η^3-Allyl Rhodium Complexes with Azolate Ligands. Crystal Structures of the Trinuclear 1,2,4-Triazolate (tz) Complexes $[Rh_3(\mu\text{-tz})_3(\eta^3\text{-}C_3H_5)_6]$ and $[Rh_3(\mu_3\text{-tz})(\mu\text{-Cl})Cl(\eta^3\text{-}C_3H_5)_2(CO)_4]\cdot 0.5C_2H_4Cl_2$†

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The η^3-allyl rhodium compound $[Rh(acac)(\eta^3\text{-}C_3H_5)_2]$ (acac = acetylacetonate) reacts with azole ligands to give the new azolate complexes $[Rh_3(\mu\text{-az})_3(\eta^3\text{-}C_3H_5)_6]$ [az = tetrazolate (ttz) (**1**), 1,2,4-triazolate (tz) (**2**), benzotriazolate (btz) (**3**), or imidazolate (im) (**4**)]. A single-crystal *X*-ray diffraction study on complex (**2**) has established that its structure consists of discrete trinuclear complexes in which each rhodium atom is bridged by the 1,2,4-triazolate ligands through the non-adjacent nitrogen atoms to form a multiatomic ring. Complexes (**2**) and (**1**) react with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ to give the mixed-valence trinuclear complexes $[Rh_3(\mu_3\text{-az})(\mu\text{-Cl})Cl(\eta^3\text{-}C_3H_5)_2(CO)_4]$ [az = tz (**10**) or ttz (**11**)]. The crystal structure of complex (**10**) has confirmed the existence of trinuclear molecules in which a chlorine atom and a triazolate bridge $Rh(CO)_2$ and $Rh(\eta^3\text{-}C_3H_5)_2$ moieties; in addition the remaining nitrogen atom of the triazolate ligand completes the square-planar co-ordination of a $RhCl(CO)_2$ unit. In the crystal, there is an intermolecular Rh–Rh distance of 3.393(1) Å. Complex (**2**) reacts with $[Rh_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_4]$ to give the trinuclear complex $[Rh_3(\mu_3\text{-tz})(\mu\text{-Cl})Cl(\eta^3\text{-}C_3H_5)_6]$. Heterobridged binuclear pyrazolate (pz) complexes of formula $[Rh_2(\mu\text{-pz})(\mu\text{-X})(\eta^3\text{-}C_3H_5)_4]$ (X = Cl, OH, or N_3) have also been prepared.

Pyrazolate (pz) complexes of the platinum metals have attracted much interest in recent years.[1–7] Our activity in this area began in 1979 when we observed that pyrazolate-type anions react with $[Rh(diolefin)(PPh_3)_2]^+$ complexes to give markedly stable $[Rh_2(\mu\text{-pz})_2(diolefin)_2]$ compounds.[8,9] The latter complexes, as well as the related $[Rh_2(\mu\text{-pz})_2(CS)_2(PPh_3)_2]$ compounds, are also easily formed by addition of triethylamine to $[Rh(Hpz)_2(diolefin)]^+$ or $[Rh(Hpz)(CS)(PPh_3)_2]^+$ complexes.[10–12] Since then, we have developed an extensive chemistry on symmetrical and unsymmetrical homobinuclear rhodium pyrazolate complexes, in which the metals are in oxidation states I,[9,11–16] II,[14,17] or III,[15–18] along with heterobinuclear compounds.[8,12,19,20]

Related chemistry involving other bi- or tri-azolate ligands has been less studied, and relatively few rhodium(I) or iridium(I) compounds with imidazolate,[19,21] 1,2,4-triazolate,[22–24] or benzotriazolate[25,26] anions are known. While binuclear structures are observed for pyrazolate-bridged complexes, higher nuclearity is found[21] for the related imidazolate (im)-bridged rhodium(I) or iridium(I) complexes $[M_x(\mu\text{-im})_x(L_2)_x]$ (L_2 = diolefin, L = CO), where *x* = 3 or 4. In particular $[Rh_4(\mu\text{-2-mim})_4(CO)_8]$ (2-mim = methylimidazolate) has been characterized by *X*-ray methods.[21] On the other hand the binuclear complexes $[M_2(\mu\text{-az})_2(L_2)_2]$ [az = 1,2,4-triazolate (tz) or benzotriazolate (btz)] are formed when triazolate ligands are used,[23,26] suggesting that the two nitrogen atoms involved in co-ordination are adjacent, as found for pyrazolate-bridged rhodium or iridium complexes,[4,9,12] and confirmed by an *X*-ray study of $[Rh_2(\mu\text{-btz})_2(cod)_2]$ (cod = cyclo-octa-1,5-diene).[26,27] Since these binuclear complexes have two unco-ordinated nitrogen atoms, one from each triazolate ligand, tri- or tetranuclear complexes have been derived from them.[23,24,26] Preliminary studies[22] on 1,2,4-triazolate complexes have shown interesting structural differences for trinuclear rhodium bis(η^3-allyl) and diolefin derivatives, suggesting that further work with the rhodium(III) moiety $Rh(\eta^3\text{-}C_3H_5)_2$ was merited. Herein we describe the preparation and properties of new bi- and trinuclear η^3-allyl rhodium complexes with representative azolate ligands.

Results and Discussion

The well known[28] mononuclear complex $[Rh(acac)(\eta^3\text{-}C_3H_5)_2]$ (acac = acetylacetonate) reacts with tetrazole (Httz), 1,2,4-triazole (Htz), benzotriazole (Hbtz), and imidazole (Him) to give the new azolate rhodium(III) complexes $[Rh_3(\mu\text{-az})_3(\eta^3\text{-}C_3H_5)_6]$ [az = ttz (**1**), tz (**2**), btz (**3**), or im (**4**)]. Elemental analysis data and representative properties of these complexes are listed in Table 1. Molecular-weight measurements on complexes (**1**)—(**3**) showed that they are trinuclear, suggesting that the nitrogen atoms involved in co-ordination are not adjacent, since for rhodium complexes containing bridging pyrazolate-type ligands only binuclear compounds are known. The low solubility of the imidazolate complex (**4**) prevented the determination of its molecular weight by osmometry, but the expected parent ion was found in the mass spectrum, along with the fragment formed by loss of one imidazolate group. The proposed structure for these complexes has been confirmed for complex (**2**) by *X*-ray methods (see below). These results suggest that the rhodium(III) moiety $Rh(\eta^3\text{-}C_3H_5)_2$ favours imidazolate-type co-ordination, while the rhodium(I) units RhL_2 (L_2 = diolefin, L = CO) favour the chemically very stable formulation

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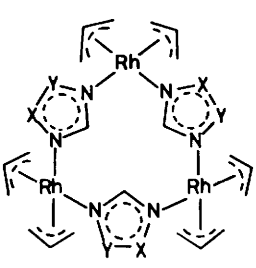
† Tris[di-η-allyl-μ-(1,2,4-triazolato-N^1N^4)-rhodium] and 1,1-di-η-allyl-2,2,3,3-tetracarbonyl-1,2-μ-chloro-3-chloro-μ_3-1,2,4-triazolato-$N^1N^2N^4$-trirhodium 1,2-dichloroethane (2/1).

Supplementary data available (No. SUP 56614, 5 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii–xx. Structure factors are available from the editorial office.

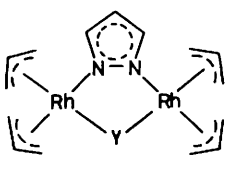
Table 1. Analytical data[a] for the compounds

Compound	Analysis (%)					
	C	H	N	M^b	Colour	Yield (%)
(**1**) $[Rh_3(\mu\text{-ttz})_3(\eta^3\text{-}C_3H_5)_6]$	32.70 (33.10)	4.20 (4.25)	23.15 (22.40)	763 (762)	White	75
(**2**) $[Rh_3(\mu\text{-tz})_3(\eta^3\text{-}C_3H_5)_6]$	38.40 (37.95)	4.85 (4.75)	17.40 (16.60)	764 (760)	White	72
(**3**) $[Rh_3(\mu\text{-btz})_3(\eta^3\text{-}C_3H_5)_6]$	47.10 (47.55)	4.65 (4.65)	14.20 (13.85)	1 007 (909)	White	75
(**4**) $[Rh_3(\mu\text{-im})_3(\eta^3\text{-}C_3H_5)_6]$	42.95 (42.90)	5.65 (5.20)	11.05 (11.10)	—	White	70
(**5**) $[RhCl(\eta^3\text{-}C_3H_5)_2(Hpz)]$	37.15 (37.45)	4.85 (4.90)	10.30 (9.70)	298 (288)	Yellow	80
(**6**) $[RhCl(\eta^3\text{-}C_3H_5)_2(Hbtz)]$	42.10 (42.45)	3.80 (4.15)	12.50 (12.35)	507 (340)	Yellow	72
(**7**) $[Rh_2(\mu\text{-pz})(\mu\text{-Cl})(\eta^3\text{-}C_3H_5)_4]$	38.20 (38.10)	4.70 (4.90)	6.15 (5.90)	496 (473)	Yellow	70
(**8**) $[Rh_2(\mu\text{-pz})(\mu\text{-OH})(\eta^3\text{-}C_3H_5)_4]$	38.70 (39.65)	5.30 (5.35)	5.90 (6.15)	—	Pale yellow	75
(**9**) $[Rh_2(\mu\text{-pz})(\mu\text{-}N_3)(\eta^3\text{-}C_3H_5)_4]$	37.25 (37.60)	4.65 (4.85)	15.15 (14.60)	470 (479)	Pale yellow	70
(**10**) $[Rh_3(\mu_3\text{-tz})(\mu\text{-Cl})Cl(\eta^3\text{-}C_3H_5)_2(CO)_4]^c$	23.70 (24.00)	2.05 (2.01)	6.90 (7.00)	709	Orange	80
(**11**) $[Rh_3(\mu_3\text{-ttz})(\mu\text{-Cl})Cl(\eta^3\text{-}C_3H_5)_2(CO)_4]^c$	20.60 (20.55)	1.80 (1.70)	9.10 (8.70)	671 (643)	Dark red	70
(**12**) $[Rh_3(\mu_3\text{-tz})(\mu\text{-Cl})Cl(\eta^3\text{-}C_3H_5)_6]$	34.30 (34.60)	4.70 (4.65)	6.70 (6.05)	760 (694)	Pale yellow	75
(**13**) $[Rh_2(\mu\text{-bim})(\eta^3\text{-}C_3H_5)_4]$	43.95 (43.05)	4.65 (4.80)	10.85 (11.15)	505 (502)	Pale yellow	50
(**14**) $[RhAu_2(\mu_3\text{-bim})(\eta^3\text{-}C_3H_5)_2(PPh_3)_2]ClO_4$	43.20 (43.20)	3.25 (3.30)	4.15 (4.20)	—	White	69

[a] Required values are given in parentheses. [b] In chloroform. [c] ν(CO) in dichloromethane: (**10**), 2 092, 2 085, 2 022, and 2 010; (**11**), 2 098, 2 081, 2 030, and 2 011 cm^{-1}.



	X	Y
(**1**)	N	N
(**2**)	N	CH
(**4**)	CH	CH



	Y
(**7**)	Cl
(**8**)	OH
(**9**)	N_3

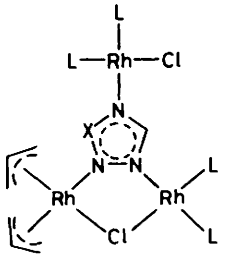
$[Rh_2(\mu\text{-az-}N^1N^2)_2(L_2)_2]$ (az = pz,[9,11] tz,[23] or btz[26]). This difference could explain our unsuccessful attempts at preparing $[Rh_2(\mu\text{-pz})_2(\eta^3\text{-}C_3H_5)_4]$ by treating $[Rh(acac)(\eta^3\text{-}C_3H_5)_2]$ with pyrazole.

On the other hand, a general and well known pathway for the synthesis of $[Rh_2(\mu\text{-az})_2(L_2)_2]$ (L_2 = diolefin, L = CO) complexes is the treatment of $[Rh_2(\mu\text{-Cl})_2(L_2)_2]$ dimers with the azole and triethylamine.[9,11,23,26] When this approach was used, starting from $[Rh_2(\mu\text{-Cl})_2(\eta^3\text{-}C_3H_5)_4]$,[28] the initial formation of the mononuclear complex $[RhCl(\eta^3\text{-}C_3H_5)_2(Hpz)]$ (**5**) was observed, after adding the stoicheiometric amount of pyrazole. Upon addition of triethylamine, loss of the acidic pyrazole proton was also observed, but the heterobridged complex $[Rh_2(\mu\text{-pz})(\mu\text{-Cl})(\eta^3\text{-}C_3H_5)_4]$ (**7**) was formed. In contrast, the expected complexes (**2**) and (**3**) are formed by this route when 1,2,4-triazole or benzotriazole is used instead of pyrazole. Thus, compound (**6**) reacts with triethylamine to give (**3**).

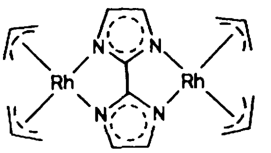
The reasons for the preference of the $Rh(C_3H_5)_2$ moiety for the formation of a 'Rh(μ-pz)(μ-Cl)Rh' arrangement over '$Rh_2(\mu\text{-pz})_2$' are not clear, but we suspect that they are mainly electronic, rather than steric. The '$Rh_2(\mu\text{-pz})_2$' framework is very flexible as seen in the wide range of intermetallic separations (Rh–Rh 2.581—3.568 Å).[23]

Complex (**7**) undergoes anion metathesis with stoicheiometric amounts of KOH or NaN_3 to give the related heterobridged complexes $[Rh_2(\mu\text{-pz})(\mu\text{-OH})(\eta^3\text{-}C_3H_5)_4]$ (**8**) and $[Rh_2(\mu\text{-pz})(\mu\text{-}N_3)(\eta^3\text{-}C_3H_5)_4]$ (**9**). Their i.r. spectra show the presence of co-ordinated $\eta^3\text{-}C_3H_5$ groups, as well as typical bands of the bridging groups [pz, 1 500—1 450; ν(OH), 3 620; ν(N≡N), 2 050 cm^{-1}].

Our interest in carbonylrhodium(I) complexes with a 'Rh(μ-



	X	L
(10)	CH	CO
(11)	N	CO
(12)	CH	C_3H_5



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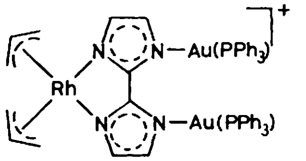

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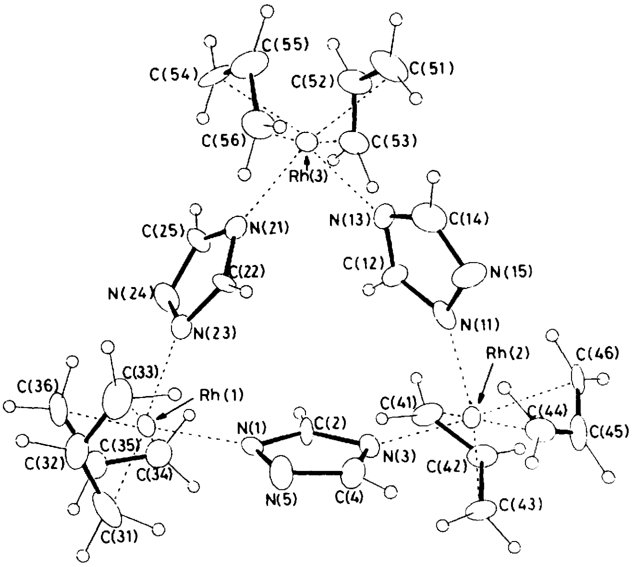

Figure 1. An ORTEP view of the complex $[Rh_3(\mu\text{-tz})_3(\eta^3\text{-}C_3H_5)_6]$ (**2**), showing the atomic numbering as projected onto the Rh_3 plane

az)(μ-X)Rh' core is related to previous observations[22–24,29] on their ability to promote extended metal–metal interactions. In a preliminary communication[22] we reported that reaction of equimolecular amounts of $[Rh(acac)L_2]$ [L_2 = tetrafluorobenzobarrelene, tfb (5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene), L = η^3-C_3H_5], 1,2,4-triazole, and $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ produces trinuclear $[Rh_3(\mu_3\text{-tz})(\mu\text{-}Cl)ClL_2(CO)_4]$ complexes exhibiting extended metal–metal interactions in different arrangements. We now report in full the structure of the allyl derivative together with a new reaction converting the '$Rh_3(\mu\text{-az})_3$' core into the '$Rh_3(\mu_3\text{-az})(\mu\text{-Cl})$.' Thus, the reaction of the trinuclear tri- and tetra-azolate complexes (**2**) and (**1**) with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ where $Rh(\eta^3\text{-}C_3H_5)_2:Rh(CO)_2 = 1:2$ gives rises to the mixed-valence trinuclear complexes $[Rh_3(\mu_3\text{-az})(\mu\text{-}Cl)Cl(\eta^3\text{-}C_3H_5)_2(CO)_4]$ [az = tz (**10**) or ttz (**11**)]. The ^1H n.m.r. spectrum of (**10**) shows the expected resonances for two inequivalent allyl groups and two triazolate protons (8.24 and 8.40 p.p.m.). Molecular-weight measurements support the proposed formulation, which has been confirmed by the crystallographic characterization of complex (**10**). Their i.r. spectra show the expected bands of the co-ordinated ligands, along with a markedly strong ν(C–H) band in the range 3 120—3 150 cm^{-1} that we consider to be a characteristic of $[Rh_2M(\mu_3\text{-tz})(\mu\text{-X})ClL_2(CO)_4]$ complexes.[23] Furthermore, their solid-state i.r. spectra are relatively complex, indicating the presence of metal–metal interactions.

It is noteworthy that complexes (**10**) and (**11**) are also formed by treating (**2**) or (**1**) with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ where $Rh(\eta^3\text{-}C_3H_5)_2:Rh(CO)_2 = 1:1$, confirming the stability of these trinuclear allylrhodium(III) complexes. Under similar reaction conditions, the dirhodium(I) compounds $[Rh_2(\mu\text{-tz})_2(L_2)_2]$ (L_2 = diolefin, L = CO) react with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ where $RhL_2:Rh(CO)_2 = 1:1$ to give tetranuclear $[Rh_4(\mu_3\text{-tz})_2Cl_2(L_2)_2(CO)_4]$ complexes, although the expected trinuclear derivatives $[Rh_3(\mu_3\text{-tz})Cl_2L_2(CO)_4]$ are obtained when $RhL_2:Rh(CO)_2 = 1:2$.[23] Attempts to prepare the binuclear mixed-valence complex $[Rh_2(\mu\text{-tz})(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)_2(CO)_2]$, by treating $[Rh_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_4]$ with 1,2,4-triazole and $[Rh(acac)(CO)_2]$, were unsuccessful, due to the formation of the markedly stable trinuclear compound $[Rh_3(\mu_3\text{-tz})(\mu\text{-}Cl)Cl(\eta^3\text{-}C_3H_5)_2(CO)_4]$ (**10**). On the other hand, the trinuclear complex $[Rh_3(\mu_3\text{-tz})(\mu\text{-}Cl)Cl(\eta^3\text{-}C_3H_5)_6]$ (**12**) has been prepared by reaction of compound (**2**) with $[Rh_2(\mu\text{-}Cl)_2(\eta^3\text{-}C_3H_5)_4]$.

Finally, we have explored the ability of the 2,2'-bi-imidazolate anion (bim) to act as quadridentate bridging ligand towards the $Rh(\eta^3\text{-}C_3H_5)_2$ moiety. $[Rh(acac)(\eta^3\text{-}C_3H_5)_2]$ reacts with 2,2'-bi-imidazole ($Rh:H_2bim = 2:1$) to give the binuclear complex $[Rh_2(\mu\text{-bim})(\eta^3\text{-}C_3H_5)_4]$ (**13**) in which the bi-imidazolate ligand is most probably chelating two rhodium atoms through the four nitrogen atoms of the two imidazole rings. Several rhodium(I) complexes of formula $[Rh_2(\mu\text{-bim})(diolefin)_2]$ (diolefin = cyclo-octa-1,5-diene,[30] norborna-2,5-diene,[8] or tetrafluorobenzobarrelene[8]) or $[Rh_4(\mu_3\text{-bim})_2(CO)_4L_4]$ (L = CO[30] or PPh_3[8,31]) are known, as well as tetranuclear palladium(II) and heteronuclear palladium(II)–rhodium(I) complexes,[32] such as $[Pd_4(\mu_3\text{-bim})_2(\eta^3\text{-}C_3H_5)_4]$ and $[Pd_2Rh_2(\mu_3\text{-bim})_2(\eta^3\text{-}C_3H_5)_2L_2]$ (L_2 = cod, L = CO). On the other hand, the complex $[Au_2(\mu\text{-bim})(PPh_3)_2]$, prepared by reacting $Tl_2(bim)$ with $[AuCl(PPh_3)]$, reacts with $[Rh(\eta^3\text{-}C_3H_5)_2(Me_2CO)_x]ClO_4$ to give the new hetero-trinuclear complex $[RhAu_2(\mu_3\text{-bim})(\eta^3\text{-}C_3H_5)_2(PPh_3)_2]ClO_4$ (**14**), in which the bim ligand should be chelating to one rhodium atom through two nitrogen atoms and unidentate to the gold atoms through the other two nitrogen atoms. The related 2,2'-bibenzimidazolate rhodium(I)–gold(I) complex $[RhAu_2(\mu_3\text{-bbzim})(cod)(PPh_3)_2]ClO_4$ has previously been reported.[33] It has a short intramolecular Au–Au distance of 3.134(4) Å.

Description of the Structures.—The solid-state structure of the complex $[Rh_3(\mu\text{-tz})_3(\eta^3\text{-}C_3H_5)_6]$ (**2**) is shown in Figure 1 together with the atomic numbering scheme. Selected bond lengths and angles are given in Table 2. Each of the three rhodium atoms is in a distorted-octahedral arrangement, and is bonded to two η^3-C_3H_5 ligands and two nitrogen atoms of two triazolates, which act as *exo*-bidentate ligands through two non-adjacent nitrogens. There is some asymmetry in the allyl–rhodium bonding.

The metal atoms and the triazolate groups form a twelve-membered ring skeleton whose conformation is shown in Figure 2. Torsion angles given in Table 2 show the pseudo-mirror plane of symmetry that this skeleton possesses, passing through Rh(2),

Table 2. Selected geometrical parameters (distances in Å, angles in °) for $[Rh_3(\mu\text{-tz})_3(\eta^3\text{-}C_3H_5)_6]$ (**2**)

Rh(1)–Rh(2)	6.259(2)	Rh(2)–Rh(3)	6.232(2)	Rh(3)–Rh(1)	6.314(2)
Rh(1)–N(1)	2.139(13)	Rh(2)–N(3)	2.147(13)	Rh(3)–N(13)	2.154(16)
Rh(1)–N(23)	2.119(15)	Rh(2)–N(11)	2.113(16)	Rh(3)–N(21)	2.170(16)
Rh(1)–C(31)	2.117(23)	Rh(2)–C(42)	2.132(22)	Rh(3)–C(51)	2.152(24)
Rh(1)–C(32)	2.172(26)	Rh(2)–C(43)	2.122(20)	Rh(3)–C(52)	2.135(21)
Rh(1)–C(33)	2.241(25)	Rh(2)–C(41)	2.187(20)	Rh(3)–C(53)	2.246(21)
Rh(1)–C(34)	2.182(21)	Rh(2)–C(44)	2.237(20)	Rh(3)–C(56)	2.169(22)
Rh(1)–C(35)	2.144(21)	Rh(2)–C(45)	2.153(18)	Rh(3)–C(54)	2.169(29)
Rh(1)–C(36)	2.148(18)	Rh(2)–C(46)	2.158(16)	Rh(3)–C(55)	2.150(25)
N(1)–N(5)	1.364(21)	N(11)–N(15)	1.412(23)	N(23)–N(24)	1.406(22)
N(1)–C(2)	1.316(21)	N(13)–C(14)	1.322(30)	N(21)–C(25)	1.343(25)
N(3)–C(2)	1.322(20)	N(11)–C(12)	1.371(25)	N(21)–C(22)	1.345(24)
N(3)–C(4)	1.374(24)	N(13)–C(12)	1.338(25)	N(23)–C(22)	1.327(23)
N(5)–C(4)	1.329(24)	C(14)–N(15)	1.296(31)	C(25)–N(24)	1.317(27)
C(31)–C(32)	1.318(38)	C(41)–C(42)	1.392(30)	C(51)–C(52)	1.430(32)
C(32)–C(33)	1.298(33)	C(42)–C(43)	1.421(26)	C(52)–C(53)	1.326(31)
C(34)–C(35)	1.354(30)	C(44)–C(45)	1.286(32)	C(54)–C(55)	1.438(38)
C(35)–C(36)	1.420(30)	C(45)–C(46)	1.431(35)	C(55)–C(56)	1.380(31)

N(23)–Rh(1)–C(31)	159.1(9)	N(3)–Rh(2)–C(46)	162.9(8)	N(13)–Rh(3)–C(54)	163.4(9)
N(1)–Rh(1)–C(36)	162.5(7)	N(11)–Rh(2)–C(43)	165.0(7)	N(21)–Rh(3)–C(51)	165.5(8)
C(33)–Rh(1)–C(34)	172.5(8)	C(41)–Rh(2)–C(44)	169.0(8)	C(53)–Rh(3)–C(56)	171.7(8)
Rh(2)–Rh(1)–Rh(3)	59.4(1)	Rh(1)–Rh(2)–Rh(3)	60.7(1)	Rh(1)–Rh(3)–Rh(2)	59.8(1)
Rh(1)–N(1)–C(2)	125.4(11)	Rh(2)–N(11)–C(12)	126.5(13)	Rh(3)–N(21)–C(22)	128.9(12)
C(2)–N(3)–Rh(2)	131.4(12)	C(12)–N(13)–Rh(3)	125.1(13)	C(22)–N(23)–Rh(1)	129.0(12)

N(3)–Rh(2)–N(11)–C(12)	−70.7(15)	N(11)–Rh(2)–N(3)–C(2)	69.2(18)
Rh(2)–N(11)–C(12)–N(13)	171.9(12)	Rh(2)–N(3)–C(2)–N(1)	−167.7(12)
N(11)–C(12)–N(13)–Rh(3)	−174.1(12)	N(3)–C(2)–N(1)–Rh(1)	177.0(12)
C(12)–N(13)–Rh(3)–N(21)	44.4(16)	C(2)–N(1)–Rh(1)–N(23)	−47.5(15)
N(13)–Rh(3)–N(21)–C(22)	44.2(16)	N(1)–Rh(1)–N(23)–C(22)	−43.0(15)
Rh(3)–N(21)–C(22)–N(23)	−176.1(12)	Rh(1)–N(23)–C(22)–N(21)	177.4(12)

[Rh(1),Rh(2),Rh(3)]–[N(1),C(2),N(3),C(4),N(5)]	67.5(6)
[Rh(1),Rh(2),Rh(3)]–[N(11),C(12),N(13),C(14),N(15)]	64.7(6)
[Rh(1),Rh(2),Rh(3)]–[N(21),C(22),N(23),N(24),C(25)]	64.8(5)
[N(1),C(2),N(3),C(4),N(5)]–[N(11),C(12),N(13),C(14),N(15)]	73.2(8)
[N(1),C(2),N(3),C(4),N(5)]–[N(21),C(22),N(23),N(24),C(25)]	57.1(7)
[N(11),C(12),N(13),C(14),N(15)]–[N(21),C(22),N(23),N(24),C(25)]	53.7(8)

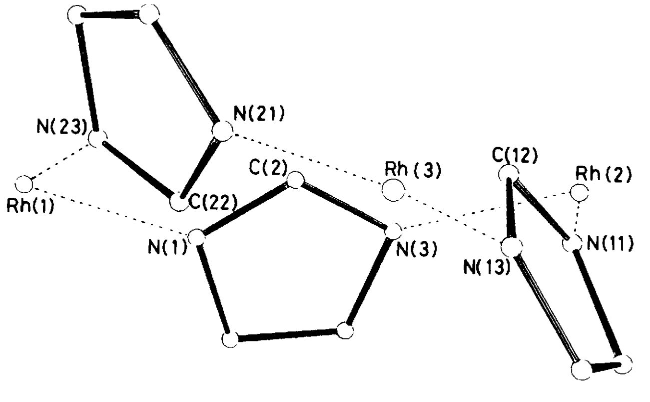

Figure 2. The $Rh_3(\mu\text{-tz})_3$ skeleton of compound (**2**) showing the conformation of the trimer

C(22), and the midpoint of N(24)–C(25). The planes of the triazolate groups are at angles of about 66° with respect to the three rhodium planes. The Rh–N bond lengths agree with those found in related binuclear pyrazolate complexes[9,12,16] or in the related tetranuclear compound $[Rh_4(\mu\text{-2-mim})_4(CO)_8]$.[21]

The structure of $[Rh_3(\mu_3\text{-tz})(\mu\text{-Cl})Cl(\eta^3\text{-}C_3H_5)_2(CO)_4]\cdot 0.5C_2H_4Cl_2$ (**10**) is illustrated in Figure 3, and the main bond parameters are given in Table 3. The rhodium(I) atoms are in a distorted square-planar environment, as illustrated by the dihedral angles in Table 3 and the angles at the rhodium atoms [88.9(5)—91.8(4)°]. There is a significant asymmetry in the allyl group in that one terminal carbon, C(20), *trans* to the bridging chlorine, is closer to the metal, as previously observed in the related binuclear complexes $[Rh_2(\mu\text{-X})_2(\eta^3\text{-}C_5H_5)_4]$.[34] Within the complex, the separation between Rh(2) and Rh(3) of 3.712(1) Å is similar to that [3.715(2) Å] found for the mixed-valence complex $[(C_5Me_5)ClRh(\mu\text{-pz})(\mu\text{-Cl})Rh(tfb)]$.[16] The central ring Rh(2),N(2),N(1),Rh(3),Cl(1) is puckered so as to adopt a distorted envelope conformation at Cl(2) (see torsion angles in Table 3). A non-planar ring conformation has also been found in the binuclear complexes $[Rh_2(\mu\text{-pz})(\mu\text{-Cl})(CO)_4]$[29] and $[(C_5Me_5)ClRh(\mu\text{-pz})(\mu\text{-Cl})Rh(tfb)]$,[16] although in the related trinuclear complex $[Rh_3(\mu_3\text{-tz})(\mu\text{-Cl})Cl(tfb)(CO)_4]$ the Rh_2N_2Cl ring is nearly planar.[23] The lengths of the Rh–N bonds are similar to those found for complex (**2**) and related rhodium azolate complexes.[9,12–16,21] The metal–ligand distances are uniformly greater for the six-co-ordinate rhodium(III) than for the four-co-ordinate rhodium(I) centres, as previously observed for other mixed-valence complexes.[16,35,36]

An interesting feature in this complex is the presence of an intermolecular contact Rh(1) • • • Rh(2) of 3.393(1) Å (see Figure 4). This value may be compared with those found for the mononuclear complexes $[Rh(acac)(CO)_2]$, 3.233(6) and 3.271(6) Å,[37] and $[RhCl(CO)_2(Hpz)]$, 3.4522(4) Å,[38] the binuclear compound $[Rh_2(\mu\text{-pz})(\mu\text{-Cl})(CO)_4]$, 3.5107(8) and 3.6201(8) Å,[29] or the recently reported trinuclear complex $[Rh_3(\mu_3\text{-tz})$-

Table 3. Selected geometrical parameters (distances in Å, angles in °) for [$Rh_3(\mu_3$-tz)(μ-Cl)Cl(η^3-$C_3H_5)_2(CO)_4]\cdot 0.5C_2H_4Cl_2$ (**10**)

Rh(2)–Rh(1)(*x*,*y*,1 + *z*)	3.393(1)	Rh(2)–Rh(3)	3.712(1)
Rh(1)–N(4)	2.096(7)	Rh(3)–N(1)	2.143(6)
Rh(1)–Cl(2)	2.358(3)	Rh(3)–Cl(1)	2.500(2)
Rh(1)–C(13)	1.846(12)	Rh(3)–C(15)	2.209(11)
Rh(1)–C(14)	1.832(9)	Rh(3)–C(16)	2.156(12)
Rh(2)–N(2)	2.087(7)	Rh(3)–C(17)	2.146(14)
Rh(2)–Cl(1)	2.356(3)	Rh(3)–C(18)	2.238(12)
Rh(2)–C(11)	1.838(12)	Rh(3)–C(19)	2.145(9)
Rh(2)–C(12)	1.814(10)	Rh(3)–C(20)	2.110(11)
N(1)–N(2)	1.376(9)	C(11)–O(11)	1.146(15)
N(1)–C(5)	1.303(10)	C(12)–O(12)	1.150(14)
N(2)–C(3)	1.306(11)	C(13)–O(13)	1.082(16)
N(4)–C(3)	1.357(12)	C(14)–O(14)	1.141(12)
N(4)–C(5)	1.346(10)		
C(15)–C(16)	1.386(14)	C(18)–C(19)	1.386(20)
C(16)–C(17)	1.432(20)	C(19)–C(20)	1.416(15)
Cl(2)–Rh(1)–C(13)	175.1(3)	Cl(1)–Rh(3)–C(20)	160.6(3)
N(4)–Rh(1)–C(14)	177.9(4)	N(1)–Rh(3)–C(17)	162.5(4)
Cl(1)–Rh(2)–C(12)	179.1(3)	C(15)–Rh(3)–C(18)	177.2(5)
N(2)–Rh(2)–C(11)	176.1(4)	Rh(2)–Cl(1)–Rh(3)	99.7(1)
Rh(1)–C(13)–O(13)	177.8(9)	Rh(2)–C(11)–O(11)	177.4(11)
Rh(1)–C(14)–O(14)	177.1(9)	Rh(2)–C(12)–O(12)	178.3(8)
Rh(1)–N(4)–C(3)	128.2(6)	Rh(2)–N(2)–N(1)	123.0(5)
Rh(1)–N(4)–C(5)	128.5(6)	Rh(3)–N(1)–N(2)	124.0(5)
N(2)–Rh(2)–Cl(1)–Rh(3)	−36.8(2)		
Rh(2)–C(1)–Rh(3)–N(1)	35.2(2)		
Cl(1)–Rh(3)–N(1)–N(2)	−24.3(5)		
Rh(3)–N(1)–N(2)–Rh(12)	−2.9(8)		
N(1)–N(2)–Rh(2)–Cl(1)	29.8(6)		
[Cl(2),C(14),C(13),N(4)]–[N(1),N(2),C(3),N(4),C(5)]	29.0(3)		
[Cl(1),C(11),C(12),N(2)]–[N(1),N(2),C(3),N(4),C(5)]	28.7(3)		
[Cl(2),C(14),C(13),N(14)]–[Cl(1),C(11),C(12),N(2)]	7.3(2)		
[Rh(1),N(4),Cl(2)]–[C(13),C(14),Rh(1)]	4.9(3)		
[Rh(2),N(2),Cl(1)] [C(11),C(12),Rh(1)]	3.9(3)		

(μ-Cl)Cl(tfb)$(CO)_4$],[23] in which stacking of square-planar rhodium units is present. The whole complex (**10**) conforms roughly with the two square planes inclined at about 7° and both at about 29° to the triazolate plane (see Table 3).

The above structural results on triazolate complexes show that the Rh(η^3-$C_3H_5)_2$ moiety (Rh^{III}, d^6 species) produces significant differences with respect to RhL_2 (L_2 = diolefin, L = CO) units (Rh^I, d^8 species). The latter favours binuclear [Rh_2(μ-tz$)_2(L_2)_2$] complexes, while the trinuclear η^3-allyl rhodium(III) compound (**2**) is formed. On the other hand, although a similar trinuclear formulation [$Rh_3(\mu_3$-tz)(μ-Cl)Cl$L_2(CO)_4$] is observed, the homovalent rhodium(I) complexes (L_2 = diolefin) presents a stacking arrangement of square-planar rhodium units involving nearly linear chains of metal atoms along one axis,[23] while the related mixed-valence complex (**10**) (L = η^3-C_3H_5) shows a different arrangement with Rh–Rh interactions between structurally different Rh atoms.

Experimental

Measurements.—Elemental analyses were carried out with a Perkin-Elmer 240 B 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 NaCl windows. Proton n.m.r. spectra were recorded in $CDCl_3$ at room temperature on a Varian XL 200 spectrometer, using $SiMe_4$ as standard. Molecular weights were determined with a Perkin-Elmer 115 osmometer using chloroform solutions.

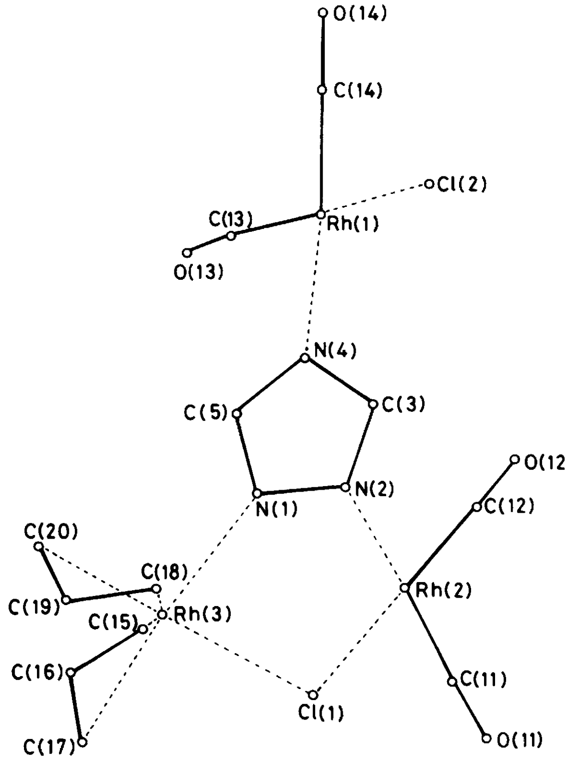

Figure 3. The molecular structure of the complex [$Rh_3(\mu_3$-tz)(μ-Cl)Cl(η^3-$C_3H_5)_2(CO)_4$] (**10**), showing the atomic numbering as projected along the *a* axis

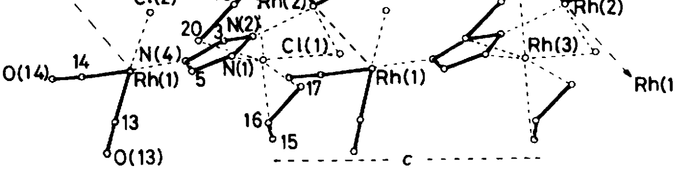

Figure 4. The packing arrangement in crystals of compound (**10**) showing the metal–metal interactions

Syntheses.—The reactions were carried out at room temperature. Prior to use, solvents were purified by standard methods. The compounds [$Rh_2(\mu$-Cl$)_2(\eta^3$-$C_3H_5)_4$], [Rh(acac)(η^3-$C_3H_5)_2$], [$Rh_2(\mu$-Cl$)_2(CO)_4$], and [Rh(η^3-$C_3H_5)_2(Me_2CO)_x$]ClO_4 were prepared according to literature methods.[28]

[$Rh_3(\mu$-az$)_3(\eta^3$-$C_3H_5)_6$] (**1**)—(**4**). To a solution of [Rh(acac)(η^3-$C_3H_5)_2$] (0.272 mmol) in acetone (20 cm^3) was added Haz (Haz = Httz, Htz, Hbtz, or Him) (0.272 mmol). In the case of complex (**4**) the solution was stirred for 12 h and it precipitated spontaneously, whilst in the cases of complexes (**1**)—(**3**) the solutions were stirred for 2 h, and the products were isolated after partial evaporation of the solvent to *ca.* 1 cm^3 and subsequent addition of diethyl ether (15 cm^3). The white solids were filtered off, washed with diethyl ether, and air-dried.

[RhCl(η^3-$C_3H_5)_2$(Haz)] [Haz = Hpz (**5**) *or* Hbtz (**6**)]. To a solution in dichloromethane (15 cm^3) of [$Rh_2(\mu$-Cl$)_2(\eta^3$-$C_3H_5)_4$][28] (60 mg, 0.136 mmol) was added Hpz (18.5 mg, 0.272

mmol). After stirring for 30 min, the solution was evaporated under vacuum to *ca.* 1 cm^3, and hexane (15 cm^3) was added. The white complex (**5**) which separated was filtered off, washed with hexane, and air-dried. The related compound $[\mathrm{RhCl}(\eta^3\text{-}\mathrm{C_3H_5})_2(\mathrm{Hbtz})]$ (**6**) was prepared in the same way as (**5**) but using acetone as solvent instead of dichloromethane.

$[\mathrm{Rh_2}(\mu\text{-pz})(\mu\text{-Cl})(\eta^3\text{-}\mathrm{C_3H_5})_4]$ (**7**). To a suspension of $[\mathrm{Rh_2}(\mu\text{-Cl})_2(\eta^3\text{-}\mathrm{C_3H_5})_4]$ (200 mg, 0.453 mmol) in methanol (75 cm^3) were added Hpz (61.76 mg, 0.907 mmol) and $\mathrm{NEt_3}$ (126.2 µl, 0.907 mmol). The starting material dissolved when the addition was complete. After stirring for 30 min, the solution was evaporated under vacuum to *ca.* 10 cm^3, and methanol–water (1:2) (10 cm^3) was added. The solid which separated was filtered off, washed with methanol–water (1:2), and air-dried.

$[\mathrm{Rh_2}(\mu\text{-pz})(\mu\text{-OH})(\eta^3\text{-}\mathrm{C_3H_5})_4]$ (**8**). To a suspension of $[\mathrm{Rh_2}(\mu\text{-pz})(\mu\text{-Cl})(\eta^3\text{-}\mathrm{C_3H_5})_4]$ (**7**) (50 mg, 0.106 mmol) in water (25 cm^3) was added 0.091 mol dm^{-3} KOH (1.16 cm^3, 0.106 mmol). After stirring for 18 h, the solid which separated was filtered off, washed with water, and air-dried.

$[\mathrm{Rh_2}(\mu\text{-pz})(\mu\text{-N_3})(\eta^3\text{-}\mathrm{C_3H_5})_4]$ (**9**). To a solution of complex (**7**) (70 mg, 0.15 mmol) in methanol (20 cm^3) was added $\mathrm{NaN_3}$ (10 mg, 0.154 mmol). After stirring for 1 h, the resulting solution was evaporated under vacuum to *ca.* 5 cm^3, and methanol–water (1:2) (15 cm^3) was added. The solid which separated was filtered off, washed with methanol–water (1:2), and air-dried.

$[\mathrm{Rh_3}(\mu_3\text{-az})(\mu\text{-Cl})\mathrm{Cl}(\eta^3\text{-}\mathrm{C_3H_5})_2(\mathrm{CO})_4]$ [az = tz (**10**) *or* ttz (**11**)]. To a solution of $[\mathrm{Rh_3}(\mu\text{-az})_3(\eta^3\text{-}\mathrm{C_3H_5})_6]$ (az = tz or ttz) (0.0343 mmol) in acetone (20 cm^3) was added $[\mathrm{Rh_2}(\mu\text{-Cl})_2(\mathrm{CO})_4]$ (0.103 mmol). After stirring for 15 min, the solution was evaporated under vacuum to *ca.* 1 cm^3, and diethyl ether (15 cm^3) was added. The solids which separated were filtered off, washed with diethyl ether, and air-dried.

$[\mathrm{Rh_3}(\mu_3\text{-tz})(\mu\text{-Cl})\mathrm{Cl}(\eta^3\text{-}\mathrm{C_3H_5})_6]$ (**12**). To a suspension of $[\mathrm{Rh_3}(\mu\text{-tz})_3(\eta^3\text{-}\mathrm{C_3H_5})_6]$ (60 mg, 0.079 mmol) in acetone (20 cm^3) was added $[\mathrm{Rh_2}(\mu\text{-Cl})_2(\eta^3\text{-}\mathrm{C_3H_5})_4]$ (104.5 mg, 0.237 mmol). After stirring for 30 min, the starting material dissolved. The resulting solution was evaporated under vacuum to *ca.* 2 cm^3 and hexane (20 cm^3) was added. The solid which separated was filtered off, washed with hexane, and air-dried.

$[\mathrm{Rh_2}(\mu\text{-bim})(\eta^3\text{-}\mathrm{C_3H_5})_4]$ (**13**). A suspension of $[\mathrm{Rh_2}(\mu\text{-Cl})_2(\eta^3\text{-}\mathrm{C_3H_5})_4]$ (60 mg, 0.136 mmol) and $\mathrm{Tl_2(bim)}$ (73.6 mg, 0.136 mmol) in acetone (30 cm^3) was stirred for 30 min, then filtered through Kieselguhr to remove TlCl. Evaporation of the filtrate to *ca.* 2 cm^3 and addition of hexane (20 cm^3) gave a pale yellow solid which was isolated by filtration.

$[\mathrm{RhAu_2}(\mu_3\text{-bim})(\eta^3\text{-}\mathrm{C_3H_5})_2(\mathrm{PPh_3})_2]\mathrm{ClO_4}$ (**14**). The compound $[\mathrm{Au_2}(\mu\text{-bim})(\mathrm{PPh_3})_2]$ prepared by treating $[\mathrm{AuCl(PPh_3)}]$ (91.46 mg, 0.185 mmol) with $\mathrm{Tl_2(bim)}$ (50 mg, 0.092 mmol) was added to an acetone solution (15 cm^3) of $[\mathrm{Rh}(\eta^3\text{-}\mathrm{C_3H_5})_2(\mathrm{Me_2CO})_x]\mathrm{ClO_4}$ (1:1 mol ratio) and stirred for 4 h. The solution was vacuum evaporated to dryness, the residue extracted with dichloromethane (10 cm^3) and filtered. Concentration of the filtrate to *ca.* 1 cm^3 and addition of diethyl ether (8 cm^3) led to the precipitation of a microcrystalline solid, which was filtered off, washed with diethyl ether, and vacuum-dried.

Crystal Structure Determinations of $[\mathrm{Rh_3}(\mu\text{-tz})_3(\eta^3\text{-}\mathrm{C_3H_5})_6]$ (**2**) *and* $[\mathrm{Rh_3}(\mu_3\text{-tz})(\mu\text{-Cl})\mathrm{Cl}(\eta^3\text{-}\mathrm{C_3H_5})_2(\mathrm{CO})_4]\cdot 0.5\mathrm{C_2H_4Cl_2}$ (**10**).—*Crystal data.* $\mathrm{C_{24}H_{36}N_9Rh_3}$, (**2**), orthorhombic, $M = 759.33$, space group $P2_12_12_1$, $a = 20.504\,5(12)$, $b = 14.149\,0(4)$, $c = 9.756\,5(2)$ Å, $U = 2\,830.5(2)$ Å^3 (by least-squares refinement of the 2θ values of 79 reflections in the range θ 2—45°, λ = 1.5418 Å), $D_c = 1.782$ g cm^{-3}, $Z = 4$ $F(000) = 1\,442$, $\mu = 145.62$ cm^{-1} (max. and min. transmission factors for the absorption correction in the range 0.274—0.502). Crystal samples obtained by vapour diffusion from dichloromethane–diethyl ether. A pale yellow transparent plate of dimensions 0.06 × 0.10 × 0.22 mm was used in the analysis.

$\mathrm{C_{12}H_{12}Cl_2N_3O_4Rh_3}\cdot 0.5\mathrm{C_2H_4Cl_2}$, (**10**), triclinic, $M = 691.35$, space group $P\bar{1}$, $a = 13.523\,6(6)$, $b = 10.641\,0(4)$, $c = 7.426\,0(1)$ Å, $\alpha = 90.038(2)$, $\beta = 87.042(2)$, $\gamma = 100.582(2)°$, $U = 1\,049.02(6)$ Å^3 (by least-squares refinement of 2θ values of 61 reflections in the range θ 2—45°, λ = 1.5418 Å), $D_c = 2.189$ g cm^{-3}, $Z = 2$, $F(000) = 662$, $\mu = 231.78$ cm^{-1} (due to the irregular shape of the sample no absorption correction was applied, dimensions were in the range 0.07—0.27 mm). Samples obtained by vapour diffusion from dichloroethane–diethyl ether were yellow-orange.

Data collection and processing. Philips PW1100 diffractometer, ω–2θ mode, scan width 1.5°, graphite monochromated Cu-K_α radiation. 2 766 and 3 116 reflections measured (θ up to 65 and 60°), of which 2 325 and 2 792 were observed [$I > 3\sigma(I)$]. Stability checked every 90 min using two standard reflections. Lorentz and polarization corrections were applied.

Structure analysis and refinement. Patterson, Fourier, and weighted full-matrix least-squares methods. Anisotropic model for the non-hydrogen atoms. Isotropic hydrogen atoms for difference synthesis. Weights were chosen as $w = K/[f(F_o)\cdot g(\sin\theta/\lambda)]$, first fitting ΔF *versus* F_o to obtain $f(F_o)$ and then

Table 4. Final atomic co-ordinates for complex (**2**)

Atom	*X/a*	*Y/b*	*Z/c*
Rh(1)	0.331 21(5)	0.079 32(9)	0.222 80(13)
Rh(2)	0.634 43(6)	0.042 19(9)	0.272 93(14)
Rh(3)	0.489 43(6)	−0.176 09(9)	−0.190 75(12)
N(1)	0.431 4(6)	0.120 6(10)	0.236 2(14)
C(2)	0.480 2(7)	0.064 5(13)	0.269 0(21)
N(3)	0.538 7(8)	0.103 5(10)	0.265 1(16)
C(4)	0.523 1(9)	0.194 0(14)	0.225 8(22)
N(5)	0.459 5(7)	0.205 4(11)	0.206 1(24)
N(11)	0.611 3(7)	−0.011 2(12)	0.076 6(17)
C(12)	0.567 2(9)	−0.081 1(15)	0.047 3(19)
N(13)	0.559 5(7)	−0.087 1(13)	−0.088 7(17)
C(14)	0.599 4(13)	−0.022 6(18)	−0.139 3(26)
N(15)	0.632 9(10)	0.025 1(13)	−0.050 4(16)
N(21)	0.419 3(7)	−0.128 2(11)	−0.039 4(17)
C(22)	0.408 7(8)	−0.040 2(13)	0.007 6(20)
N(23)	0.364 3(7)	−0.037 8(10)	0.106 6(15)
N(24)	0.345 6(8)	−0.132 3(12)	0.127 5(20)
C(25)	0.378 6(9)	−0.181 4(14)	0.036 1(21)
C(31)	0.299 8(11)	0.218 5(16)	0.266 9(31)
C(32)	0.277 8(10)	0.199 9(20)	0.142 8(26)
C(33)	0.318 1(11)	0.177 9(18)	0.045 2(25)
C(34)	0.330 8(10)	−0.012 5(15)	0.402 6(22)
C(35)	0.270 5(9)	0.024 3(18)	0.382 9(22)
C(36)	0.240 4(8)	0.006 9(17)	0.254 3(23)
C(41)	0.594 9(11)	−0.074 7(13)	0.393 9(22)
C(42)	0.647 4(11)	−0.032 6(13)	0.460 6(23)
C(43)	0.642 1(11)	0.065 9(13)	0.487 1(20)
C(44)	0.691 2(10)	0.159 7(13)	0.176 5(22)
C(45)	0.729 0(8)	0.106 0(16)	0.247 3(35)
C(46)	0.734 4(7)	0.006 2(18)	0.227 2(28)
C(51)	0.568 8(12)	−0.243 0(17)	−0.297 7(23)
C(52)	0.535 6(12)	−0.310 4(14)	−0.213 6(22)
C(53)	0.532 1(12)	−0.300 2(14)	−0.078 6(23)
C(54)	0.407 2(14)	−0.226 5(21)	−0.310 0(29)
C(55)	0.442 5(14)	−0.155 9(16)	−0.385 6(24)
C(56)	0.450 3(11)	−0.068 3(15)	−0.325 6(24)

Table 5. Final atomic co-ordinates for complex (**10**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cl(2)	0.206 8(2)	0.028 5(2)	0.569 1(4)
C(14)	0.067 8(7)	0.079 8(9)	0.295 0(13)
O(14)	0.049 6(7)	0.021 8(8)	0.167 7(10)
C(13)	0.013 5(8)	0.278 9(10)	0.441 9(13)
O(13)	−0.041 0(7)	0.338 5(9)	0.415 5(12)
Rh(1)	0.103 67(4)	0.175 00(5)	0.494 90(8)
N(1)	0.199 7(5)	0.450 6(6)	0.892 0(8)
N(2)	0.217 7(5)	0.343 1(6)	0.977 7(9)
C(3)	0.187 7(7)	0.246 6(8)	0.872 7(12)
N(4)	0.150 1(5)	0.284 7(6)	0.720 2(9)
C(5)	0.158 7(6)	0.411 8(8)	0.742 0(11)
Rh(2)	0.287 60(5)	0.349 29(6)	0.222 44(8)
C(12)	0.341 0(7)	0.210 0(9)	0.160 2(14)
O(12)	0.376 9(6)	0.123 6(8)	1.118 9(15)
C(11)	0.355 8(9)	0.363 6(11)	1.431 5(15)
O(11)	0.397 1(8)	0.376 9(10)	1.563 0(13)
Cl(1)	0.220 7(2)	0.532 4(2)	1.301 6(3)
Rh(3)	0.233 67(5)	0.639 68(5)	0.999 63(8)
C(15)	0.075 2(8)	0.661 7(11)	1.047 5(17)
C(16)	0.136 7(9)	0.779 5(10)	1.014 3(17)
C(17)	0.219 3(11)	0.816 7(11)	1.128 1(26)
C(18)	0.396 4(8)	0.627 8(16)	0.951 5(17)
C(19)	0.372 7(7)	0.734 8(10)	0.870 1(15)
C(20)	0.294 5(8)	0.717 6(11)	0.747 8(15)
Cl(3)	0.519 8(6)	0.907 5(8)	0.250 4(11)
C(21)	0.508 8(22)	0.949 1(24)	0.470 7(39)
Cl(4)	0.452 1(8)	0.834 6(11)	0.342 5(15)

$\Delta^2 F/f^2(F_o)$ *versus* $(\sin\theta)/\lambda$ to obtain the g function, K is a scale factor to ensure $< w\Delta^2 F > \sim 1$. For complex (**2**) there was some doubt as to the assignment of either N or C to the atoms numbered as 4 and 5, 14 and 15, 24 and 25 but several attempts to obtain a possible model of disorder, with variation in the assignments and taking into account thermal factors and populations, led to the structure presented as the most probable. Hydrogen atoms were not refined. Final R and R' were 0.056 and 0.067, with a maximum residual electron density of 1.2 e Å^{-3} near Rh(3) and with a maximum thermal parameter of 0.12(2) Å^2 for U_{33} of C(45). For complex (**10**) the $C_2H_4Cl_2$ group is situated at a crystallographic centre of symmetry which relates both halves of the molecule. Moreover the Cl atom is disordered over two possible positions, Cl(3) and Cl(4), with populations of 0.42(2) and 0.58(2), respectively. Hydrogen atoms were refined isotropically. Final R and R' were 0.043 and 0.048, with a maximum residual electron density of 1.0 e Å^{-3} near Rh(1), and a maximum thermal parameter of 0.139(8) Å^2 for U_{33} of O(12).

The scattering factors were taken from ref. 39. Most of the calculations were performed with the *X*-RAY 76 system[40] on a VAX11/750. Final atomic co-ordinates for the non-hydrogen atoms are given in Tables 4 and 5.

Acknowledgements

We thank 'Comisión Asesora de Investigacion Cientifica y Técnica (CAICYT)' for financial support, and Professor S. Garcia-Blanco for facilities.

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Received 8th November 1985; *Paper* 5/1969