Isomeric clusters $[Ru_4(\mu_4\text{-}PPh)(\mu_4\text{-}C_4H_3N)(CO)_{11}]$ containing diagonal C,C and parallel C,N bonded pyrrolyne ligands

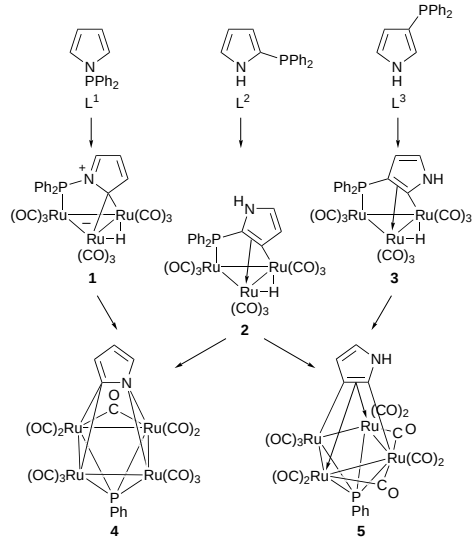
Alejandro J. Arce,[b] Antony J. Deeming,*[a] Ysaura De Sanctis,[b] Sharnjit K. Johal,[a] Caroline M. Martin,[a] Mukesh Shinhmar,[a] Despo M. Speel[a] and Alexander Vassos[a]

[a] *Department of Chemistry, University College London, 20 Gordon Street, London, UK WC1H 0AJ*
[b] *Centro de Quimíca, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 21827, Caracas 1020-A, Venezuela*

The three isomeric tertiary phosphines, diphenyl-*n*-pyrrolylphosphine (*n* = 1, 2 or 3) lead to two isomeric tetranuclear clusters $[Ru_4(\mu_4\text{-}PPh)(\mu_4\text{-}C_4H_3N)(CO)_{11}]$ which contain the diagonal C,C bonded and parallel C,N bonded pyrrolyne ligands.

The organometallic chemistry of pyrrole is important from the point of view of the hydrodenitrogenation (HDN) process.[1] There are few examples of mononuclear pyrrole complexes but it coordinates as pyrrolyl in complexes related to cyclopentadienyl compounds.[2] However, in clusters there are both aromatic and non-aromatic, doubly and triply bridging ligands derived from pyrrole, mostly by C–H bond activation and hydrogen atom transfer.[3] Up to now it has been unknown as a μ_4 ligand. This paper describes the synthesis and structure of two isomeric pyrrolyne ligands that bridge square faces of tetranuclear ruthenium complexes.

Treatment of $[Ru_3(CO)_{12}]$ with equimolar amounts of any of the three isomeric pyrrolyl phosphines, $Ph_2P(n\text{-}C_4H_4N)$ (L^1, n = 1; L^2, n = 2; L^3 n = 3),[4] leads firstly to simple substitution products $[Ru_3(CO)_{11}L^n]$ with L^n coordinated through phosphorus, closely related to known tertiary phosphine clusters.[5] The clusters $[Ru_3(CO)_{11}L^n]$ were only formed in small quantities because they readily lose CO to allow metallation at the pyrrolyl rings, in preference to the phenyl rings, to give products **1**–**3** (Scheme 1). For **2** and **3** pure samples were isolated and in the case of **3** the crystal structure has been determined (to be reported elsewhere). Compound **1** was not detected, however, and its intermediacy can only be reasoned from the isolation and full characterisation, including X-ray structure, of the corresponding osmium complex formed from L^1 and $[Os_3(CO)_{12}]$.[6] Compounds **1** to **3** react further with $[Ru_3(CO)_{12}]$ under the reaction conditions to give isomers of $[Ru_4(\mu_4\text{-}PPh)(\mu_4\text{-}C_4H_3N)(CO)_{11}]$, C,N-bonded **4** or C,C-bonded **5** as shown in Scheme 1. Clusters **4** and **5** gave similar but different IR ν(CO) spectra, both showing bridging CO bands.† Whereas **4** showed three sharp ^{1}H NMR signals for the pyrrolyne ligand at δ 7.43, 6.19 and 7.07 consistent with these all being CH groups, **5** gave signals at δ 6.62, 5.90 and 7.90. The broad signal at δ 7.90 for **5** is assigned to NH, while the other two signals are much sharper.



Scheme 1 Formation of clusters **4** and **5** from L^n and $[Ru_3(CO)_{12}]$

The X-ray structures of two red crystalline modifications of **4** have been determined: a triclinic crystal deposited from heptane on cooling and a monoclinic crystal formed by evaporation of a hexane–CH_2Cl_2 mixture.‡ Their molecular structures are very similar and only one is shown (Fig. 1). The molecular structure of **5** is shown in Fig. 2.

Fig. 3 shows the cores of these molecules to emphasize the clearly different ways that the C_4H_3N ligands coordinate in clusters **4** and **5**. In the C,C-bonded form **5** [Fig. 2 and 3(*b*)] the geometry is closely related to known structures of the type $[Ru_4(\mu_4\text{-}PR)(\mu_4\text{-}X)(CO)_{11}]$, where X = alkyne,[7] thiophyne,[8] *etc.*, with the diagonal vertical arrangement with the ligand vertical. Like other diagonally coordinated complexes of the type, there are two bridging CO ligands along the shorter Ru–Ru edges. The angle between the C_4H_2NH plane and the Ru_4 plane is 90.3°. Benzyne analogues $[Ru_4(\mu_4\text{-}PR)(\mu_4\text{-}C_6H_4)(CO)_{11}]$ **6** have been synthesised from $[Ru_3(CO)_{12}]$ and arylphosphines[9] and are also formed as a minor byproduct from $[Ru_3(CO)_{12}]$ and L^2. The μ_4-C_6H_4 ligand behaves as a six-electron donor and adopts a parallel tilted orientation; the

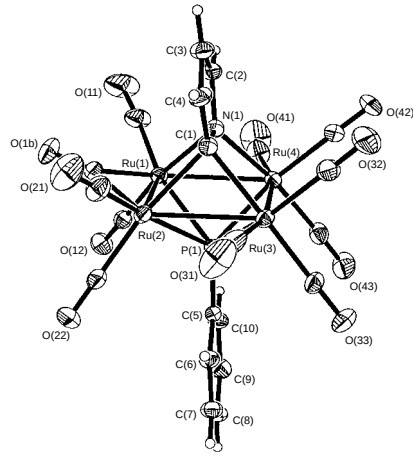


Fig. 1 Molecular structure of **4**. The monoclinic form is shown; the triclinic form is similar. Selected bond lengths (Å) are given for the monoclinic crystal with those for the triclinic crystal in square brackets: Ru(1)–Ru(2) 2.8316(7) [2.8035(9)], Ru(2)-Ru(3) 2.8752(8) [2.8318(7)], Ru(3)–Ru(4) 2.9069(7) [2.8637(9)], Ru(4)–Ru(1) 2.8720(8) [2.8522(8)], Ru(1)–N(1) 2.211(4) [2.177(5)], Ru(2)–C(1) 2.217(4) [2.188(5)], Ru(3)–C(1) 2.193(4) [2.178(5)], Ru(4)–N(1) 2.194(4) [2.170(5)], C(1)–N(1) 1.462(6) [1.441(7)], C(1)–C(4) 1.400(7) [1.374(8)], C(2)–C(3) 1.388(9) [1.381(10)], C(3)–C(4) 1.385(8) [1.400(9)], C(2)–N(1) 1.407(7) [1.373(8)].

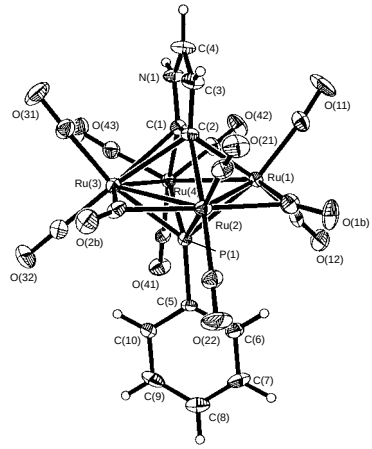


Fig. 2 Molecular structure of **5**. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 2.7553(13), Ru(2)–Ru(3) 2.7533(11), Ru(3)–Ru(4) 2.9035(13), Ru(1)–Ru(4), 2.8730(11), Ru(1)–C(1) 2.456(8), Ru(1)–C(2) 2.372(7), Ru(2)–C(2) 2.182(7), Ru(3)–C(1) 2.468(8), Ru(3)–C(2) 2.366(8), Ru(4)–C(1) 2.081(8), C(1)–C(2) 1.418(11), C(1)–N(1) 1.383(11), C(2)–C(3) 1.450(10), C(3)–C(4) 1.350(12), C(4)–N(1) 1.367(11).

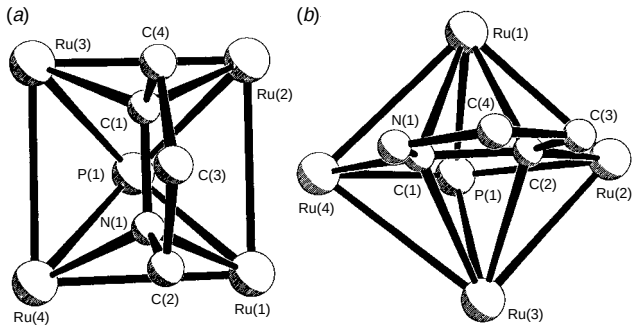


Fig. 3 A comparison of (*a*) the C,N bonded **4** and (*b*) the C,C bonded **5**

coordinated C–C bond is parallel to a Ru–Ru edge and the C_6H_4 plane is 49.7 and 54.7° to the Ru_4 plane (two independent molecules) when R = Ph. A related 1,2-naphthyne cluster is also known.[10] In C,N-bonded pyrrolyne cluster **4** [Fig. 1 and 3(*a*)] a parallel arrangement is found with the C(1)–N(1) bond parallel to the Ru(1)–Ru(2) and Ru(3)–Ru(4) edges of the Ru_4 square. However, in this case the organic ring is essentially vertical with a dihedral angle to the metal plane of 84.2° (monoclinic form) and 85.2° (triclinic form). In many ways the isomers **4** and **5** correspond to the C,N-bonded (ligand vertical) and the C,C-bonded (ligand tilted) forms of pyrrolyne in trisomium clusters $[Os_3(\mu\text{-}H)(\mu\text{-}C_4H_3N)(CO)_9]$ **7**[3c] and $[Os_3(\mu\text{-}H)(\mu\text{-}C_4H_2NMe)(CO)_9]$ **8**.[3b] The existence of these different isomers at both triangular and square metal faces in trinuclear and tetranuclear clusters respectively strongly points to the possibility of having similar isomeric forms for pyrrolyne at metal surfaces.

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Footnotes and References

* E-mail: a.j.deeming@ucl.ac.uk

† *Syntheses*: Reaction of L^1 with $[Ru_3(CO)_{12}]$: a solution of L^1 [4a] (0.057 g) and $[Ru_3(CO)_{12}]$ (0.145 g) in refluxing octane gave after TLC separation three products: $[Ru_3(CO)_{11}(Ph_2PC_4H_4N)]$ as an orange solid (0.025 g, 17%), $[Ru_3(CO)_9(Ph_2PC_4H_4N)_3]$ as a dark red solid (0.041 g, 28%) and **4** as red crystals (0.016 g, 11%).

Reaction of L^2 with $[Ru_3(CO)_{12}]$: a solution of L^2 [4b] (0.059 g) and $[Ru_3(CO)_{12}]$ (0.150 g) in refluxing toluene gave after TLC separation **2** as a yellow oil (10%), $[Ru_3(\mu\text{-}H)(\mu_3\text{-}Ph_2PC_4H_2NH)(CO)_8(Ph_2PC_4H_3NH)]$ as a yellow oil (10%), **4** as red crystals (7%) and **6** as an orange oil (3%).

Reaction of L^3 with $[Ru_3(CO)_{12}]$: a solution of L^3 [4b] (0.0903 g) and $[Ru_3(CO)_{12}]$ (0.22 g) in refluxing toluene gave after TLC separation **3** as orange crystals (20%), $[Ru_3(\mu\text{-}H)(\mu_3\text{-}Ph_2PC_4H_2NH)(CO)_8(Ph_2PC_4H_3NH)]$ as dark orange crystals (25%) and **5** as a brown solid (5%).

‡ *Crystal data*: cluster **4**, $C_{21}H_8NO_{11}PRu_4$, M = 885.53, monoclinic, space group $P2_1/n$, a = 9.241(2), b = 17.182(3), c = 17.891(4) Å, β = 90.51(3)°, U = 2840.6(10) Å^3, Z = 4, D_c = 2.071 Mg m^{-3}, $F(000)$ = 1680, red plate, 0.70 × 0.50 × 0.01 mm, μ(Mo-Kα) = 21.96 cm^{-1}. 5900 unique data collected in the range $5 \leqslant 2\theta \leqslant 53°$, final R = 0.0373 [$I > 2\sigma(I)$], wR_2 = 0.1008 (all data), GOF = 1.005, maximum Δ/σ = 0.001, max. peak, hole in final difference Fourier = 0.846, −1.380 e Å^{-3}. Cluster **4**, triclinic, space group $P\bar{1}$, a = 9.4707(13), b = 9.621(2), c = 15.855(4) Å, α = 92.41(2), β = 95.65(2), γ = 110.990(12)°, U = 1337.7(4) Å^3, Z = 2, D_c = 2.199 Mg m^{-3}, $F(000)$ = 840, red plate, 0.40 × 0.38 × 0.03 mm, μ(Mo-Kα) = 23.31 cm^{-1}. 4642 unique data collected in the range $5 \leqslant 2\theta \leqslant 50°$, final R = 0.0375 [$I > 2\sigma(I)$], wR_2 = 0.1109 (all data), GOF = 1.059, max. Δ/σ = 0.001, max. peak, hole in final difference Fourier = 0.63, −1.11 e Å^{-3}. Cluster **5**, $C_{21}H_8NO_{11}PRu_4$, M = 885.53, triclinic, space group $P\bar{1}$, a = 9.110(2), b = 9.577(3), c = 16.298(4) Å, α = 89.93(2), β = 105.11(2), γ = 107.89(2)°, U = 1301.6(6) Å^3, Z = 2, D_c = 2.260 Mg m^{-3}, $F(000)$ = 840, red plate, 0.22 × 0.18 × 0.03 mm, μ(Mo-Kα) = 23.96 cm^{-1}. 4519 unique data collected in the range $5 \leqslant 2\theta \leqslant 50°$, final R = 0.0421 [$I > 2\sigma(I)$], wR_2 = 0.1271 (all data), GOF = 1.089, maximum Δ/σ = 0.001, max. peak, hole in final difference Fourier = 0.74, −0.89 e Å^{-3}. For each structure, data were collected at 273(2) K on a Nicolet R3v/m diffractometer in the ω–2θ scan mode, absorption corrections (ψ-scans) were applied, relative transmission factors: 0.924–0.189 (**4**, monoclinic), 1.000–0.661 (**4**, triclinic), 0.961–0.699 (**5**). Structures were solved by direct methods (SHELXTL PLUS)[11] and full-matrix least-squares refinement on F^2 (SHELXL 93).[12] All non-hydrogen atoms were refined anisotropically except the coordinated C and N atoms of the pyrrolyne in **4** (both forms) which were refined isotropically. In the two modifications of **4** a model was refined with disorder involving two enantiomeric orientations of the pyrrolyne ligand. The orientation shown in Fig. 1 is the major one in each case with C(1) and N(1) reversed in the other. CCDC 182/682.

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