Weak Intermetallic Bonding in Unusual Trinuclear Complexes: Crystal Structure of [Rh₃(μ₃-tz)(μ₂-Cl)Cl(η⁴-tfb)(CO)₄]·½CH₂Cl₂ and [Rh₃(μ₃-tz)(μ₂-Cl)Cl(η³-C₃H₅)₂(CO)₄]·½C₂H₄Cl₂ (Htz = 1,2,4-Triazole; tfb = Tetrafluorobenzobarrelene: 5,6,7,8-Tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene)

Luis A. Oro,*[a] M. Teresa Pinillos,[a] Cristina Tejel,[a] Concha FocesFoces,[b] and Felix H. Cano[b]

[a] Departamento de Química Inorgánica, Universidad de Zaragoza, Zaragoza, Spain

[b] Departamento de Rayos-X, Instituto Rocasolano, C.S.I.C., Serrano, 119, Madrid-6, Spain

[Rh(acac)L₂] [Hacac = acetylacetone; L₂ = η⁴-tfb (tetrafluorobenzobarrelene), L = η³-C₃H₅] react with 1,2,4-triazole (Htz) and [RhCl(CO)₂]₂ to give trinuclear complexes of formula [Rh₃(μ₃-tz)(μ₂-Cl)ClL₂(CO)₄] whose crystal structures, determined by X-ray methods, show intermetallic Rh–Rh distances of 3.425(4) and 3.393(1) Å, respectively.

There has been considerable interest recently in one-dimensional metallic complexes;[1,2] this has concentrated on square-planar d⁸ complexes, particularly those of platinum-(II).[3] Here, we describe a simple route leading to the preparation of unexpected trinuclear complexes that show Rh–Rh interactions and appear to be the first structurally

characterized rhodium complexes in which a triazolate ligand is simultaneously bonded to three metal atoms.

The compounds [Rh₃(μ₃-tz)(μ₂-Cl)ClL₂(CO)₄] [L₂ = η⁴-tfb, (1); L = η³-C₃H₅, (2)] were prepared at room temperature by the reaction of [Rh(acac)L₂] (Hacac = acetylacetone; L₂ = tfb or L = η³-C₃H₅) (0.20 mmol), 1,2,4-triazole (0.20
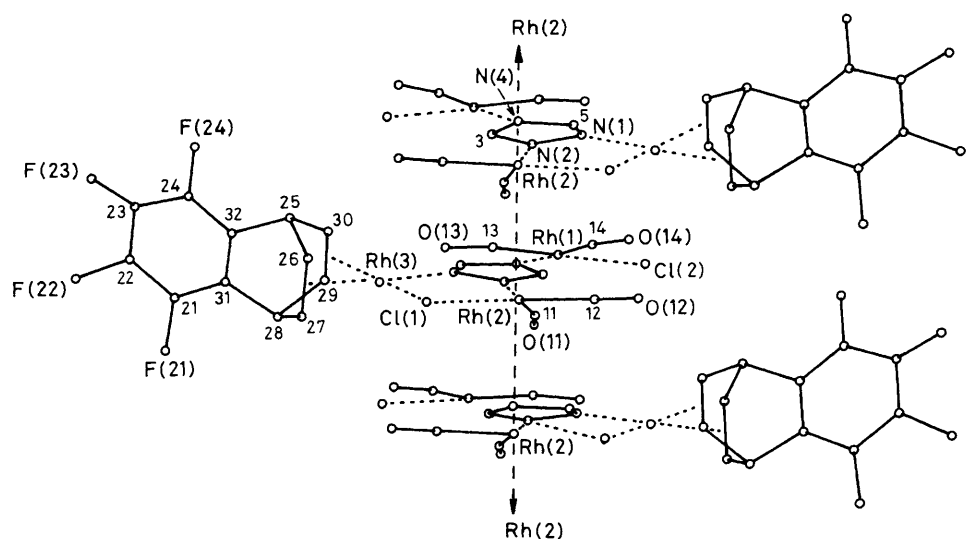
Figure 1. Molecular structure and columnar stacking arrangement in crystals of [Rh₃(μ₃-tz)(μ₂-Cl)Cl(η⁴-tfb)(CO)₄]·½CH₂Cl₂ (1). Carbon atoms are identified by number only. Selected interatomic distances (Å): Rh(2)–Rh(2') (x, ½−y, ½+z) 3.425(4), Rh(2)–Rh(3) 3.817(3), Rh(1)–Cl(2) 2.355(8), Rh(1)–N(4) 2.047(20), Rh(2)–Cl(1) 2.347(7), Rh(2)–N(2) 2.085(26), Rh(3)–Cl(1) 2.346(7), Rh(3)–N(1) 2.086(23), Rh(3)–C(26) 2.128(26), Rh(3)–C(27) 2.171(25), Rh(3)–C(29) 2.101(26), Rh(3)–C(30) 2.112(31).
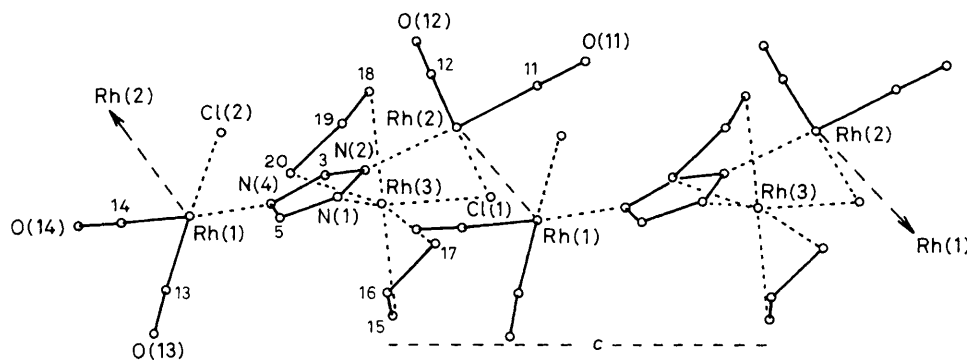

Figure 2. Molecular structure of [Rh₃(μ₃-tz)(μ₂-Cl)Cl(η³-C₃H₅)₂(CO)₄]·½C₂H₄Cl₂ (2). Carbon atoms are identified by number only. Selected bond distances (Å): Rh(2)–Rh(1') (x, y, 1+z) 3.393(1), Rh(2)–Rh(3) 3.712(1), Rh(1)–Cl(2) 2.358(3), Rh(1)–N(4) 2.096(7), Rh(2)–Cl(1) 2.356(3), Rh(2)–N(2) 2.087(7), Rh(3)–Cl(1) 2.500(2), Rh(3)–N(1) 2.143(6), Rh(3)–C(15) 2.209(11), Rh(3)–C(16) 2.156(12), Rh(3)–C(17) 2.146(14), Rh(3)–C(18) 2.238(12), Rh(3)–C(19) 2.145(9), Rh(3)–C(20) 2.110(11).

mmol), and $[RhCl(CO)_2]_2$ (0.20 mmol) in acetone (15 ml). Complex (1) precipitated immediately as a red solid with a metallic sheen (70% yield). The orange complex (2) was obtained by addition of diethyl ether (85% yield). The triazole molecule was deprotonated in these reactions.

The crystal structures† consist of trinuclear complexes in which a chlorine atom and a triazolate group bridge $Rh(CO)_2$ and RhL_2 [L_2 = tfb, (1); L = η^3-C_3H_5, (2)] moieties. In addition the remaining nitrogen atom of the triazolate ligand

---

† *Crystal data* for (1): $C_{18}H_8Cl_2F_4N_3O_4Rh_3\cdot\frac{1}{2}CH_2Cl_2$, M = 828.4, monoclinic, space group $P2_1/c$, a = 13.8906(15), b = 26.8586(39), c = 6.8480(4) Å, β = 98.668(11)°, Z = 4, D_c = 2.178 g cm^{-3}, Cu-K_α radiation (λ = 1.5418 Å), μ = 196.5 cm^{-1}. Final R factor 0.108 for 2103 observed reflections [$I > 3\sigma(I)$].

Crystal data for (2): $C_{12}H_{12}Cl_2N_3O_4Rh_3\cdot\frac{1}{2}C_2H_4Cl_2$, M = 691.3, triclinic, space group $P\bar{1}$, a = 13.5236(6), b = 10.6410(4), c = 7.4260(1) Å, α = 90.038(2), β = 87.042(2), γ = 100.582(2)°, Z = 2, D_c = 2.189 g cm^{-3}, Cu-K_α radiation, μ = 231.78 cm^{-1}. Final R factor 0.043 for 2792 observed reflections [$I > 3\sigma(I)$].

Intensities were collected on a Philips PW 1100 diffractometer ($2 < \theta < 65°$) using ω–2θ scan techniques. Absorption corrections were not applied owing to the irregular shape of the samples. The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares. The positions of some H atoms were located in the Fourier difference syntheses and refined isotropically although some had to be fixed in the refinement.

The atomic co-ordinates 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.

---

completes the square-planar co-ordination of a $RhCl(CO)_2$ unit.

Interestingly a stacking arrangement (Figure 1) of square-planar Rh(2)-centred units along the c axis, forming linear [∠ Rh–Rh–Rh 177.6(3)°] chains of metal atoms, with a Rh–Rh distance of 3.425(4) Å, is present in complex (1). This distance is shorter by *ca.* 0.03 Å than that recently observed in the mononuclear complex [RhCl(CO)$_2$(pyrazole)],[4] and only 0.1 Å longer than that found in [Rh(acac)(CO$_2$)], a compound which seems to exhibit semiconductor properties.[5] Columnar stacking remains rare for rhodium complexes, and this molecule represents the first example of this arrangement in trinuclear complexes.

A different arrangement is observed in complex (2) (Figure 2), the rhodium atoms Rh(1) and Rh(2) having an intermolecular distance of 3.393(1) Å. These structural differences explain the marked dichroism observed for (1), but absent for (2).

References

1 A. E. Underhill and D. M. Watkins, *Chem. Soc. Rev.*, 1980, **9**, 429.
2 P. B. Hitchcock, S. Morton, and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1984, 603.
3 J. M. Williams, *Adv. Inorg. Chem. Radiochem.*, 1983, **26**, 235.
4 M. J. Decker, D. O. Kimberley Fjeldsted, S. R. Stobart, and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1983, 1525.
5 R. S. Dickson, in 'Organometallic Chemistry of Rhodium and Iridium,' eds. P. M. Maitlis, F. G. A. Stone, and R. West, Academic Press, London, 1983, p. 110.