Reactions of μ-η^2-Allenyl Complexes: Coupling of Diphenylacetylene with $Ru_2(CO)_6[\mu$-σ,η^2-$PhCC{=}CH_2](\mu$-$PPh_2)$ and the *X*-Ray Crystal Structure of a Novel Tetranuclear Cyclopentadienyl Complex $[Ru_2(CO)_4\{\mu$-$\sigma(C,O),\eta^7$-$C_5MePh_2(C_6H_4)(O)\}(\mu$-$PPh_2)]_2{\cdot}2C_7H_8$

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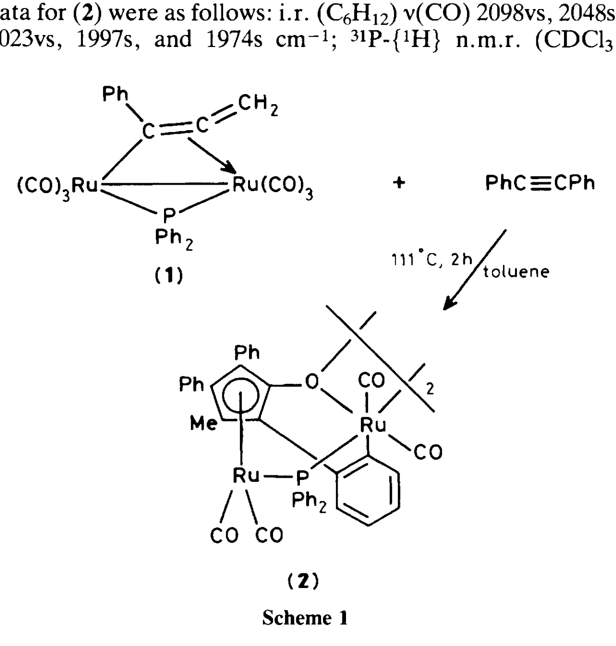
The μ-σ,η^2-allenyl complex $Ru_2(CO)_6[\mu$-σ,η^2-$PhCC{=}CH_2](\mu$-$PPh_2)$ reacts with diphenylacetylene to afford a novel tetranuclear cyclopentadienyl complex $[Ru_2(CO)_4\{\mu$-$\sigma(C,O),\eta^7$-$C_5MePh_2(C_6H_4)(O)\}(\mu$-$PPh_2)]_2$ *via* allenyl–alkyne coupling: the structure has been determined by *X*-ray diffraction.

The chemistry of binuclear complexes containing μ-σ,η^2-allenyl groups $R^1C{=}C{=}CR^2R^3$ is of interest for several reasons: (i) these hydrocarbyls have cumulated double bonds, one of which is co-ordinated while the other is free when the ligand functions as a three-electron donor;[1] (ii) their isomeric counterparts, the μ-η^3-allyl $\{R'CC(R^2)C(R^3)\}$ compounds are well known and synthetically useful;[2,3] and (iii) the parent allenyl ligand $-CH{=}C{=}CH_2$ is composed of three C_1 fragments, carbide (C), methylidyne (CH), and methylene (CH_2), which have been implicated in various catalytic processes.[4] However, the chemistry of these binuclear allenyl compounds is relatively unexplored.[2] We have previously[1] synthesised a series of binuclear allenyl complexes $[M_2(CO)_6\{\mu$-σ,η^2-$PhC{=}C{=}CRR'\}(\mu$-$PPh_2)]$ (M = Fe, Ru, or Os; R = R' = H, Me, or Ph) *via* the addition of diazoalkanes to acetylides $[M_2(CO)_6(\mu$-σ,η^2-$C{\equiv}CPh)(\mu$-$PPh_2)]$ and we describe here an unusual coupling reaction with diphenylacetylene which affords a novel tetranuclear cyclopentadienyl complex.

Treatment of the allenyl complex (**1**) (0.25 g, 0.37 mmol) with PhC_2Ph (0.10 g, 0.56 mmol) in refluxing toluene (35 ml) for 2 h followed by column chromatography [Florisil; eluant n-C_7H_{16}–C_7H_8 (5 : 1)] afforded a yellow band which gave pale yellow crystals of the cyclopentadienyl complex (**2**) (57%) (from CH_2Cl_2–C_7H_8 at −5 °C) (Scheme 1). The only other band (red–brown) afforded, as an orange powder (11%), an as yet uncharacterised complex (from n-heptane). Spectroscopic data for (**2**) were as follows: i.r. (C_6H_{12}) ν(CO) 2098vs, 2048s, 2023vs, 1997s, and 1974s cm^{-1}; ^{31}P-$\{^1H\}$ n.m.r. ($CDCl_3$;



Scheme 1

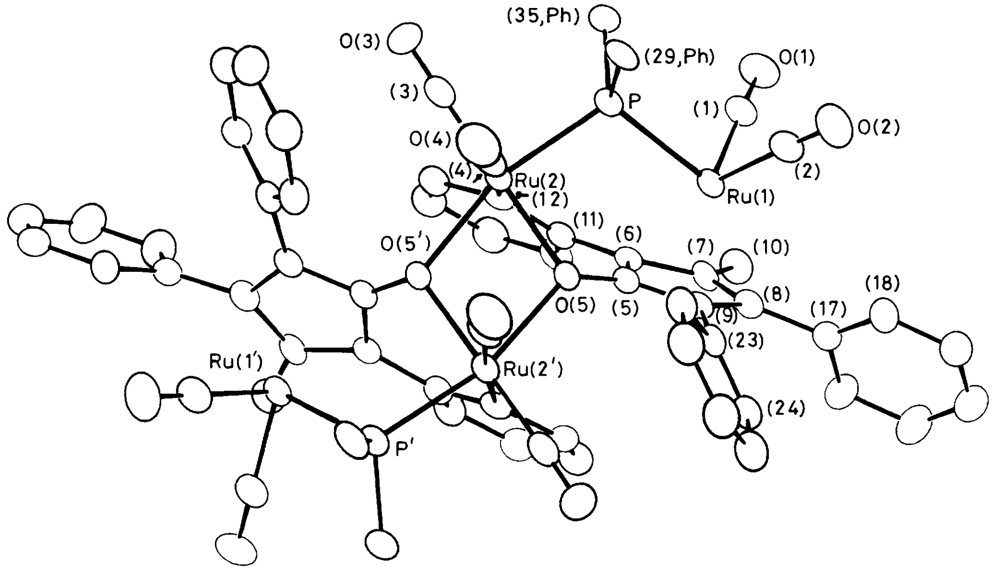


Figure 1. The molecular structure of $[Ru_2(CO)_4\{\mu\text{-}\sigma(C,O),\eta^7\text{-}C_5MePh_2(C_6H_4)(O)\}(\mu\text{-}PPh_2)]_2\cdot 2C_7H_8$ (**2**) showing the atomic numbering. Important bond distances (Å) and angles (°) not included in the text are: Ru(1)–P 2.409(2), Ru(2)–P 2.346(2), Ru(2)–O(5) 2.119(3), Ru(2)–O(5') 2.229(3), Ru(1)–C(5) 2.288(5), Ru(1)–C(6) 2.233(5), Ru(1)–C(7) 2.231(5), Ru(1)–C(8) 2.270(5), Ru(1)–C(9) 2.277(5), C(5)–C(6) 1.439(7), C(5)–O(5) 1.318(6), C(6)–C(7) 1.441(7), C(7)–C(8) 1.431(8), C(9)–C(5) 1.428(7), C(8)–C(9) 1.450(8); Ru(2)–O(5)–Ru(2') 105.0(1), Ru(2)–O(5)–C(5) 115.0(2), Ru(2')–O(5)–C(5) 128.1(2), C(4)–Ru(2)–C(12) 175.7(5), C(3)–Ru(2)–O(5) 179.0(2), P–Ru(2)–O(5) 89.9(1), P–Ru(2)–O(5') 163.5(1).

101.26 MHz; 298 K) δ +52.5; ^{1}H n.m.r. ($CDCl_3$; 250.13 MHz; 298 K) δ 2.4 (d, 6 H, J_{PH} 1.5 Hz, CH_3) and 7.0—8.0 (m, 48 H, C_6H_5 and C_6H_4); ^{13}C-{^{1}H} n.m.r. ($CDCl_3$; 62.87 MHz; for numbering see Figure 1) δ 201.6 (d, CO, $^2J_{PC}$ 7.6 Hz), 198.5 (d, CO, $^2J_{PC}$ 6.7 Hz), 196.2 (d, CO, $^2J_{PC}$ 9.6 Hz), 185.0 (d, CO, $^2J_{PC}$ 5.2 Hz), 170.2 [d, C(5,5'), $^3J_{PC}$ 5.6 Hz], 161.9 [d, C(12,12'), $^2J_{PC}$ 10.9 Hz], 145.9 (d, P–C_i, $^1J_{PC}$ 22.0 Hz), 144.3 [s, C(23,23')], 141.9 (d, P–C_i, $^1J_{PC}$ 27.5 Hz), 133.7 [d, C(11,11'), $^3J_{PC}$ 3.6 Hz], 132.9 [s, C(14,16,14',16')], 132.1 (d, *P*–C_o, $^2J_{PC}$ 11.3 Hz), 132.0 [s, C(17,17')], 131.9 [s, C(13,13'], 131.1 (d, P–C_o, $^2J_{PC}$ 9.4 Hz), 129.8 [s, C(24,28,24', 28')], 128.5 (d, *P*–C_p, $^4J_{PC}$ 2.5 Hz), 128.4 [s, C(18,22,18',22')], 128.3 (d, P–C_p, $^4J_{PC}$ 2.4 Hz), 128.1 (d, P–C_m, $^3J_{PC}$ 10.7 Hz), 128.0 (d, P–C_m, $^3J_{PC}$ 9.8 Hz), 127.9 [s, C(15,15')], 127.7 [s, C(25,27,25',27')], 126.5 [s, C(19,21,19',21')], 125.2 [s, C(26,26')], 124.4 [s, C(20,20')], 101.9 [s, C(8,8')], 98.3 [d, C(9,9'), $^4J_{PC}$ 4.7 Hz], 91.3 [d, C(6,6'), $^4J_{PC}$ 2.5 Hz], 86.1 [d, C(7,7'), $^5J_{PC}$ 2.4 Hz], and 15.1 [s, C(10,10')]. These suggested the presence of four terminal carbonyl groups, an opened phosphido bridge, and a new ligand system with two unique deshielded carbon atoms. Full details of the molecular structure (Figure 1) were revealed by a single-crystal *X*-ray diffraction study.† The molecule lies on a two-fold crystallographic axis passing through the centre of the Ru(2),Ru(2'),O(5),O(5') ring. None of the metal–metal distances [Ru(1)---Ru(2) 3.8312(6), Ru(2)---Ru(2') 3.4501(7) Å] are bonding, and a remarkable feature is that the two halves of the molecule are held together by only the two bridging oxygen atoms O(5) and O(5'). We are unaware of any precedent for such an open chain Ru_4 structure in organoruthenium chemistry. Within each of the binuclear fragments, the two ruthenium atoms are bridged by an open phosphido group, Ru(1)–P–Ru(2) 107.36(3)°, and by a new organometallic moiety best described as a deprotonated and *ortho*-metallated 1-hydroxy-2,4,5-triphenyl-3-methylcyclopentadienyl ligand. The five membered C(5)—C(9) ring system is η^5-bound to Ru(1), with the C(6)-phenyl ring bound to Ru(2) *via* a σ-bond to the *ortho* position C(12) [Ru(2)–C(12) 2.115(6) Å]. The oxygen atom O(5) acts as a three-electron donor to the two symmetry-related ruthenium atoms Ru(2) and Ru(2') such that all four metal atoms obey the eighteen-electron rule. The stereochemistry at Ru(1) and Ru(1') is typical for an η^5-$C_5R_5Ru(CO)_2X$ fragment; Ru(2) and Ru(2') are octahedral. The new cyclopentadienyl ligand is constituted from a molecule of diphenylacetylene, a CO group, and the original allenyl ligand ($PhC{=}C{=}CH_2$) of (**1**) which provides two ring carbon atoms and two substituents for the five-membered ring. Although the mechanism of formation of (**2**) has not been established, substituent connectivities indicate addition of alkyne and CO to the η^2-co-ordinated double bond of the allenyl ligand. Furthermore, since complexes η^5-$C_5H_5Ru(CO)(PR_3)(R)$ are known to undergo metallation readily,[5] it is tempting to suggest that *ortho*-metallation of the phenyl ring of the allenyl fragment occurs subsequent to ring formation. The overall reaction to form (**2**) is reminiscent of the coupling of a Fischer-type carbene with CO and alkynes leading to 4-methoxy-1-naphthols, which has been developed into a useful synthetic strategy by Dotz.[6] The formation of the cyclopentadienyl complex (**2**) in good yield from (**1**) and

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† *Crystal data:* $C_{80}H_{54}Ru_4P_2O_{10}\cdot 2C_7H_8$, M = 1825.83, monoclinic, space group $C2/c$, a = 14.123(2), b = 20.352(4), c = 28.070(4) Å, β = 98.88(1)°, U = 7971(2) Å^3, Z = 4, D_c = 1.521 g cm^{-3}, μ(Mo-K_α) = 10.31 cm^{-1}, F(000) = 3680. Diffraction data were collected with a Syntex P2$_1$ diffractometer (ω scans; 294 ± 1 K). The structure solution (Patterson, Fourier methods) and refinement (full-matrix least-squares; all non-hydrogen atoms anisotropic) were based on 4246 observed intensities ($I \geqslant 3\sigma(I)$) from 7032 measured data ($2\theta \leqslant 50°$). Final R and R_w values were 0.036 and 0.040. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

PhC_2Ph contrasts sharply not only with the sporadic appearance of cyclopentadienyl compounds as trace products in metal carbonyl–alkyne reactions[7] but also with the coupling pathways observed for acetylenes with binuclear η^2-bound alkynes[2,8] and σ,η-acetylides.[9] A significantly different chemistry for σ,η-allenyl species can thus be predicted.

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