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CLUSTER CHEMISTRY

L *. TRAPPING OF ARYLNITRENES FORMED BY CLEAVAGE OF AZOARENES IN REACTIONS WITH $M_3(CO)_{12}$ (M = Fe or Ru): X-RAY STRUCTURE OF $Ru_3(\mu_3\text{-NPh})_2(\mu\text{-dppm})(CO)_7$

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Summary

Trinuclear products obtained from reactions between $M_3(CO)_{12}$ (M = Fe or Ru) and azobenzenes are shown to have the structure $M_3(\mu_3\text{-NAr})_2(CO)_9$, rather than the *o*-semidine formulation proposed earlier. ETC CO-substitution reactions are similar to those of $Ru_3(CO)_{12}$, with isocyanides occupying axial sites and tertiary phosphines and phosphites occupying equatorial sites on the Ru_3 cluster as shown in the latter instance by an X-ray structure of $Ru_3(\mu_3\text{-NPh})_2(\mu\text{-dppm})(CO)_7$, in which the dppm ligand spans the non-bonded Ru ··· Ru vector.

In 1966, it was reported that the binuclear complex formed in reactions between azobenzene and iron carbonyls [1] had the *o*-semidine-derived structure **1** [2]. Later, minor products obtained from azoanisole and $Fe(CO)_5$, or from azotoluene and $Fe_2(CO)_9$, the purple trinuclear complexes **2a**, were formulated with similar μ_3-$NH(C_6H_3R)N(C_6H_4R)$ (R = OMe or Me) ligands. Related reactions of $Ru_3(CO)_{12}$ were described in 1971, the trinuclear complexes **2b** so obtained being supposed to contain the semidine ligand on the basis of comparisons of the IR spectra with those of the iron complexes [3]. To our knowledge, these formulations have not been challenged.

We now report X-ray structural studies which show that these complexes contain two μ_3-arylimido ligands capping a triangular M_3 cluster. Several examples of complexes $Ru_3(\mu_3\text{-NAr})_2(CO)_9$ (**3**) containing the same or different Ar groups have been prepared directly from $Ru_3(CO)_{12}$ and the appropriate azoarene (refluxing

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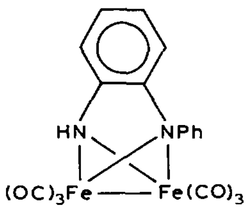
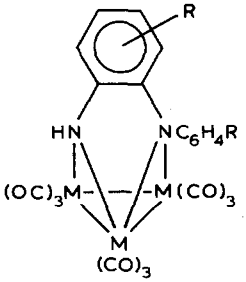
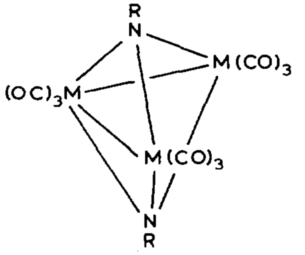


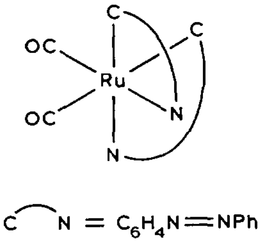
(1)



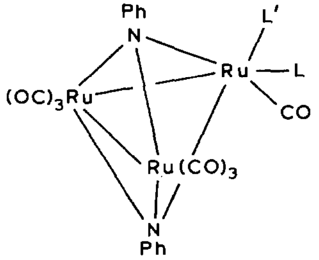
(**2a**: M = Fe, R = Me-4 or OMe-4;
2b: M = Ru, R = H)



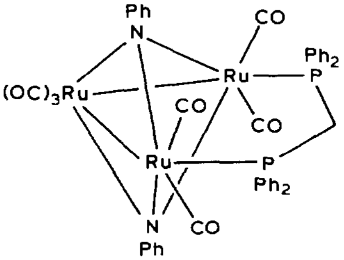
(**3a**: M = Ru, R = aryl;
3b: M = Fe, R = C_6H_4Me-4)



(**4**)



(**5**: L = CO, L′ = $CN(C_6H_3Me_2$-2,6);
6: L = PPh_3, L′ = CO;
7: L = $P(OMe)_3$, L′ = CO) .



(**8**)

octane, 15–20% yield). Reactions between $Fe_3(CO)_{12}$ and azoarenes similarly afford low yields of $Fe_3(\mu_3\text{-NAr})_2(CO)_9$ *. Other products from the reactions of $Ru_3(CO)_{12}$ include the cyclometallated complexes $Ru(C_6H_3RN{=}NC_6H_4R)_2(CO)_2$ (**4**) (the osmium analogue of **4** has been structurally characterised as one of several complexes obtained from $Os_3(CO)_{12}$ and azobenzene in refluxing octane [4]) and a dark

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* For example: $Fe_3(\mu_3\text{-NPh})_2(CO)_9$, ν(CO) (cyclohexane) 2059vs, 2037vs, 2017vs, 2011s, 1986s, 1972s cm^{-1} (lit. [5] 2050vs, 2028vs, 2008s, 1987m, 1970w cm^{-1}); $Ru_3(\mu_3\text{-NC}_6H_4\text{Me-3})_2(CO)_9$, ν(CO) (cyclohexane) 2098w, 2077vs, 2053vs, 2027vs, 2020vs, 2016vs, 1995s, 1984m cm^{-1}.

brown, apparently polymeric material which has not been fully characterised. The bis(phenylimido) complexes of iron and ruthenium have been reported earlier as products from reactions between $PhNO_2$ and $M_3(CO)_{12}$ (M = Fe or Ru) [5]; the complex $Ru_3(\mu_3\text{-}NCF_2CHFCF_3)_2(CO)_{10}$ is formed in reactions between $Ru_3(CO)_{12}$ and the azide $CF_3CHFCF_2N_3$ [6]. The X-ray structures of $M_3(\mu_3\text{-}NR)_2(CO)_9$ (R = Me, M = Fe [7]; R = Ph, M = Fe [8], Ru [9]) have been described *, and the spectroscopic properties of complexes **2** correspond with the literature values. Formally, at least, the formation of these complexes represents a facile cleavage of the N=N double bond in the azoarene, trapping the two resultant arylnitrene fragments on the cluster carbonyl. Similar reactions of alkynes to form bis-μ_3-carbyne cluster complexes are well-known [10].

We have found that the electron transfer-catalysed (ETC) substitution reactions of $Ru_3(\mu\text{-}NPh)_2(CO)_9$ with Group 14 or 15 ligands proceed similarly to those of $Ru_3(CO)_{12}$ [11]. Thus, with $CN(C_6H_3Me_2\text{-}2,6)$, complex **5** was obtained, in which the isocyanide occupies an axial position on an outer Ru atom **. On the other hand, tertiary phosphines or phosphites occupy equatorial coordination sites in complexes containing these ligands (as in **6** or **7**), probably as a result of steric interactions. This is illustrated by the X-ray structure of $Ru_3(\mu_3\text{-}NPh)_2(\mu\text{-}dppm)(CO)_7$ (**8**).

Intensity data for **8** were collected on an Enraf–Nonius CAD4F diffractometer fitted with Mo-K_α (graphite monochromator) radiation, λ 0.71073 Å. The ω-2θ scan technique was employed to measure the intensities of 11429 ($1 \leq \theta \leq 22.5°$) reflections of which 10296 were unique and of these 8204 satisfied the $I \geq 2.5\sigma(I)$ criterion. Corrections were applied for Lorentz and polarization effects and for absorption [12].

*Crystal data for **8**.* $Ru_3(NPh)_2(dppm)(CO)_7 \equiv C_{44}H_{32}N_2O_7P_2Ru_3$, $M = 1065.9$, monoclinic, space group $P2_1/n$ (variant $P2_1/c$, C^5_{2h}, No. 14), a 11.499(5), b 33.063(6), c 22.231(4) Å, β 98.57(3)°, U 8358(2) Å^3, D_m 1.69, $Z = 8$, D_c 1.694 g cm^{-3}, μ 11.44 cm^{-1}, T 293 K; analytical absorption correction, max/min transmission factors 0.7832, 0.5847.

The structure was solved by direct methods [12] and refined by a full-matrix least-squares procedure. Phenyl groups were refined as hexagonal rigid groups and remaining non-hydrogen atoms were refined anisotropically. Hydrogen atoms were not included in the model. The refinement converged with R 0.046, R_w 0.060 for $w = [\sigma^2(F) + 0.0054|F|^2]^{-1}$ ***.

As can be seen from Fig. 1, the dppm ligand spans the non-bonded Ru $\cdots$ Ru edge, the P atoms occupying approximate equatorial coordination sites, with the resulting six-membered C(20)P(1)Ru(1)Ru(2)Ru(3)P(2) ring adopting a boat conformation. The Ru $\cdots$ Ru separation (3.321(1) Å, average for two independent mole-

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* The X-ray structural characterisation of **4** (R = H), $Ru_3(\mu_3\text{-}NPh)(\mu_3\text{-}NC_6H_4F\text{-}3)(CO)_9$, and **5** will be described elsewhere.

** $Ru_3(\mu_3\text{-}NPh)_2(CO)_8(CNC_6H_3Me_2\text{-}2,6)$ (**5**), ν(CN) (cyclohexane) 2156m(br), ν(CO) 2086m, 2078s, 2061m, 2045vs, 2038s, 2018(sh), 2011vs, 1996s, 1984s, 1975m, 1969m cm^{-1}; $Ru_3(\mu_3\text{-}NPh)_2(\mu\text{-}dppm)(CO)_7$ (**8**), ν(CO) 2057(sh), 2053vs, 2022vs, 2003s, 1994s, 1970s, 1950m cm^{-1}.

*** The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

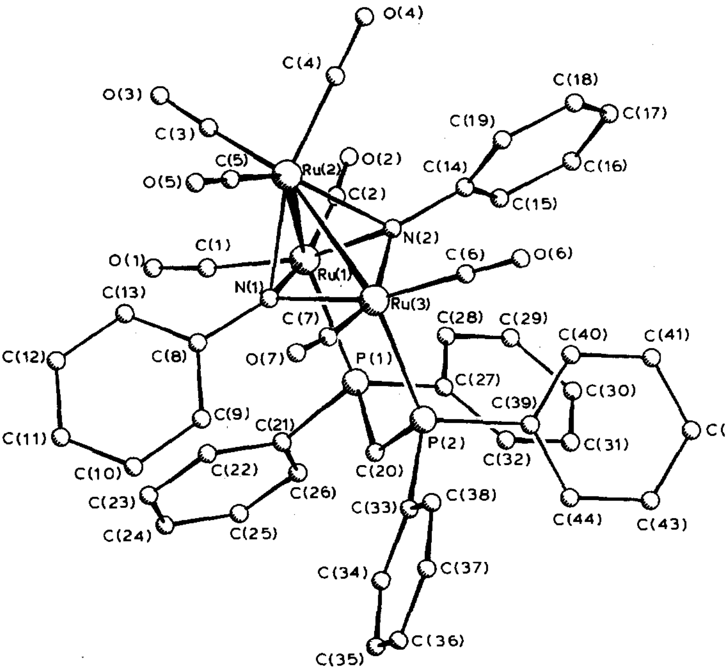

Fig. 1. Molecular structure of $Ru_3(\mu_3\text{-NPh})_2(\mu\text{-dppm})(CO)_7$ (**8**). Bond distances (values for molecules A, B given): Ru(1)–Ru(2) 2.680(1), 2.633(1), Ru(2)–Ru(3) 2.664(1), 2.699(1), Ru(1) · · · Ru(3) 3.320(1), 3.321(1), Ru(1)–P(1) 2.335(2), 2.340(2), Ru(3)–P(2) 2.310(2), 2.304(2), Ru(1)–N(1) 2.100(5), 2.084(6), Ru(1)–N(2) 2.058(5), 2.071(6), Ru(2)–N(1) 2.117(6), 2.130(6), Ru(2)–N(2) 2.166(5), 2.120(6), Ru(3)–N(1) 2.081(5), 2.101(6), Ru(3)–N(2) 2.085(6), 2.077(5) Å. Bond angles: Ru(1)–Ru(2)–Ru(3) 76.8(1), 77.0(1), Ru(1)–N(1)–Ru(3) 105.1(2), 105.1(2), Ru(1)–N(2)–Ru(3) 106.5(2), 106.4(2)°.

cules) is longer than that found in **3a** (3.290(1) Å) [8]. An asymmetry in the Ru(1)–Ru(2) and Ru(2)–Ru(3) separations (difference 0.026 Å in molecule A, 0.066 Å in molecule B) is similar to that found for **3a** (Ar = Ph). The two Ru–P distances in **8** are not equal, but while the shorter Ru–P distance in molecule B is associated with the longer Ru–Ru bond, in molecule A the opposite is true. These asymmetries appear to result from the relative dispositions of the CO, N-Ph and P-Ph groups.

These and other complexes have been obtained by the radical-anion ($Na^+[Ph_2CO]^{\cdot-}$) initiated reactions, which in the case of $Ru_3(CO)_{12}$, probably proceed by initial transfer of an electron to a metal–metal antibonding orbital to generate a substitution-labile metal centre in the cluster. The recent elegant studies of Ohst and Kochi [13] on electrochemically-induced substitution of the analogous $Fe_3(\mu_3\text{-PPh})_2(CO)_9$ cluster, in which they demonstrated opening of one of the Fe_2P triangular faces, suggest that similar opening of an Ru_2N face occurs in the reactions described above.

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