves must be identical in solution, because only two hydride signals and one phosphorus resonance are seen in the NMR spectra. The aryne ligand is bound to the Os$_3$ cluster in an unsymmetrical manner previously observed only for open clusters such as **1** and **6**, and the present result is the first finding of such bonding in a closed cluster. The C–Os bond lengths (Figure 4) show this to good effect. The torsion angle Os(4)C(3)C(4)Os(6) is 22.1 (7)° with Os(4) 0.49 Å from the aryne plane: Os(6) is 0.26 Å distant but on the opposite side, the same side as Os(5) that is 1.99 Å from this plane. The Os$_3$ planes are almost parallel with a dihedral angle of 171.0°. The two C$_5$ rings are considerably tilted, the dihedral angle being 10.55°. The aryne ring C(1)–C(5) is tilted at an angle of 68.3° to the Os$_3$ plane.

As mentioned above, the bond lengths in the aryne fragment are longer than in a normal cyclopentadiene ring.

The ^{1}H NMR spectra of Os$_3$(CO)$_9$(H)$_2$(μ_3-C$_6$H$_4$) (**9**) shows two signals for the two equivalent hydrides only at low temperature.[14] The motion that gives rise to averaged signals at higher temperatures has been studied by Kneuper and Shapley and involves a rapid, reversible exchange between protons on the Os$_3$ moiety and those on the aryne ring.[14b] It seems that this process is not possible for **3** because the rings are locked in position by the coordinated phosphorus atoms.

In summary, this paper describes some novel binding modes found in the new class of organometallic aryne moieties connected to M$_3$P (M = Os, Ru) open and Os$_3$ closed clusters. Ferrocyne acts as a symmetrical four-electron donor to the open cluster in **2**. (Benzyne)chromium tricarbonyl acts as a four-electron donor in **1**, again an open cluster, but two electrons come from the η^2-carbon atoms and the other two predominantly from the chromium atom. The ferrodicyne moiety of **3** is unsymmetrically bound to the closed Os$_3$ moiety. The 18-electron rule again requires that each C$_5$ ring act as a four-electron donor, presumably through contributions from resonance forms similar to those invoked to account for the bonding in **6**.[15]

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Supplementary Material Available: Stereo ORTEP diagrams and tables of hydrogen atom parameters, anisotropic thermal parameters, and torsion or conformation angles for 2, 3, and 6, tables of least-squares planes for 2 and 6, and a table of angles involving the hydrogen atoms for 6 (39 pages); tables of observed and calculated structure factors for 2, 3, and 6 (197 pages). Ordering information is given on any current masthead page.