Tetra- and Tri-nuclear Rhodium–Palladium Complexes with the 1,2,4-Triazolate Ligand. Crystal Structure of $(\eta^3\text{-}C_3H_5)_2Pd_2Rh_2(\mu_3\text{-}tz)_2Cl_2(CO)_4$

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As part of our studies [1–3] exploring the use of multidentate nitrogens donor ligands for the construction of polynuclear rhodium complexes, we have shown a useful synthetic strategy based on the ability of ligands containing N–H bonds (*e.g.* 7-azaindole [3], 1,2,4-triazole [4], 1,8-diaminonaphthalene [5]) to abstract the acetylacetonate group from $Rh(acac)L_2$ complexes. Here we report on the use of this method for the synthesis of new tetra- or tri-nuclear rhodium–palladium complexes.

The reaction of $Pd_2Cl_2L_2$ (0.169 mmol) ($L = \eta^3\text{-}C_3H_5$, $\eta^3\text{-}C_4H_7$) with 1,2,4-triazole (Htz) (0.318 mmol)* in methanol (30 ml) followed by the addition of $Rh(acac)(CO)_2$ (0.318 mmol) yields orange tetranuclear complexes of formula $Rh_2Pd_2(\mu_3\text{-}tz)_2Cl_2(CO)_4L_2$. Analytical data and molecular weight measurements support the tetranuclear formulation. Complete characterization of $(\eta^3\text{-}C_3H_5)_2Pd_2Rh_2(\mu_3\text{-}tz)_2Cl_2(CO)_4$ was achieved by an X-ray analysis on a single crystal grown from dichloromethane–ether. Crystal data: $C_{14}H_{14}Cl_2N_6O_4Pd_2Rh_2$, M 819.82, tetragonal, space group $I\bar{4}2d$, a 21.702(4), c 10.386(3) Å, V 4892(2) Å^3, Z 8, D_c 2.226 g cm^{-3}, $F(000)$ 3104, $\mu(\text{Cu-K}_\alpha)$ 253.46 cm^{-1}. Final R and R_w values were 0.055 and 0.064 for 559 observed reflections [$I \geqslant 2\sigma(I)$] of 1028 independent observations measured ($3 \leqslant \theta \leqslant 60°$) on a Siemens AED diffractometer using Ni-filtered Cu-K$_\alpha$ radiation. Intensity data were corrected for absorption (maximum and minimum transmission factors were 1.3206 and 0.7190). The structure was solved by direct and Fourier methods and refined by full-matrix least-squares, with anisotropic thermal parameters for Pd, Rh and Cl atoms in the last cycles. It was not possible to localize clearly the hydrogen atoms. The final atomic coordinates are given in Table I. Thermal parameters and a list of structure factors have been deposited and are also available from the authors.

TABLE I. Fractional Atomic Coordinates ($\times 10^4$) with e.s.d.s in Parentheses for the Non-hydrogen Atoms.

Atom	*x/a*	*y/b*	*z/c*
Pd	425(1)	5735(1)	5320(3)
Rh	2040(1)	3835(1)	2417(3)
Cl	2412(4)	4807(4)	1809(10)
O1	1627(15)	2586(18)	3002(40)
O2	3096(16)	3257(17)	1009(40)
N1	1331(11)	4233(11)	3336(23)
N2	782(12)	4936(12)	4420(23)
N3	463(12)	4399(11)	4461(26)
C1	1775(23)	3111(24)	2847(58)
C2	2605(19)	3450(17)	1428(45)
C3	1287(14)	4818(13)	3868(31)
C4	796(14)	3966(13)	3869(36)
C5	1260(16)	6009(16)	6152(40)
C6	786(22)	6309(23)	6883(55)
C7	216(14)	6577(15)	6260(44)

The structure of $(\eta^3\text{-}C_3H_5)_2Pd_2Rh_2(\mu_3\text{-}tz)_2Cl_2(CO)_4$ is represented in Fig. 1, together with the most important bond parameters. The complex, having an

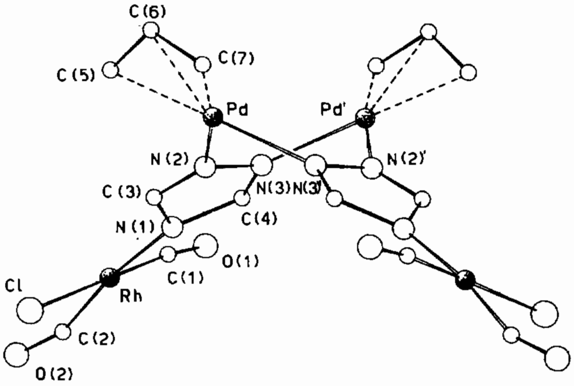

Fig. 1. View of the complex $(\eta^3\text{-}C_3H_5)_2Pd_2Rh_2(\mu_3\text{-}tz)_2Cl_2(CO)_4$ with the atomic numbering scheme. Important bond distances (Å): Rh–Cl 2.345(9), Rh–N(1) 2.01(2), Rh–C(1) 1.73(5), Rh–C(2) 1.80(4), Pd–N(2) 2.12(3), Pd–N(3)' 2.14(3), Pd–C(5) 2.09(4), Pd–C(6) 2.19(5), Pd–C(7) 2.12(4), N(2)–N(3) 1.36(4), N(3)–C(4) 1.34(4), N(1)–C(4) 1.41(4), N(1)–C(3) 1.39(4), N(2)–C(3) 1.26(4). Important bond angles (°): Cl–Rh–N(1) 90(1), Cl–Rh–C(2) 92(1), N(1)–Rh–C(1) 91(2), C(1)–Rh–C(2) 87(2), N(2)–Pd–N(3)' 92(1). Primed atoms are related to the corresponding unprimed ones by a two-fold axis (symmetry equivalent position: $-x$, $1-y$, z).

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*PdClL (Htz) complexes are presumably formed '*in situ*'.

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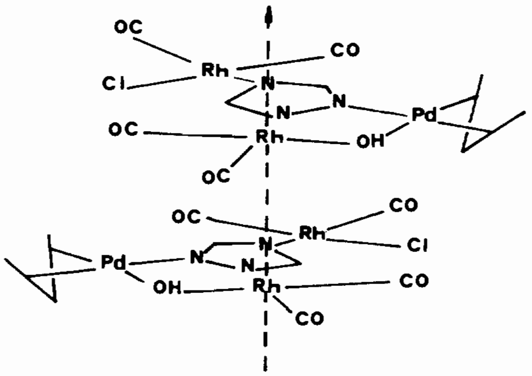

Fig. 2. Hypothesized structure for $\mathrm{Rh_2Pd(\mu_3\text{-}tz)(\mu\text{-}OH)Cl(CO)_4L}$ complexes.

imposed crystallographic C_2 symmetry, is tetranuclear with two triazolate anions acting as tridentate ligands. Each triazolate bridges two Pd atoms through the two adjacent nitrogen atoms and is bound to a rhodium atom through the third nitrogen atom. The coordination around the Pd atoms is completed by an allyl ligand, η^3-interacting through the three carbon atoms. The one around the two Rh atoms, being roughly square-planar, is completed by a chlorine atom and two carbon atoms from terminal carbonyl groups. The two triazolates, nearly planar, make a dihedral angle of 64(1)°. The $\mathrm{Pd_2N_4}$ ring is in a boat conformation in which the two Pd atoms are 0.916(3) Å out of the plane passing through the four nitrogen atoms. The situation around the two Pd atoms is very similar to that found in the complex $(\eta^3\text{-}\mathrm{C_3H_5})_2\mathrm{Pd_2}(\mu\text{-}\mathrm{Me_2pz})_2$ [6], in which $\mathrm{Me_2pz}$ is 3,5-dimethylpyrazolate.

Interestingly, addition of $\mathrm{Rh_2Cl_2(CO)_4}$ (0.073 mmol) to $\mathrm{Rh_2Pd_2(\mu_3\text{-}tz)_2Cl_2(CO)_4L_2}$ (0.073 mmol) in acetone (20 ml) results in the formation of trinuclear compounds of formula $\mathrm{Rh_2Pd(\mu_3\text{-}tz)(\mu\text{-}OH)Cl(CO)_4L}$*, which exhibit very complex IR spectra in the $\nu(\mathrm{C{\equiv}O})$ region. These spectra and the deep blue colours of the isolated complexes point to the existence of intermolecular interactions. Figure 2 shows a hypothesized structure for these complexes. We have recently characterized a related trinuclear complex, $\mathrm{Rh_3(\mu_3\text{-}tz)(\mu\text{-}Cl)Cl(\eta^4\text{-}tfb)(CO)_4}$, which shows a similar stacking arrangement of square-planar rhodium centred units along one axis, forming linear chains of metal-atoms with an intermetallic distance of 3.425(4) Å [4]. The latter complex, as well as the trinuclear rhodium–palladium complexes reported in this communication, all crystallize as long needles.

A possible pathway for the formation of the trinuclear complexes from the tetranuclear compounds could be related to the known ability of $\mathrm{Rh_2Cl_2(CO)_4}$ to abstract chloride ions from metal complexes (in this case from $\mathrm{RhCl(CO)_2}$ units). This reaction should lead to $[\mathrm{RhCl_2(CO)_2}]^-$ [7], and $[\mathrm{LPd(\mu\text{-}tz)Rh(CO)_2}]_x^{x+}$ (x = 1 or 2) intermediates, that give rise to the formation of the trinuclear complexes in which hydroxo (most probably from small amounts of water in the solvent) and triazolate groups bridge $\mathrm{Rh(CO)_2}$ and PdL units, whilst the remaining N atom of the triazolate ligand completes the coordination of the $\mathrm{RhCl(CO)_2}$ unit.

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*Analytical data, molecular weight measurements and ^{1}H NMR spectra support the proposed formulation.