Tetrazolate Rhodium(I) Complexes. Crystal Structures of the Trinuclear Complexes $[Rh_3(\mu_3\text{-ttz})(\mu\text{-Cl})Cl(cod)_2(CO)_2]$ (ttz = tetrazolate, cod = cyclo-octa-1,5-diene) and $[Rh_3(\mu_3\text{-ttz})(\mu\text{-Cl})Cl(CO)_6]$,† an Unusual Example of Metal–Metal Interactions

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Homo- and hetero-bridged binuclear complexes of general formulae $[Rh_2(\mu\text{-ttz})_2(L_2)_2]$ [ttz = tetrazolate, L_2 = diolefin or $(CO)_2$] and $[Rh_2(\mu\text{-ttz})(\mu\text{-X})L_2L'_2]$ [X = Cl, $L_2 = L'_2$ = diolefin; X = N_3, $L_2 = L'_2$ = diolefin, L_2 = cyclo-octa-1,5-diene (cod), $L'_2 = (CO)_2$] have been prepared. The heterobridged complexes, having unco-ordinated N atoms from the tetrazolate group, react with $[Rh_2(\mu\text{-Cl})_2(L''_2)_2]$ (2:1 molar ratio) [L''_2 = cod or $(CO)_2$] to give trinuclear compounds of general formula $[Rh_3(\mu_3\text{-ttz})(\mu\text{-X})ClL_2L'_2L''_2]$ (X = Cl or N_3). The latter complexes can also be obtained by reaction of $[Rh_2(\mu\text{-ttz})_2(L_2)_2]$ with $[Rh_2(\mu\text{-Cl})_2(L'_2)_2]$ (1:2 molar ratio). *X*-Ray crystallographic studies of the complexes $[Rh_3(\mu_3\text{-ttz})(\mu\text{-Cl})Cl(cod)_2(CO)_2]$ (**12**) and $[Rh_3(\mu_3\text{-ttz})(\mu\text{-Cl})Cl(CO)_6]$ (**13**) show them to contain trinuclear units, with bridging Cl atoms and tetrazolate groups. In complex (**13**) the units pack in the crystal with infinite chains, through Rh ··· Rh interactions of 3.457(2), 3.229(2), and 3.399(2) Å. In compound (**12**) the complex consists only of two units, related by a symmetry centre with a Rh ··· Rh distance equal to 3.519(2) Å.

There is considerable interest in the chemical and physical properties of new anisotropic materials.[1–4] In particular, studies on one-dimensional metal systems of square-planar d^8 complexes have usually involved platinum(II) and iridium(I). Some mononuclear rhodium(I) complexes such as $[Rh(acac)(CO)_2]$ (acac = acetylacetonate),[5] which exhibit semiconductor properties,[6] and $[RhCl(CO)_2(Hpz)]$[7] (Hpz = pyrazole), form linear stacks. Very recently it has been reported that the bi- and tri-nuclear complexes $[Rh_2(\mu\text{-pz})(\mu\text{-Cl})(CO)_4]$[8] and $[Rh_3(\mu_3\text{-tz})(\mu\text{-Cl})Cl(tfbb)(CO)_4]$[9] [tz = triazolate, tfbb = tetrafluorobenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene (tetrafluorobenzobarrelene)] present stacking arrangements of square-planar rhodium units (Figure 1) along one axis, forming nearly linear chains of metal atoms. The above mentioned complexes contain clearly defined and largely isolated parallel stacks of the constituent molecules. Due to the possibility of unusual solid-state properties for related complexes with interchain electronic interactions, and following our interest in rhodium azolate complexes,[9–11] we have attempted the preparation of bi- and tri-nuclear tetrazolate rhodium(I) complexes containing sterically undemanding and/or planar ligands.

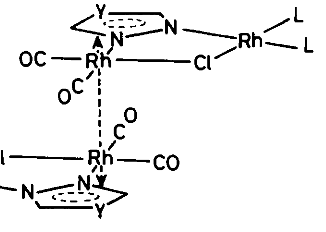

Figure 1. Stacking arrangements in the complexes $[Rh_3(\mu_3\text{-tz})(\mu\text{-Cl})Cl(tfbb)(CO)_4]$[9] [Y = N-RhCl(CO)$_2$, L_2 = tfbb] and $[Rh_2(\mu\text{-pz})(\mu\text{-Cl})(CO)_4]$[8] (Y = HC, L = CO)

Results and Discussion

The reaction of $[Rh_2(\mu\text{-Cl})_2(diolefin)_2]$ complexes [diolefin = cyclo-octa-1,5-diene (cod) or tfbb] with tetrazole (Httz) and triethylamine results in the isolation in good yields of $[Rh_2(\mu\text{-ttz})_2(diolefin)_2]$ complexes [diolefin = cod (**1**) or tfbb (**2**)]. Bubbling of carbon monoxide through a dichloromethane solution of these complexes gives the carbonyl derivative $[Rh_2(\mu\text{-ttz})_2(CO)_4]$ (**3**).

Complexes (**1**)—(**3**) can also be obtained by reaction of $[Rh(acac)L_2]$ [L_2 = diolefin or $(CO)_2$] with equimolar amounts of tetrazole. Molecular weight measurements on complexes (**1**) and (**2**) showed that they are binuclear, suggesting that the nitrogen atoms involved in co-ordination are adjacent; the low solubility of complex (**3**) prevented confirmation of the molecular weight.

Heterobridged dirhodium complexes of general formula $[Rh_2(\mu\text{-ttz})(\mu\text{-}N_3)L_2L'_2]$, containing tetrazolate and azide bridging ligands, can be obtained by treating $[Rh_2(\mu\text{-Cl})_2(L_2)_2]$ with tetrazole, $[Rh(acac)L'_2]$, and the stoicheiometric amount of NaN_3 according to equation (1). The proposed intermediate with a 'Rh(μ-ttz)(μ-Cl)Rh' core has been isolated in the solid state for $L_2 = L'_2$ = cod (**7**). Osmometric molecular weight measurements on these complexes in chloroform confirm the proposed binuclear formulation.

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† 1,1-Dicarbonyl-2,3-μ-chloro-1-chloro-2,3-bis(η-cyclo-octa-1,5-diene)-μ_3-[tetrazolato-$N^1(Rh^2)N^2(Rh^3)N^4(Rh^1)$]-trirhodium(I) and 1,1,2,2,3,3-hexacarbonyl-2,3-μ-chloro-1-chloro-μ_3-[tetrazolato-$N^1(Rh^2)N^2(Rh^3)N^4(Rh^1)$]-trirhodium(I).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

$$\tfrac{1}{2}[\mathrm{Rh_2(\mu\text{-}Cl)_2(L_2)_2}] \xrightarrow[-\mathrm{Hacac}]{\mathrm{Httz,\ [M(acac)L'_2]}} [\mathrm{Rh_2(\mu\text{-}ttz)(\mu\text{-}Cl)L_2L'_2}] \xrightarrow[-\mathrm{NaCl}]{\mathrm{NaN_3}} [\mathrm{Rh_2(\mu\text{-}ttz)(\mu\text{-}N_3)L_2L'_2}] \quad (1)$$

$\mathrm{L_2 = L'_2 =}$ cod (**4**) or tfbb (**5**); $\mathrm{L_2 =}$ cod, $\mathrm{L'_2 = (CO)_2}$ (**6**)

The binuclear complexes (**1**)—(**7**) still have unco-ordinated nitrogen atoms and therefore can act as donor centres for the construction of compounds of higher nuclearity. Thus, complexes (**4**)—(**6**) react with $[\mathrm{Rh_2(\mu\text{-}Cl)_2(L_2)_2}]$, in a 2:1 molar ratio, according to equation (2). Analytical data and molecular weight measurements support the trinuclear formulation. These complexes still present an unco-ordinated nitrogen atom on the tetrazolate group; however attempts at preparing tetranuclear compounds by treating complex (**9**) with $[\mathrm{Rh_2(\mu\text{-}Cl)_2(CO)_4}]$ (2:1 molar ratio) were unsuccessful due to the formation of complex (**11**).

$$2[\mathrm{Rh_2(\mu\text{-}ttz)(\mu\text{-}N_3)L_2L'_2}] + [\mathrm{Rh_2(\mu\text{-}Cl)_2(L''_2)_2}] \longrightarrow 2[\mathrm{Rh_3(\mu_3\text{-}ttz)(\mu\text{-}N_3)ClL_2L'_2L''_2}] \quad (2)$$

$\mathrm{L_2 = L'_2 =}$ cod, $\mathrm{L''_2 =}$ cod (**8**), or $\mathrm{(CO)_2}$ (**9**)
$\mathrm{L_2 = L'_2 =}$ tfbb, $\mathrm{L''_2 = (CO)_2}$ (**10**)
$\mathrm{L_2 =}$ cod, $\mathrm{L'_2 = L''_2 = (CO)_2}$ (**11**)

Similarly, complex (**7**) reacts with $[\mathrm{Rh_2(\mu\text{-}Cl)_2(CO)_4}]$ (2:1 molar ratio) to give $[\mathrm{Rh_3(\mu_3\text{-}ttz)(\mu\text{-}Cl)Cl(cod)_2(CO)_2}]$ (**12**). It is noteworthy that the latter complex is also formed if 2 mol of $[\mathrm{Rh_2(\mu\text{-}Cl)_2(cod)_2}]$ are treated with 1 mol of complex (**3**), confirming the stability of these trinuclear complexes. Complex (**12**) was obtained as an orange solid. As expected, bubbling of carbon monoxide through a dichloromethane solution of it leads to the displacement of cod and to formation of the carbonyl derivative $[\mathrm{Rh_3(\mu_3\text{-}tzz)(\mu\text{-}Cl)Cl(CO)_6}]$ (**13**), which precipitated immediately as a green solid with a metallic sheen. Complex (**13**) can also be obtained by reaction of (**3**) with $[\mathrm{Rh_2(\mu\text{-}Cl)_2(CO)_4}]$ (molar ratio 1:2). The preparation of the complexes (**12**) and (**13**) is shown in Scheme 1. The latter method [(*iv*)] has also been used for the synthesis of $[\mathrm{Rh_3(\mu_3\text{-}ttz)(\mu\text{-}Cl)Cl(diolefin)(CO)_4}]$ [diolefin = cod (**14**) or tfbb (**15**)], starting from the diolefin complexes (**1**) and (**2**). Table 1 collects analytical and physical data for the isolated complexes.

$$\begin{tikzcd}
{[\mathrm{Rh_2(\mu\text{-}ttz)(\mu\text{-}Cl)(cod)_2}]} \arrow[r, "(i)"] & {[\mathrm{Rh_3(\mu_3\text{-}ttz)(\mu\text{-}Cl)Cl(cod)_2(CO)_2}]} \arrow[dd, "(iii)"] \\
{[\mathrm{Rh_2(\mu\text{-}ttz)_2(CO)_4}]} \arrow[ur, "(ii)"] \arrow[dr, "(iv)"'] & \\
& {[\mathrm{Rh_3(\mu_3\text{-}ttz)(\mu\text{-}Cl)Cl(CO)_6}]}
\end{tikzcd}$$

Scheme 1. (*i*) $+\tfrac{1}{2}[\mathrm{Rh_2(\mu\text{-}Cl)_2(CO)_4}]$; (*ii*) $+2[\mathrm{Rh_2(\mu\text{-}Cl)_2(cod)_2}]$; (*iii*) +CO; (*iv*) $+2[\mathrm{Rh_2(\mu\text{-}Cl)_2(CO)_4}]$

Our interest in carbonylrhodium complexes with a '$\mathrm{Rh(\mu_3\text{-}azolate)(\mu\text{-}X)Rh}$' core is related to previous observations on their ability to promote extended metal–metal interactions (X = Cl[9] or $\mathrm{N_3}$[11c]), but the structural properties of these materials are strongly dependent on the nature of the ancillary

Table 1. Analytical data[a] for the compounds

Compound	Analysis (%)						
	C	H	N	M[b]	Colour	Yield (%)	$\tilde{\nu}$(CO)[c]/cm^{-1}
(1) $[\mathrm{Rh_2(\mu\text{-}ttz)_2(cod)_2}]$	37.95 (38.60)	4.50 (4.65)	19.30 (19.90)	555 (560)	Yellow	80	—
(2) $[\mathrm{Rh_2(\mu\text{-}ttz)_2(tfbb)_2}]$	39.90 (39.20)	1.70 (1.75)	13.50 (14.05)	838 (796)	Yellow	85	—
(3) $[\mathrm{Rh_2(\mu\text{-}ttz)_2(CO)_4}]$	15.90 (15.80)	0.60 (0.45)	25.20 (24.55)	—	Red	80	—
(4) $[\mathrm{Rh_2(\mu\text{-}ttz)(\mu\text{-}N_3)(cod)_2}]$	37.65 (38.30)	4.95 (4.70)	18.80 (18.85)	562 (533)	Yellow	84	—
(5) $[\mathrm{Rh_2(\mu\text{-}ttz)(\mu\text{-}N_3)(tfbb)_2}]$	39.10 (39.05)	2.00 (1.70)	12.80 (12.75)	806 (769)	Yellow	81	—
(6) $[\mathrm{Rh_2(\mu\text{-}ttz)(\mu\text{-}N_3)(cod)(CO)_2}]$	27.45 (27.45)	2.90 (2.70)	20.05 (20.40)	552 (481)	Dark red	70	2 025, 2 065, 2 095
(7) $[\mathrm{Rh_2(\mu\text{-}ttz)(\mu\text{-}Cl)(cod)_2}]$	38.80 (38.75)	4.70 (4.80)	11.00 (10.65)	673 (527)	Yellow	75	—
(8) $[\mathrm{Rh_3(\mu_3\text{-}ttz)(\mu\text{-}N_3)Cl(cod)_3}]$	38.80 (38.50)	4.80 (4.80)	12.15 (12.55)	660 (779)	Yellow	85	—
(9) $[\mathrm{Rh_3(\mu_3\text{-}ttz)(\mu\text{-}N_3)Cl(cod)_2(CO)_2}]$	30.80 (31.35)	3.35 (3.45)	13.70 (13.45)	728 (742)	Yellow	70	2 025, 2 062, 2 090
(10) $[\mathrm{Rh_3(\mu_3\text{-}ttz)(\mu\text{-}N_3)Cl(tfbb)_2(CO)_2}]$	33.45 (33.65)	1.55 (1.35)	10.10 (10.15)	—	Yellow	80	2 020, 2 060, 2 090
(11) $[\mathrm{Rh_3(\mu_3\text{-}ttz)(\mu\text{-}N_3)Cl(cod)(CO)_4}]$	22.85 (23.10)	1.95 (1.95)	13.95 (14.50)	620 (675)	Dark blue	70	2 015, 2 030, 2 063, 2 085, 2 100
(12) $[\mathrm{Rh_3(\mu_3\text{-}ttz)(\mu\text{-}Cl)Cl(cod)_2(CO)_2}]$	31.65 (31.65)	2.90 (3.50)	7.70 (7.75)	726 (721)	Yellow-orange	80	2 015, 2 090
(13) $[\mathrm{Rh_3(\mu_3\text{-}ttz)(\mu\text{-}Cl)Cl(CO)_6}]$	13.60 (13.65)	0.15 (0.15)	9.85 (9.10)	—	Green	78	2 020, 2 045, 2 090, 2 100
(14) $[\mathrm{Rh_3(\mu_3\text{-}ttz)(\mu\text{-}Cl)Cl(cod)(CO)_4}]$	23.15 (23.35)	1.70 (1.95)	8.65 (8.35)	704 (668)	Dark blue	75	2 010, 2 025, 2 080, 2 090
(15) $[\mathrm{Rh_3(\mu_3\text{-}ttz)(\mu\text{-}Cl)Cl(tfbb)(CO)_4}]$	25.10 (25.95)	1.00 (0.90)	7.25 (7.10)	723 (786)	Dark blue	78	2 020, 2 035, 2 087, 2 100

[a] Required values are given in parentheses. [b] In chloroform. [c] In dichloromethane. For all the mixed-bridged carbonyl complexes azide vibrations are reported together with ν(CO).

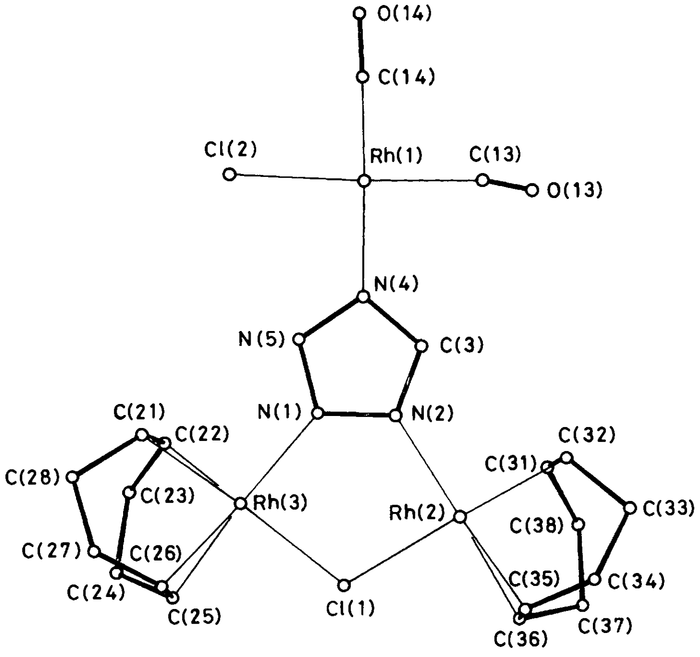

Figure 2. ORTEP drawing of complex (**12**) showing the atomic numbering

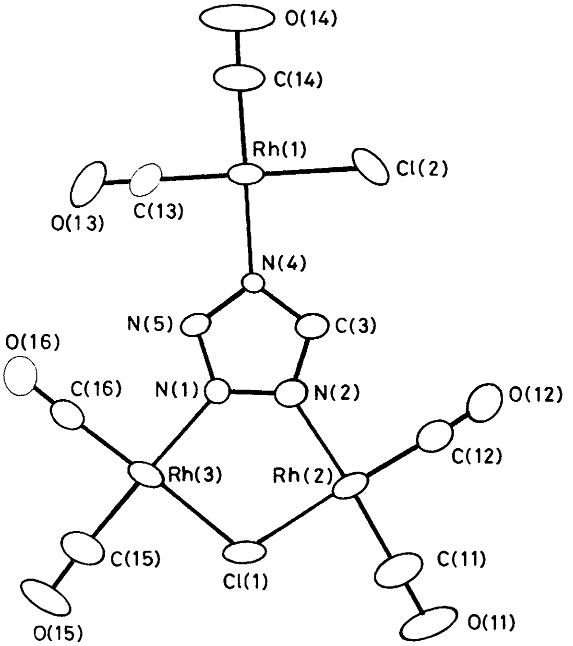

Figure 3. ORTEP drawing of complex (**13**) showing the atomic numbering

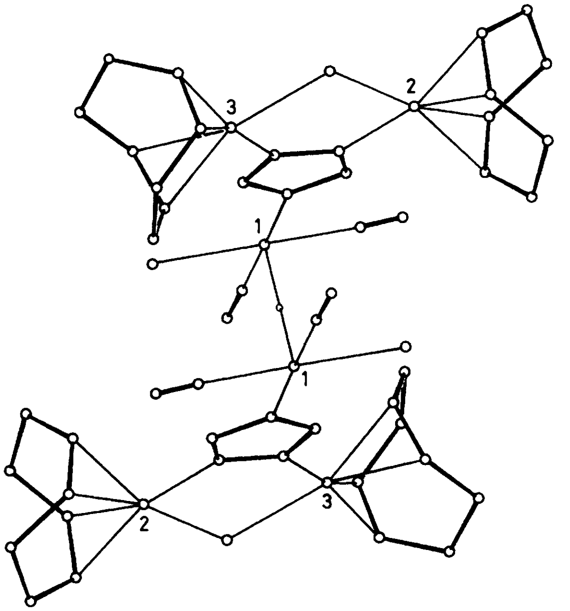

Figure 4. Packing of complex (**12**). The numbers refer to Rh atoms. The symmetry centre at $(\frac{1}{4}, \frac{1}{4}, 0)$ is also shown

ligands. Small non-bulky ligands such as CO have the correct steric requirements for close stacking involving two or more metal centres, as confirmed by *X*-ray methods for complex [Rh$_3$(μ_3-ttz)(μ-Cl)Cl(CO)$_6$] (**13**). In contrast, the previously reported [Rh$_3$(μ_3-tz)(μ-Cl)Cl(tfbb)(CO)$_4$][9] containing one bulky diolefin as ancillary ligand avoids stacking involving more than one rhodium atom. Finally the *X*-ray structure of complex (**12**), which contains two cyclo-octa-1,5-diene ligands, lacks a stacking arrangement.

Description of the Structures.—The *X*-ray crystallographic study of complexes (**12**) (Figure 2) and (**13**) (Figure 3) shows them to be trinuclear units, with bridging Cl atoms and tetrazolate groups. The main geometrical parameters are in Tables 2 and 3.

The rhodium atoms are in a distorted square-planar environment [considering the midpoints of the olefinic bonds, complex (**12**)]. The intramolecular separations Rh(2) ··· Rh(3) are equal to 3.826(1) and 3.818(1) Å for compounds (**12**) and (**13**) respectively. The central five-membered ring [N(2), Rh(2), Cl(1), Rh(3), N(1)] shows different conformations in the two

Table 2. Bond distances (Å) and angles (°) for complexes (**12**) and (**13**)

	(**12**)	(**13**)		(**12**)	(**13**)
Rh(2) • • • Rh(3)	3.826(1)	3.818(1)			
Rh(1)–N(4)	2.063(11)	2.075(10)	Rh(1)–C(13)	2.046(92)	1.871(15)
Rh(2)–N(2)	2.121(13)	2.085(10)	Rh(1)–C(14)	1.838(17)	1.848(25)
Rh(3)–N(1)	2.086(11)	2.090(10)	Rh(1)–Cl(2)*	2.364(16)	2.358(4)
Rh(3)–M(5)/C(15)	2.014(12)	1.915(18)	Rh(1)–Cl(3)*	2.302(13)	—
Rh(3)–M(6)/C(16)	1.983(12)	1.842(14)	Rh(2)–M(1)/C(11)	2.015(13)	1.857(22)
Rh(3)–Cl(1)	2.368(4)	2.371(5)	Rh(2)–M(2)/C(12)	1.998(11)	1.780(18)
			Rh(2)–Cl(1)	2.369(3)	2.358(5)
C(10)–O(10)*	1.103(43)	—	N(1)–N(4)	1.344(15)	1.355(12)
C(11)–O(11)	—	1.124(27)	N(2)–C(3)	1.304(17)	1.313(17)
C(12)–O(12)	—	1.191(23)	C(3)–N(4)	1.353(18)	1.367(15)
C(13)–O(13)*	0.895(104)	1.147(18)	N(4)–N(5)	1.347(16)	1.319(13)
C(14)–O(14)	1.115(23)	1.105(31)	N(5)–N(1)	1.336(18)	1.296(15)
C(15)–O(15)	—	1.090(23)			
C(16)–O(16)	—	1.117(19)			
Cl(2)–Rh(1)–C(14)	85.5(6)	91.7(8)	Rh(2)–N(2)–N(1)	124.0(9)	125.1(18)
Cl(2)–Rh(1)–N(4)	92.9(5)	89.6(3)	Rh(1)–N(4)–C(3)	129.6(8)	131.4(8)
C(13)–Rh(1)–C(14)	92.5(26)	87.7(9)	Rh(1)–N(4)–N(5)	124.5(9)	122.9(7)
C(13)–Rh(1)–N(4)	89.2(26)	91.0(5)	Rh(1)–C(13)–O(13)	170.5(89)	174.8(12)
Cl(1)–Rh(2)–M(1)/C(11)	90.8(4)	98.8(7)	Rh(1)–C(14)–O(14)	178.0(16)	175.8(27)
Cl(1)–Rh(2)–N(2)	89.2(3)	90.5(3)	Rh(2)–C(11)–O(11)	—	176.8(17)
M(1)/C(11)–Rh(2)–M(2)/C(12)	88.0(5)	89.7(8)	Rh(2)–C(12)–O(12)	—	175.3(17)
N(2)–Rh(2)–M(2)/C(12)	92.0(5)	92.1(8)	Rh(3)–C(15)–O(15)	—	174.2(15)
Cl(1)–Rh(3)–N(1)	88.3(3)	89.4(2)	Rh(3)–C(16)–O(16)	—	178.3(14)
Cl(1)–Rh(3)–M(5)/C(15)	91.1(4)	91.4(6)	N(5)–N(1)–N(2)	106.1(10)	110.1(8)
M(6)/C(16)–Rh(3)–M(5)/C(15)	87.4(5)	87.8(6)	N(1)–N(2)–C(3)	109.3(12)	105.0(10)
M(6)/C(16)–Rh(3)–N(1)	93.2(5)	91.3(5)	N(2)–C(3)–N(4)	109.3(11)	109.9(10)
Rh(3)–N(1)–N(2)	128.2(9)	127.2(8)	C(3)–N(4)–N(5)	105.4(11)	105.8(9)
Rh(3)–N(1)–N(5)	125.7(8)	122.5(7)	N(4)–N(5)–N(1)	109.9(11)	109.1(9)
Rh(2)–N(2)–C(3)	126.4(9)	129.9(8)			

M(1), M(2), M(5), and M(6) are the midpoints of the C(35)–C(36), C(31)–C(32), C(25)–C(26), and C(21)–C(22) olefinic bonds, respectively.

* Cl(2), Cl(3), C(10), C(13), O(10), and O(13) are involved in disorder.

Table 3. Conformational characteristics

(*a*) Torsion angles (°)

	(**12**)	(**13**)
N(1)–N(2)–Rh(2)–Cl(1)	−6.4(10)	4.9(9)
N(2)–Rh(2)–Cl(1)–Rh(3)	13.0(3)	−2.6(3)
Rh(2)–Cl(1)–Rh(3)–N(1)	−14.5(3)	1.0(3)
Cl(1)–Rh(3)–N(1)–N(2)	13.9(10)	2.4(9)
Rh(3)–N(1)–N(2)–Rh(2)	−5.7(15)	−5.6(13)
Cl(2)–Rh(1)–N(4)–C(3)	−8.6(12)	2.3(10)
M(6)/C(16)–Rh(3)–N(1)–N(2)	−162.6(11)	−178.6(10)
M(2)/C(12)–Rh(2)–N(2)–N(1)	148.8(7)	177.8(10)

(*b*) Least-squares planes

i	N(1), N(2), C(3), N(4), N(5)
ii	N(2), Rh(2), Cl(1), Rh(3), N(1)
iii	Rh(1), C(13), C(14)
iv	Rh(1), Cl(2), N(4)
v	Rh(2), M(1)/C(11), M(2)/C(12)
vi	Rh(1), Cl(1), N(2)
vii	Rh(3), M(6)/C(16)–M(5)/C(15)
viii	Rh(1), Cl(1), N(1)

(*c*) Dihedral angles (°)

	(**12**)	(**13**)
i—ii	8.1(4)	2.3(3)
ii—iv	1.9(24)	2.7(3)
v—vi	7.5(7)	7.1(6)
vii—viii	5.3(6)	1.5(5)

complexes: distorted half-chair for (**12**) with a binary axis through N(2), and envelope conformation in (**13**) with a symmetry plane through the same N(2) atom (see Table 3). This ring, conformed as an envelope, is less puckered than in other cases,[9,11b] and so the Rh(2) • • • Rh(3) distance is a bit longer, while in complex (**12**) the puckering is greater.

Complex (**12**) consists of just two units related by a symmetry centre at ($\frac{1}{4}$, $\frac{1}{4}$, 0) and interacting with Rh(1) • • • Rh(1) 3.519(2) Å (Figure 4).

Complex (**13**) packs in the crystal with finite pieces of chains, involving six metal atoms (Figure 5) along the *c* axis with contacts of Rh(2) • • • Rh(3) 3.457(2), Rh(3) • • • Rh(1) 3.229(2), and Rh(1) • • • Rh(1) 3.399(2) Å and angles Rh(2) • • • Rh(3) • • • Rh(1) 168.48(1) and Rh(3) • • • Rh(1) • • • Rh(1) 175.58(4)°. The Cl(1) • • • Cl(1) distance between units related by the binary axis is 3.574(8) Å, close to the sum of van der Waals radii.[12] This contact could be related with the different Rh • • • Rh distances observed.

Experimental

Measurements.—Elemental analyses were carried out with a Perkin-Elmer 240B microanalyser. Infrared spectra (range 4 000—200 cm^{-1}) were recorded on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets or dichloromethane solutions in sodium chloride windows. Molecular weights were determined with a Knauer osmometer using chloroform solutions.

Syntheses.—The reactions were carried out at room temperature. Prior to use, solvents were purified by standard methods.

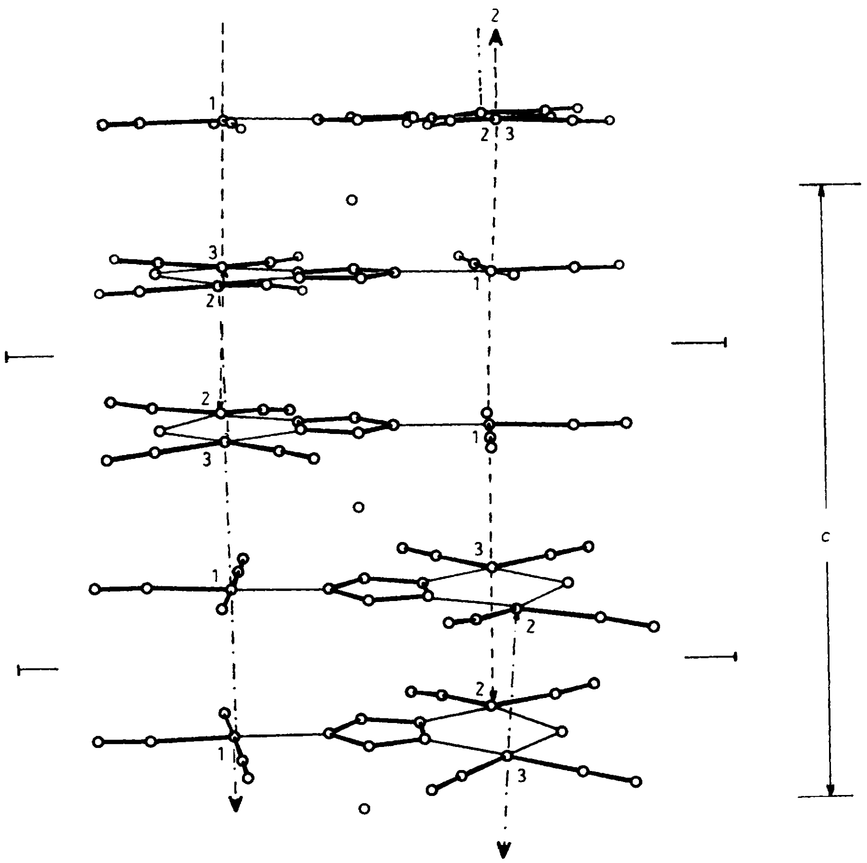

Figure 5. Stacking of units in complex (**13**) along the *c* axis of the crystal. Numbers represent the Rh atoms forming the finite chains of contacts and involving six metal atoms. Symmetric elements relating the chains are also shown. The units displayed follow, upwards, the sequence of symmetry operations: $-x, y, -\frac{1}{2} - z$; x, y, z; $-x, -y, -z$; $x, -y, \frac{1}{2} + z$; and $-x, y, \frac{1}{2} - z$

The compounds $[Rh_2(\mu\text{-}Cl)_2(diolefin)_2]$ (diolefin = cod[13] or tfbb[14]) and $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$[15] were prepared according to literature methods.

$[Rh_2(\mu\text{-}ttz)_2(diolefin)_2]$ (**1**) *and* (**2**). *Method* (*a*). A suspension of $[Rh_2(\mu\text{-}Cl)_2(diolefin)_2]$ (diolefin = cod or tfbb) (0.1 mmol) in methanol (20 cm^3) was added dropwise to a solution of tetrazole (14 mg, 0.2 mmol) and triethylamine (30 μl, 0.2 mmol) in methanol (5 cm^3). The yellow complexes $[Rh_2(\mu\text{-}ttz)_2(diolefin)_2]$ precipitated spontaneously. The resulting suspension was stirred for 30 min. The complexes were filtered off, washed with methanol–water (2:1, 10 cm^3), and air-dried.

Method (*b*). To a solution of [Rh(acac)(diolefin)] (0.1 mmol) in acetone (20 cm^3), tetrazole (7 mg, 0.1 mmol) was added. The yellow complexes precipitated spontaneously, and were isolated after partial evaporation to *ca.* 5 cm^3 and addition of hexane (10 cm^3). They were recovered by filtration, washed with hexane, and air-dried.

$[Rh_2(\mu\text{-}ttz)_2(CO)_4]$ (**3**). Carbon monoxide was bubbled through a solution of $[Rh_2(\mu\text{-}ttz)_2(cod)_2]$ (100 mg, 0.18 mmol) in dichloromethane (20 cm^3) for 30 min; complex (**3**) separated almost quantitatively. The suspension was filtered off, washed with hexane, and air-dried. This compound was also prepared starting from $[Rh(acac)(CO)_2]$ using the synthetic route (*b*) described above for complexes (**1**) and (**2**).

$[Rh_2(\mu\text{-}ttz)(\mu\text{-}N_3)(diolefin)_2]$ (**4**) *and* (**5**). Tetrazole (14 mg, 0.2 mmol) was added to a suspension of $[Rh_2(\mu\text{-}Cl)_2(diolefin)_2]$ (diolefin = cod or tfbb) (0.1 mmol) in acetone (20 cm^3). The resulting solution was stirred (30 min) and vacuum-evaporated to dryness. The residue was dissolved in methanol (20 cm^3), and solid [Rh(acac)(diolefin)] (0.2 mmol) and NaN_3 (14.3 mg, 0.2 mmol) were added. The yellow complexes precipitated spontaneously. They were filtered off, washed with cold methanol–water (2:1, 10 cm^3), and air-dried.

The asymmetric complex $[Rh_2(\mu\text{-}ttz)(\mu\text{-}N_3)(cod)(CO)_2]$ (**6**) was also prepared by this procedure starting from $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$, tetrazole, $[Rh(acac)(CO)_2]$, and NaN_3.

$[Rh_2(\mu\text{-}ttz)(\mu\text{-}Cl)(cod)_2]$ (**7**). To a mixture of $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ (50 mg, 0.1 mmol) and tetrazole (14 mg, 0.2 mmol) in acetone (30 cm^3) was added [Rh(acac)(cod)] (62 mg, 0.2 mmol). The starting material dissolved and after stirring for 30 min the solution was evaporated under vacuum to *ca.* 1 cm^3, and hexane (30 cm^3) was added. The complex which separated was filtered off, washed with hexane, and air dried.

$[Rh_3(\mu_3\text{-}ttz)(\mu\text{-}N_3)Cl(diolefin)_2(L_2)]$ (**8**)—(**10**). To a suspension of $[Rh_2(\mu\text{-}ttz)(\mu\text{-}N_3)(diolefin)_2]$ (diolefin = cod or tfbb) (0.12 mmol) in acetone (20 cm^3) was added $[Rh_2(\mu\text{-}Cl)_2(L_2)_2]$ [L_2 = cod or $(CO)_2$] (0.6 mmol). The starting materials dissolved and the yellow complexes precipitated spontaneously. After stirring for 30 min the suspension was concentrated to *ca.* 5 cm^3 and hexane (30 cm^3) was added. The solids which separated out were filtered off, washed with hexane, and air-dried.

$[Rh_3(\mu_3\text{-}ttz)(\mu\text{-}N_3)Cl(cod)(CO)_4]$ (**11**). The reaction was carried out as above but the starting materials were replaced by $[Rh_2(\mu\text{-}ttz)(\mu\text{-}N_3)(cod)(CO)_2]$ and $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$.

$[Rh_3(\mu_3\text{-}ttz)(\mu\text{-}Cl)Cl(cod)_2(CO)_2]$ (**12**). *Method* (*a*). To a suspension of $[Rh_2(\mu\text{-}ttz)(\mu\text{-}Cl)(cod)_2]$ (52.6 mg, 0.1 mmol) in acetone (20 cm^3) was added $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ (19.4 mg, 0.05 mmol). The starting material dissolved and the yellow-orange complex $[Rh_3(\mu_3\text{-}ttz)(\mu\text{-}Cl)Cl(cod)_2(CO)_2]$ precipitated spon-

Table 4. Final atomic co-ordinates for complex (**12**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Rh(1)	0.206 55(4)	0.409 44(14)	0.014 70(5)
Rh(2)	0.360 32(4)	0.779 60(14)	−0.121 11(5)
Rh(3)	0.417 53(4)	0.714 92(15)	0.047 18(5)
Cl(1)	0.426 1(1)	0.869 6(5)	−0.043 5(2)
Cl(2)	0.244 4(6)	0.353 4(21)	0.116 8(8)
Cl(3)	0.163 5(4)	0.443 7(14)	−0.083 2(6)
C(10)	0.234 4(13)	0.378 4(56)	0.102 8(18)
O(10)	0.264 2(10)	0.382 6(34)	0.143 2(12)
C(13)	0.170 7(33)	0.460 6(132)	−0.072 1(45)
O(13)	0.160 0(13)	0.486 6(56)	−0.111 6(20)
C(14)	0.152 7(6)	0.286 9(22)	0.034 4(7)
O(14)	0.120 3(5)	0.214 7(20)	0.047 9(8)
N(1)	0.345 2(4)	0.646 0(13)	0.006 5(5)
N(2)	0.324 6(4)	0.659 4(15)	−0.052 9(6)
C(3)	0.278 5(5)	0.602 1(19)	−0.059 8(6)
N(4)	0.268 2(4)	0.544 3(14)	−0.005 2(5)
N(5)	0.310 3(5)	0.572 9(19)	0.035 1(6)
C(21)	0.406 1(6)	0.648 3(26)	0.137 0(7)
C(22)	0.421 6(7)	0.500 8(25)	0.106 6(7)
C(23)	0.473 5(7)	0.419 9(30)	0.116 5(10)
C(24)	0.513 9(7)	0.553 4(32)	0.113 9(11)
C(25)	0.497 4(6)	0.711 0(31)	0.075 0(9)
C(26)	0.477 5(6)	0.854 7(34)	0.096 4(8)
C(27)	0.469 2(7)	0.888 2(30)	0.160 5(8)
C(28)	0.441 4(7)	0.745 3(32)	0.186 9(9)
C(31)	0.323 7(6)	0.609 7(23)	−0.187 1(7)
C(32)	0.296 1(5)	0.756 1(30)	−0.190 0(8)
C(33)	0.296 0(7)	0.897 5(27)	−0.240 7(9)
C(34)	0.336 1(7)	1.039 8(28)	−0.223 4(8)
C(35)	0.381 5(6)	0.975 6(21)	−0.181 6(7)
C(36)	0.407 2(7)	0.814 1(26)	−0.190 9(7)
C(37)	0.394 2(8)	0.697 4(31)	−0.244 4(8)
C(38)	0.359 1(8)	0.549 0(30)	−0.230 9(9)

taneously. After stirring for 10 min, the suspension was evaporated under vacuum to *ca.* 5 cm^3 and hexane was added. The solid was filtered off, washed with hexane, and air-dried.

Method (*b*). To a suspension of [Rh$_2$(μ-ttz)$_2$(CO)$_4$] (30 mg, 0.066 mmol) in dichloromethane (20 cm^3) was added [Rh$_2$(μ-Cl)$_2$(cod)$_2$] (65.1 mg, 0.132 mmol). After stirring for 30 min, the starting material dissolved. The resulting yellow solution was evaporated under vacuum to *ca.* 5 cm^3, and hexane (30 cm^3) was added. The solid which separated was filtered off, washed with hexane, and air-dried.

[Rh$_3$(μ$_3$-ttz)(μ-Cl)Cl(CO)$_6$] (**13**). *Method* (*a*). Carbon monoxide was bubbled through a solution of complex (**12**) (100 mg, 0.162 mmol) in dichloromethane (20 cm^3) for 30 min, and the green compound (**13**) precipitated spontaneously. The solvent was evaporated under vacuum to *ca.* 1 cm^3, and diethyl ether (20 cm^3) was added. The solid was filtered off, washed with diethyl ether, and air-dried.

Method (*b*). To a suspension of [Rh$_2$(μ-ttz)$_2$(CO)$_4$] (**3**) (80 mg, 0.17 mmol) in acetone (20 cm^3) was added [Rh$_2$(μ-Cl)$_2$(CO)$_4$] (136 mg, 0.35 mmol). Complex (**13**) precipitated spontaneously. The solid was filtered off, washed with diethyl ether, and air-dried.

[Rh$_3$(μ$_3$-ttz)(μ-Cl)Cl(diolefin)(CO)$_4$] (**14**) *and* (**15**). To a suspension of [Rh$_2$(μ-ttz)$_2$(diolefin)$_2$] (diolefin = cod or tfbb) (0.1 mmol) in acetone (25 cm^3) was added [Rh$_2$(μ-Cl)$_2$(CO)$_4$] (0.2 mmol). The dark blue complexes (**14**) and (**15**) precipitated spontaneously. They were isolated after partial evaporation of the solvent and subsequent addition of diethyl ether.

Table 5. Final atomic co-ordinates for complex (**13**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Rh(1)	0.027 36(6)	−0.211 77(7)	−0.129 41(7)
Rh(3)	−0.066 29(6)	0.217 77(8)	−0.103 51(7)
Rh(2)	0.145 70(6)	0.224 89(8)	−0.161 31(8)
Cl(2)	0.159 6(2)	−0.227 7(4)	−0.153 8(3)
Cl(1)	0.039 0(3)	0.325 4(3)	−0.127 8(3)
N(1)	0.004 8(4)	0.094 9(8)	−0.125 6(6)
N(2)	0.080 7(5)	0.096 3(8)	−0.141 9(8)
C(3)	0.100 8(6)	0.002 0(10)	−0.146 0(9)
N(4)	0.038 8(4)	−0.057 6(7)	−0.131 5(7)
N(5)	−0.018 9(5)	0.003 7(8)	−0.118 0(7)
C(11)	0.200 9(10)	0.341 7(18)	−0.178 4(15)
O(11)	0.231 2(9)	0.414 8(11)	−0.188 7(13)
C(12)	0.231 3(10)	0.154 4(16)	−0.171 5(13)
O(12)	0.287 9(7)	0.105 0(11)	−0.171 5(13)
C(13)	−0.076 7(8)	−0.200 5(10)	−0.103 8(8)
O(13)	−0.139 0(6)	−0.187 8(13)	−0.083 5(10)
C(14)	0.014 9(16)	−0.348 7(18)	−0.126 1(17)
O(14)	0.011 6(18)	−0.431 1(14)	−0.126 6(17)
C(15)	−0.133 2(8)	0.329 1(14)	−0.086 6(11)
O(15)	−0.166 1(8)	0.397 0(11)	−0.075 0(12)
C(16)	−0.149 3(7)	0.135 7(11)	−0.086 8(11)
O(16)	−0.198 9(6)	0.085 2(11)	−0.074 4(10)
H(3)	0.154(—)*	−0.023(—)*	−0.161(—)*

* Fixed in the last cycle of the refinement.

Crystal Structure Determination.—Crystal data. C$_{19}$H$_{25}$Cl$_2$N$_4$O$_2$Rh$_3$ (**12**), monoclinic, space group *C*2/*c*, *M* = 721.06, *a* = 26.975 5(18), *b* = 7.681 2(2), *c* = 22.059 9(11) Å, β = 98.908(5)° (by least-squares fit of the angular positions of 76 reflections with θ up to 45°, Cu-K_α radiation, λ = 1.5418 Å), *U* = 4 515.8(4) Å^3, D_c = 2.121 g cm^{-3}, *Z* = 8, *F*(000) = 2 816, μ = 204.14 cm^{-1} (empirical absorption corrections[16] applied).

C$_7$HCl$_2$N$_4$O$_6$Rh$_3$ (**13**), monoclinic, space group *C*2/*c*, *M* = 616.73, *a* = 17.507 1(12), *b* = 13.393 2(8), *c* = 13.634 9(10) Å, β = 91.728(7)° (48 reflections), *U* = 3 195.6(4) Å^3, D_c = 2.564 g cm^{-3}, *Z* = 8, *F*(000) = 2 304, μ = 288.85 cm^{-1} (empirical absorption corrections[16] applied).

Crystals of 0.03 × 0.08 × 0.28 and 0.05 × 0.08 × 0.33 mm were used to collect 3 831 and 2 296 independent reflections respectively (up to θ = 65°) on a Philips PW1100 diffractometer, bisecting geometry, Cu-K_α graphite monochromatized radiation with ω—2θ scans of widths 1.5 and 1.4°. The standard reflections monitored exhibited no significant variation. Totals of 2 991[$I > 3\sigma(I)$] and 1 946[$I > 2\sigma(I)$] reflections were considered as observed.

Solution and refinement. The structures were solved by Patterson methods and refined by one-block-matrix least-squares procedures operated on $F_{\text{obs.}}$. Around the Rh(1) atom in complex (**12**), disorder involving the Cl atom and the opposite CO group was detected. An occupancy factor of 0.5 was assigned to those atoms. Hydrogen atoms were obtained from a difference synthesis and their positions were fixed in the refinement. Weights were chosen to give no trends in $\langle w\Delta^2F\rangle$ *vs.* $\langle F_o\rangle$ and $\langle \sin\theta/\lambda\rangle$. The final *R* and *R′* were 0.065, 0.082 and 0.061, 0.066 for complexes (**12**) and (**13**) respectively. Final atomic co-ordinates are given in Tables 4 and 5 respectively.

The scattering factors were taken from ref. 17. All calculations were done on a VAX 11/750, mostly using the *X*-RAY 76 system.[18]

Additional material available from the Cambridge Crystallographic Data Centre comprises the H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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