1,2,4-Triazolate (tz) Complexes of Rhodium(I), Iridium(I), and Palladium(II). Crystal Structure of $[Rh_3(\mu_3\text{-tz})(\mu\text{-Cl})Cl(\eta^4\text{-tfbb})(CO)_4]\cdot0.5CH_2Cl_2$† (tfbb = tetrafluorobenzobarrelene), a Trinuclear Complex with Extended Metal–Metal Interactions

Luis A. Oro,* M. Teresa Pinillos, and Cristina Tejel
Departamento de Química Inorgánica, Instituto de Ciencias de Materiales de Aragón, Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas, 50009 Zaragoza, Spain
Concha Foces-Foces and Félix H. Cano
Departamento de Rayos-X, Instituto de Química Física Rocasolano, Consejo Superior de Investigaciones Científicas, Serrano 119, 28006 Madrid, Spain

---

New binuclear complexes of formula $[M_2(\mu\text{-tz})_2(L_2)_2]$ [tz = triazolate; M = Rh or Ir, L_2 = diolefin, $(CO)_2$, or $(CO)(PPh_3)$; M = Pd, L_2 = $\eta^3\text{-}C_3H_5$ or $\eta^3\text{-}C_4H_7$] have been prepared. These binuclear complexes, having unco-ordinated N atoms from the triazolate ligands, react with $[M_2(\mu\text{-Cl})_2(L_2)_2]$ (M = Rh, Ir, or Pd) to give tetranuclear compounds of formula $[Rh_2M_2(\mu_3\text{-tz})_2Cl_2(L_2)_4]$. The latter complexes can also be prepared by reacting triazole and $[Rh(acac)(CO)_2]$ with $[M_2(\mu\text{-Cl})_2(L_2)_2]$. The heteronuclear rhodium–gold complex $[Rh_2Au_2(\mu_3\text{-tz})_2Cl_2(cod)_2]$ (cod = cyclo-octa-1,5-diene) has been synthesized. Trinuclear complexes of formula $[Rh_2M(\mu_3\text{-tz})(\mu\text{-X})ClL_2(CO)_4]$ (X = Cl or OH) have been isolated by several routes starting from the above mentioned tetra-, bi-, or mononuclear complexes. In general, these trinuclear complexes show metallic lustre and marked dichroism, suggesting metal–metal interactions which were confirmed by the *X*-ray determination of $[Rh_3(\mu_3\text{-tz})(\mu\text{-Cl})Cl(tfbb)(CO)_4]$ (tfbb = tetrafluorobenzobarrelene). This complex shows a stacking arrangement of centred rhodium units with an intermetallic separation of 3.425(4) Å.

Binuclear rhodium or iridium pyrazolate complexes have attracted considerable interest in recent years.[1–7] In these complexes the individual metal centres, in oxidation state I or II, are generally joined to one another by a pair of bridging *exo*-bidentate pyrazolate (pz) ligands, in such a way that the cyclic bridged framework deviates from planarity, adopting a boat conformation, which results in a wide range of intermetallic separations [Rh–Rh 2.581—3.568, Ir–Ir 2.623—3.290 Å].[1,7,8] As expected, the presence of a third bridging ligand decreases the intermetallic distance. It is noteworthy that although for analogous pyrazolate complexes, Ir–Ir distances are generally shorter than Rh–Rh separations, the shortest intermetallic distances so far reported are found in the binuclear triply-bridged rhodium complexes, $[Rh_2(\mu\text{-pz})_2\{\mu\text{-P}(C_6F_4)Ph_2\}Br(CO)\{P(o\text{-BrC}_6F_4)Ph_2\}]$ [2.581(1) Å][8] and $[Rh_2(\mu\text{-pz})_2I_2(CO)_2(\mu\text{-dppm})]$ [dppm = bis(diphenylphosphino)methane] [2.612(3) Å].[6] Very recently, a related analogue of the latter complex, $[Rh_2(\mu\text{-dmpz})I_2(CO)_2(\mu\text{-dppm})_2]^+$ (dmpz = 3,5-dimethylpyrazolate), that shows a Rh–Rh distance of 2.725(2) Å, has been prepared by *trans*-annular oxidative addition of the A-frame complex $[Rh_2(\mu\text{-dmpz})(CO)_2(\mu\text{-dppm})_2]^+$.[9]

Interestingly, recent studies by Gray and co-workers[10] on pyrazolate-bridged iridium complexes have shown that C_{2v} d^8–d^8 complexes may prove to be versatile photoreagents for the reductive activation of otherwise inert substrates.

On the other hand, the pyrazolate groups,[1b,11] as well as other azolate ligands [*e.g.* imidazolate,[11] 2,2′-bi-imidazolate,[12] 2,2′-bibenzimidazolate,[12] or 2-(2′-pyridyl)benzimidazole[13]], are useful for the construction of heteronuclear Rh–M complexes (M = Pd, Pt, Au, or Ag). Furthermore, some binuclear palladium(II) pyrazolate complexes have been reported.[14]

We recently described the co-ordinative behaviour of benzotriazolate (btz) type ligands, where three nitrogen atoms are potentially available as donor sites, showing the formation of bi- and tetra-nuclear rhodium(I) complexes.[15] Interestingly, the properties of the heterobridged complex $[Rh_2(\mu\text{-btz})(\mu\text{-}N_3)(CO)_4]$ suggest the presence of intermolecular Rh–Rh interactions. Of particular interest is the use of sterically undemanding and/or planar ligands for the design of systems with extended metal–metal interactions.[16]

In this paper we report the preparation of bi-, tri-, and tetranuclear complexes of rhodium and other d^8 metal ions, as well as the *X*-ray structure of $[Rh_3(\mu_3\text{-tz})(\mu\text{-Cl})Cl(\eta^4\text{-tfbb})(CO)_4]\cdot0.5CH_2Cl_2$ (tfbb = tetrafluorobenzobarrelene), an unusual example of molecular stacking in a trinuclear rhodium complex. A preliminary communication on the latter complex has been given.[17]

Results and Discussion

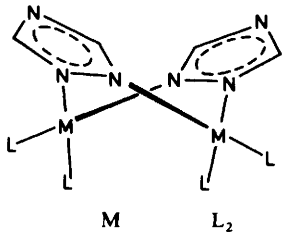
Binuclear Complexes.—The complexes $[M_2(\mu\text{-Cl})_2(cod)_2]$ (M = Rh or Ir, cod = cyclo-octa-1,5-diene) react with stoicheiometric amounts of triazole (Htz) and triethylamine (M = Rh only), or potassium hydroxide (M = Ir only), in methanol solution to give $[M_2(\mu\text{-tz})_2(cod)_2]$ [M = Rh, (**1**), or Ir, (**7**)]. Bubbling of carbon monoxide through a dichloromethane solution of the above mentioned complexes leads to the displacement of cod and to the formation of carbonyl derivatives of formula $[M_2(\mu\text{-tz})_2(CO)_4]$ [M = Rh, (**5**), or Ir, (**8**)], although the low solubility of these complexes prevented confirmation of the molecular weight.

As expected, the addition of triphenylphosphine to suspensions of $[M_2(\mu\text{-tz})_2(CO)_4]$ complexes led to evolution of

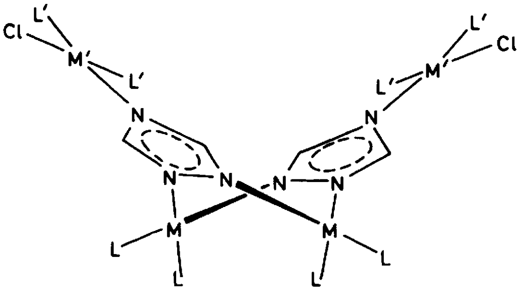
---

† 2,2,3,3-Tetracarbonyl-1,2-μ-chloro-3-chloro-1-(2—3-η,7—8-η′-tetrafluorobenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene)-[μ₃-triazolato-N^1(Rh¹),N^2(Rh²),N^4(Rh³)]-trirhodium–dichloromethane (1/0.5).

Supplementary data available (No. SUP 56480, 4 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.



	M	L_2
(1)	Rh	cod
(2)	Rh	nbd
(3)	Rh	tfbb
(4)	Rh	tmtfbb
(5)	Rh	$(CO)_2$
(6)	Rh	$(CO)(PPh_3)$
(7)	Ir	cod
(8)	Ir	$(CO)_2$
(9)	Ir	$(CO)(PPh_3)$
(10)	Pd	η^3-C_3H_5
(11)	Pd	η^3-C_4H_7



	M	L_2	M′	L'_2
(12)	Rh	cod	Rh	cod
(13)	Rh	cod	Rh	$(CO)_2$
(14)	Rh	$(CO)_2$	Rh	$(CO)_2$
(15)	Rh	cod	Ir	cod
(16)	Pd	η^3-C_3H_5	Rh	$(CO)_2$
(17)	Pd	η^3-C_4H_7	Rh	$(CO)_2$

carbon monoxide and formation of derivatives of the type *trans*-$[M_2(\mu\text{-tz})_2(CO)_2(PPh_3)_2]$ [M = Rh, **(6)** or Ir, **(9)**]. This route has been previously used by our group[1a] and Stobart and co-workers[7] for the synthesis of the related pyrazolate complexes of formula *trans*-$[M_2(\mu\text{-pz})_2(CO)_2(PPh_3)_2]$. Only one ν(CO) band is observed in solution for complexes **(6)** and **(9)** in agreement with the *trans* structure revealed by *X*-ray determinations on related pyrazolate complexes.[1a,3a]

Complexes **(5)** and **(1)**, as well as the diolefin compounds $[Rh_2(\mu\text{-tz})_2(\text{diolefin})_2]$ [diolefin = norborna-2,5-diene (nbd), **(2)**, tfbb, **(3)**, or tmtfbb, **(4)**],* can also be obtained by reaction of $[Rh(acac)L_2]$ [acac = acetylacetonate, $L_2 = (CO)_2$ or diolefin] with equimolar amounts of triazole, or alternatively by treatment of $[Rh_2(\mu\text{-Cl})_2(L_2)_2]$ complexes (L = CO or L_2 = diolefin) with triazole and potassium hydroxide. The latter method has also been used for the synthesis of $[Pd_2(\mu\text{-tz})_2(L_2)_2]$ [$L_2 = \eta^3$-C_3H_5 (allyl), **(10)**, or η^3-C_4H_7 (2-methylallyl), **(11)**], starting from the chloro-bridged complexes $[Pd_2(\mu\text{-Cl})_2(L_2)_2]$ or, alternatively, from $[Pd(acac)L_2]$.

The above mentioned complexes were isolated as stable microcrystalline solids, and show i.r. vibrations characteristic of the co-ordinated triazolate groups and ancillary ligands. Molecular weight measurements on the soluble complexes show that they are dimeric in chloroform (Table 1).

Tetranuclear Complexes.—The binuclear complexes **(1)**—**(11)** still have two unco-ordinated nitrogen atoms, one from each triazolate group, and therefore could act as donor centres for the construction of homo- and hetero-tetranuclear complexes. In fact, the cleavage of chloro-bridged binuclear rhodium(I) or iridium(I) complexes by nitrogen-donor ligands to form square-planar derivatives is a general reaction.[18] Thus, complex **(1)** reacts with $[M_2(\mu\text{-Cl})_2(cod)_2]$ (M = Rh or Ir) or $[Rh_2(\mu\text{-Cl})_2(CO)_4]$ to give $[Rh_2M_2(\mu_3\text{-tz})_2Cl_2(cod)_4]$ [M = Rh, **(12)**, or Ir, **(15)**] or $[Rh_4(\mu_3\text{-tz})_2Cl_2(cod)_2(CO)_4]$ **(13)**. The latter complex and the related compound $[Rh_4(\mu_3\text{-tz})_2Cl_2(CO)_8]$ **(14)** can be prepared by reaction of complex **(5)** with the binuclear compounds $[Rh_2(\mu\text{-Cl})_2(L_2)_2]$ (L_2 = cod or L = CO) (Scheme). As expected, complexes **(13)** and **(14)** were also formed by adding triazole and $[Rh(acac)(CO)_2]$ to acetone solutions of $[Rh_2(\mu\text{-Cl})_2(L_2)_2]$ compounds.

Bubbling of carbon monoxide through a methanol suspension of **(12)** causes the displacement of all cyclo-octadiene groups and the formation of **(14)**. However, when the carbonylation reaction of **(12)** was performed in dichloromethane solution, although the presence of i.r. bands at 2 109, 2 097, 2 087, 2 047, and 2 013 cm^{-1} is consistent with the presence of **(14)**, attempts to precipitate these species from the solutions which contain the displaced cyclo-octadiene, by addition of hexane, yield complex **(13)**.

Interestingly, rhodium–palladium complexes of formula $[Rh_2Pd_2(\mu_3\text{-tz})_2Cl_2(L_2)_2(CO)_4]$ [$L_2 = \eta^3$-C_3H_5, **(16)**, or η^3-C_4H_7, **(17)**] can be prepared by reacting $[Pd_2(\mu\text{-tz})_2(L_2)_2]$ complexes with $[Rh_2(\mu\text{-Cl})_2(CO)_4]$ (Scheme) or, alternatively, $[Rh_2(\mu\text{-tz})_2(CO)_4]$ with $[Pd_2(\mu\text{-Cl})_2(L_2)_2]$. Complexes **(16)** and **(17)** were also formed in high yields by reacting $[Pd_2(\mu\text{-Cl})_2(L_2)_2]$ with triazole and $[Rh(acac)(CO)_2]$. The heteronuclear complex $[Rh_2Au_2(\mu_3\text{-tz})_2Cl_2(cod)_2]$ **(18)** has been prepared by displacement of the co-ordinated tetrahydrothiophene (tht) from [AuCl(tht)] by the unco-ordinated nitrogen atom of the bridging triazolate groups in compound **(1)**. Molecular weight measurements on these complexes, determined osmometrically in chloroform, seem to confirm the proposed tetranuclear formulation, although some deviation is observed especially for complex **(18)**.

Most probably the triazolate ligands bridge two rhodium or palladium atoms through the two adjacent nitrogen atoms and are bound to rhodium, iridium, or gold atoms through the third nitrogen with formation of $RhCl(L_2)$(N-donor) (L_2 = cod, L = CO), IrCl(cod)(N-donor) or AuCl(N-donor) units. This proposal has recently been confirmed in a preliminary communication[19] by *X*-ray studies on complex **(16)**, prepared by treating $[Pd_2(\mu\text{-Cl})_2(\eta^3\text{-}C_3H_5)_2]$ with triazole and $[Rh(acac)(CO)_2]$.

Finally, a cationic tetranuclear complex of formula $[Rh_4(\mu_3\text{-tz})_2(cod)_4(PPh_3)_2][ClO_4]_2$ **(19)** can be obtained by reacting **(1)** with $[Rh(cod)(Me_2CO)_x][ClO_4]$ and triphenylphosphine, suggesting the formation of $Rh(cod)(PPh_3)$(N-donor) units. This cationic complex can also be prepared by treating **(12)** with $Ag[ClO_4]$ and triphenylphosphine.

Trinuclear Complexes.—While the above mentioned tetranuclear $[Rh_2M_2(\mu_3\text{-tz})_2Cl_2(L_2)_2(CO)_4]$ complexes are obtained by reaction of stoicheiometric amounts of $[M_2(\mu\text{-tz})_2(L_2)_2]$ and $[Rh_2(\mu\text{-Cl})_2(CO)_4]$, an interesting family of trinuclear compounds can be prepared if two moles of $[Rh_2(\mu\text{-Cl})_2(CO)_4]$ are reacted with one mole of $[M_2(\mu\text{-tz})_2(L_2)_2]$. In particular, $[Rh_3(\mu_3\text{-tz})(\mu\text{-Cl})Cl(\text{diolefin})(CO)_4]$ complexes [diolefin = cod, **(20)**, nbd, **(21)**, or tfbb, **(22)**] and the related

---

* tfbb = tetrafluorobenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene, tmtfbb = trimethyltetrafluorobenzobarrelene = 1,3,8-trimethyl(tetrafluorobenzo[5,6])bicyclo[2.2.2]octa-2,5,7-triene.

Table 1. Analytical[a] and physical data for the compounds

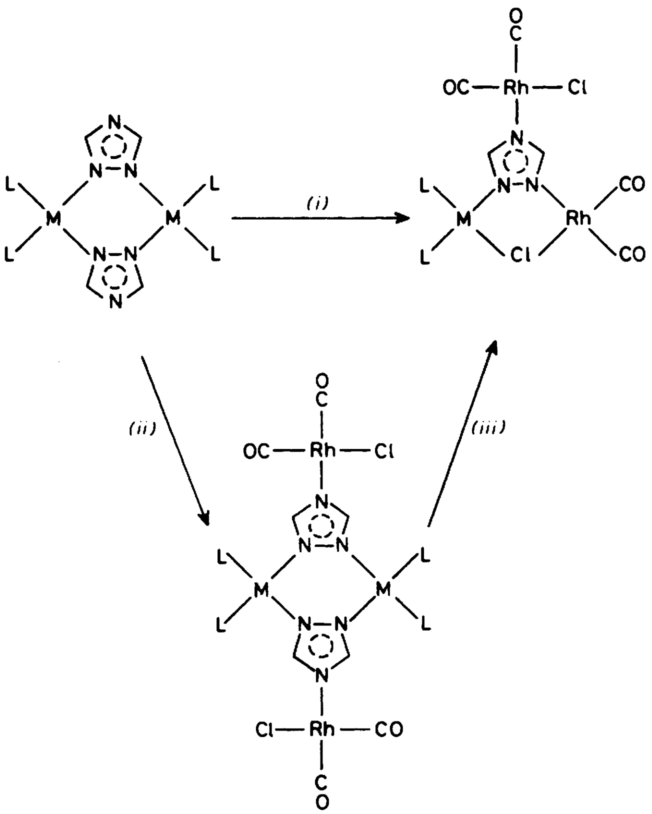
	Compound	Yield	Colour	Analysis (%)			M[a,b]	ν(CO)[c]/cm^{-1}
				C	H	N		
(1)	$[Rh_2(\mu\text{-}tz)_2(cod)_2]$	96	Yellow	42.5 (43.0)	4.8 (5.0)	14.6 (15.0)	568 (555)	
(2)	$[Rh_2(\mu\text{-}tz)_2(nbd)_2]$	89	Yellow	41.1 (41.1)	3.6 (3.8)	16.4 (15.9)	549 (526)	
(3)	$[Rh_2(\mu\text{-}tz)_2(tfbb)_2]$	84	Yellow	42.2 (42.3)	2.1 (2.0)	10.3 (11.6)	789 (793)	
(4)	$[Rh_2(\mu\text{-}tz)_2(tmtfbb)_2]$	82	Yellow	45.8 (46.4)	3.4 (3.2)	9.5 (9.6)		
(5)	$[Rh_2(\mu\text{-}tz)_2(CO)_4]$	92	Orange	21.7 (21.2)	1.1 (0.9)	18.2 (18.5)		2 090, 2 080, 2 025
(6)	$[Rh_2(\mu\text{-}tz)_2(CO)_2(PPh_3)_2]$	85	Yellow	54.0 (54.7)	4.6 (3.7)	8.8 (9.1)	1 010 (922)	1 985
(7)	$[Ir_2(\mu\text{-}tz)_2(cod)_2]$	60	Red	32.2 (32.6)	4.2 (3.8)	11.3 (11.4)	762 (737)	
(8)	$[Ir_2(\mu\text{-}tz)_2(CO)_4]$	60	Dark blue	13.75 (13.30)	16.15 (15.20)	0.70 (0.65)		2 080, 2 070, 2 010
(9)	$[Ir_2(\mu\text{-}tz)_2(CO)_2(PPh_3)_2]$	45	Orange	46.1 (45.8)	3.8 (3.1)	6.9 (7.6)		1 970
(10)	$[Pd_2(\mu\text{-}tz)_2(\eta^3\text{-}C_3H_5)_2]$	47	White	26.9 (27.8)	3.3 (3.3)	19.4 (19.5)	440 (431)	
(11)	$[Pd_2(\mu\text{-}tz)_2(\eta^3\text{-}C_4H_7)_2]$	50	White	30.7 (31.4)	3.8 (3.9)	18.0 (18.3)	449 (459)	
(12)	$[Rh_4(\mu_3\text{-}tz)_2Cl_2(cod)_4]$	86	Yellow	41.4 (41.2)	5.1 (4.6)	7.9 (8.0)	1 050 (1 051)	
(13)	$[Rh_4(\mu_3\text{-}tz)_2Cl_2(cod)_2(CO)_4]$	77	Yellow-orange	30.6 (30.4)	3.2 (3.0)	8.6 (8.9)		2 090, 2 018
(14)	$[Rh_4(\mu_3\text{-}tz)_2Cl_2(CO)_8]$	78	Orange	17.0 (17.1)	0.5 (0.4)	10.0 (10.0)	886 (843)	2 109, 2 097, 2 087, 2 047, 2 013
(15)	$[Rh_2Ir_2(\mu_3\text{-}tz)_2Cl_2(cod)_4]$	50	Orange	36.1 (36.1)	5.1 (4.3)	7.1 (6.8)		
(16)	$[Rh_2Pd_2(\mu_3\text{-}tz)_2Cl_2(\eta^3\text{-}C_3H_5)_2(CO)_4]$	84	Yellow-orange	20.3 (20.5)	1.7 (1.7)	10.5 (10.3)	753 (816)	2 082, 2 008
(17)	$[Rh_2Pd_2(\mu_3\text{-}tz)_2Cl_2(\eta^3\text{-}C_4H_7)_2(CO)_4]$	89	Yellow-orange	22.0 (22.6)	2.2 (2.1)	10.2 (9.9)	924 (848)	2 090, 2 020
(18)	$[Rh_2Au_2(\mu_3\text{-}tz)_2Cl_2(cod)_2]$	60	Yellow	24.1 (23.5)	2.8 (2.7)	8.0 (8.2)	880 (1 023)	
(19)	$[Rh_4(\mu_3\text{-}tz)_2(cod)_4(PPh_3)_2][ClO_4]_2$[d]	75	Yellow	50.1 (50.7)	5.1 (4.8)	4.5 (4.9)		
(20)	$[Rh_3(\mu_3\text{-}tz)(\mu\text{-}Cl)Cl(cod)(CO)_4]$	68	Red	24.9 (25.2)	1.9 (2.1)	6.5 (6.3)	713 (668)	2 090, 2 080, 2 025, 2 010
(21)	$[Rh_3(\mu_3\text{-}tz)(\mu\text{-}Cl)Cl(nbd)(CO)_4]$	76	Dark blue	24.2 (23.9)	1.4 (1.5)	6.2 (6.4)	700 (652)	2 095, 2 087, 2 025, 2 012
(22)	$[Rh_3(\mu_3\text{-}tz)(\mu\text{-}Cl)Cl(tfbb)(CO)_4]$	80	Red	28.5 (27.5)	1.4 (1.0)	5.1 (5.3)	807 (786)	2 105, 2 095, 2 040, 2 025
(23)	$[Rh_3(\mu_3\text{-}tz)(\mu\text{-}Cl)Cl(CO)_6]$	78	Green	15.6 (15.6)	0.6 (0.3)	7.2 (6.8)		
(24)	$[Rh_3(\mu_3\text{-}tz)(\mu\text{-}OH)Cl(CO)_6]$[e]	60	Purple	15.8 (16.1)	0.4 (0.5)	6.9 (7.0)		
(25)	$[Rh_2Ir(\mu_3\text{-}tz)(\mu\text{-}Cl)Cl(cod)(CO)_4]$	60	Violet	21.3 (22.2)	1.8 (1.9)	5.7 (5.5)		2 075, 2 065, 2 000, 1 986
(26)	$[Rh_2Pd(\mu_3\text{-}tz)(\mu\text{-}OH)Cl(\eta^3\text{-}C_3H_5)(CO)_4]$[e]	74	Dark blue	17.8 (18.4)	1.8 (1.2)	7.2 (7.2)	624 (586)	2 100, 2 090, 2 030, 2 015
(27)	$[Rh_2Pd(\mu_3\text{-}tz)(\mu\text{-}OH)Cl(\eta^3\text{-}C_4H_7)(CO)_4]$[e]	50	Dark blue	19.3 (20.0)	1.5 (1.7)	6.9 (7.0)	623 (600)	2 090, 2 085, 2 025, 2 010
(28)	$[Rh_3(\mu_3\text{-}tz)(\mu\text{-}N_3)(N_3)(nbd)(CO)_4]$	84	Red	23.0 (23.5)	1.3 (1.5)	19.3 (19.0)		2 095, 2 080, 2 060, 2 020, 2 010
(29)	$[Rh_3(\mu_3\text{-}tz)(\mu\text{-}N_3)(N_3)(tfbb)(CO)_4]$	75	Red	27.0 (27.0)	1.1 (1.0)	16.0 (15.8)		2 100, 2 085, 2 070, 2 020, 2 010

[a] Required values are given in parentheses. [b] In chloroform. [c] In dichloromethane. [d] $\Lambda_M = 123\ \Omega^{-1}\ cm^2\ mol^{-1}$ (*ca.* 5×10^{-4} mol dm^{-3} acetone solutions). [e] ν(OH) in Nujol: **(24)**, 3 560; **(26)**, 3 610; **(27)**, 3 610 cm^{-1}.

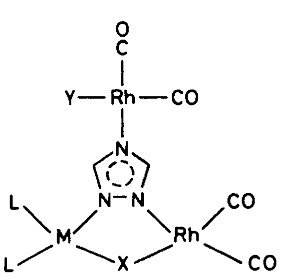
$[Rh_2Ir(\mu_3\text{-}tz)(\mu\text{-}Cl)Cl(cod)(CO)_4]$ **(25)** are obtained (Scheme), but μ-hydroxo derivatives of formula $[Rh_2M(\mu_3\text{-}tz)(\mu\text{-}OH)Cl(L_2)(CO)_4]$ [M = Rh, L = CO, **(24)**; M = Pd, $L_2 = \eta^3\text{-}C_3H_5$, **(26)**, or $\eta^3\text{-}C_4H_7$, **(27)**] are formed most probably from small amounts of water in the solvent.

In fact the reaction of **(5)** with two moles of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ gives $[Rh_3(\mu_3\text{-}tz)(\mu\text{-}Cl)Cl(CO)_6]$ **(23)** in dry acetone, whereas $[Rh_3(\mu_3\text{-}tz)(\mu\text{-}OH)Cl(CO)_6]$ **(24)** is formed in aqueous acetone.

Complexes **(20)**—**(22)** or **(26)**—**(27)** can also be prepared by



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



	M	L_2	X	Y
(20)	Rh	cod	Cl	Cl
(21)	Rh	nbd	Cl	Cl
(22)	Rh	tfbb	Cl	Cl
(23)	Rh	$(CO)_2$	Cl	Cl
(24)	Rh	$(CO)_2$	OH	Cl
(25)	Ir	cod	Cl	Cl
(26)	Pd	$\eta^3\text{-}C_3H_5$	OH	Cl
(27)	Pd	$\eta^3\text{-}C_4H_7$	OH	Cl
(28)	Rh	nbd	N_3	N_3
(29)	Rh	tfbb	N_3	N_3

reacting stoicheiometric amounts of $[M(acac)L_2]$, triazole, and $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$, or alternatively by adding stoicheiometric quantities of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ to the tetranuclear $[Rh_2M_2(\mu_3\text{-}tz)_2Cl_2(L_2)_2(CO)_4]$ complexes. The latter reaction shows that the addition of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ to the tetranuclear triazolate produces important modifications, not observed for the related tetranuclear benzotriazolate analogues.[15]

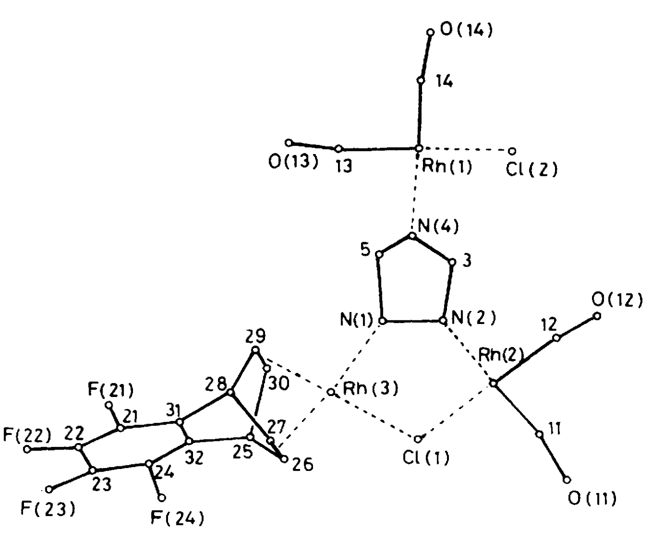


Figure 1. A projection of the structure of **(22)** along the *c* axis, showing the numbering scheme

A possible pathway could be related to the abstraction of a chloride ion from the $RhCl(CO)_2$(N-donor) units[19,20] by the chloro-bridged carbonyl rhodium complex, leading to the formation of $[RhCl_2(CO)_2]^-$ and $[\{L_2M(\mu\text{-}tz)Rh(CO)_2\}_x]^{x+}$ (x = 1 or 2) as intermediates, or more simply to the symmetrical cleavage of the tetranuclear complex with subsequent formation of $[L_2M(\mu\text{-}tz)RhCl(CO)_2]$ intermediates.

On the other hand, related trinuclear azide complexes of formula $[Rh_3(\mu_3\text{-}tz)(\mu\text{-}N_3)(N_3)(diolefin)(CO)_4]$ [diolefin = nbd, **(28)**, or tfbb, **(29)**] can be prepared by reacting complexes **(2)** or **(3)** with $[Rh_2(\mu\text{-}N_3)_2(CO)_4]$.

Molecular weight measurements support the proposed formulation (Table 1). All these trinuclear complexes present a characteristic strong i.r. band at 3 150—3 140 cm^{-1} [ν(C–H)] along with a complex spectrum in the carbonyl region (in the solid state). Furthermore, they present metallic lustre, deep colours, and marked dichroism, suggesting some intermetallic interaction. In general they crystallised as long needles. All these facts suggest some stacking arrangement. After many attempts to obtain suitable crystals, a low-quality crystal of **(22)** has been used for confirming the proposed arrangement.

The structure of the complex, showing the co-ordination around the Rh atoms, is in Figure 1. The main bond lengths and angles are in Table 2. The three metal atoms are in a square planar environment, considering the midpoints of the olefinic bonds [C(67) and C(90)], for Rh(3). The central ring Rh(2)–N(2)–N(1)–Rh(3)–Cl(1) is quite planar, as observed for the related $[Pt_2(\mu\text{-}pz)(\mu\text{-}Cl)Cl_2(C_2H_4)_2]$ complex,[21] and is almost coplanar [4.2(9)°] with the plane of the triazolate group. This ligand presents the usual features observed for bridging azolate ligands.[1a,19]

Within the complex the separation between Rh(2) and Rh(3) is 3.817(3) Å, similar to those found for related complexes containing the $M_2(\mu\text{-}Z)(\mu\text{-}Cl)$ framework {M = Rh, Z = pyrazolate (pz) [3.715(2) Å][22] or tz [3.712(1) Å];[17] M = Pt, Z = pz [3.717(1) Å][21]}. The most interesting feature in the complex is the presence of a stacking arrangement of parallel units, centred on a line of Rh(2) atoms along the *c* axis (see Figure 2). These chains are linear [Rh–Rh–Rh 177.6(3)°] and the metal atoms are separated by 3.425(4) Å. Columnar stacking is still rare for rhodium complexes, and the present case is the first example of such an arrangement in a trinuclear complex. Some mononuclear rhodium complexes also form

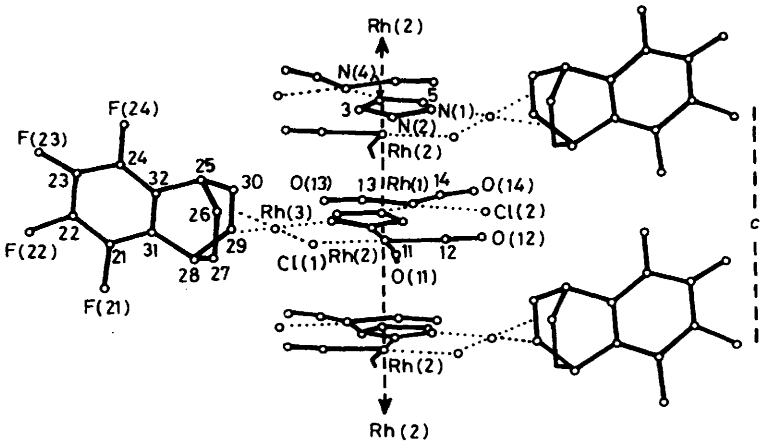


Figure 2. Structure and stacking arrangement in crystal of (22)

Table 2. Selected bond distances (Å) and bond angles (°) for compound (22)*

Rh(1)–Cl(2)	2.355(8)	Rh(2)–Cl(1)	2.347(7)	Rh(3)–C(67)	2.01(2)	Rh(3)–C(90)	2.01(2)
Rh(3)–Cl(1)	2.346(7)	Rh(1)–N(4)	2.05(2)	Rh(2)–Rh(3)	3.817(3)	N(1)–N(2)	1.38(3)
Rh(2)–N(2)	2.08(3)	Rh(3)–N(1)	2.09(2)	N(1)–C(5)	1.27(3)	N(2)–C(3)	1.41(4)
Rh(1)–C(13)	1.76(5)	Rh(2)–C(11)	1.67(4)	N(4)–C(3)	1.37(3)	N(4)–C(5)	1.39(3)
Rh(2)–C(12)	1.88(4)	Rh(1)–C(14)	1.74(5)	O(11)–C(11)	1.31(5)	O(12)–C(12)	1.13(4)
Rh(3)–C(26)	2.13(3)	Rh(3)–C(27)	2.17(3)	O(13)–C(13)	1.24(6)	O(14)–C(14)	1.26(3)
Rh(3)–C(29)	2.10(3)	Rh(3)–C(30)	2.11(3)	C(26)–C(27)	1.54(4)	C(29)–C(30)	1.28(5)

N(4)–Rh(1)–Cl(2)	90.5(6)	N(4)–Rh(1)–C(14)	178.7(6)	Cl(1)–Rh(3)–C(90)	167(1)	C(67)–Rh(3)–C(90)	71(1)
N(4)–Rh(1)–C(13)	95(1)	Cl(2)–Rh(1)–C(13)	175(1)	Rh(2)–Cl(1)–Rh(3)	108.8(3)	C(5)–N(1)–Rh(3)	128(2)
Cl(2)–Rh(1)–C(14)	88(1)	C(13)–Rh(1)–C(14)	87(1)	N(2)–N(1)–Rh(3)	122(2)	C(3)–N(2)–Rh(2)	127(2)
N(2)–Rh(2)–Cl(1)	88.6(7)	N(2)–Rh(2)–C(11)	177(1)	N(1)–N(2)–Rh(2)	129(2)	C(3)–N(4)–Rh(1)	124(2)
N(2)–Rh(2)–C(12)	93(1)	Cl(1)–Rh(2)–C(11)	94(1)	C(5)–N(4)–Rh(1)	133(2)	Rh(1)–C(13)–O(13)	171(4)
Cl(1)–Rh(2)–C(12)	178(1)	C(11)-Rh(2)–C(12)	84(1)	Rh(1)–C(14)–O(14)	174(5)	Rh(2)–C(11)–O(11)	165(2)
N(1)–Rh(3)–Cl(1)	91.0(7)	N(1)–Rh(3)–C(67)	169(1)	Rh(2)–C(12)–O(12)	178(3)		
N(1)–Rh(3)–C(90)	98(1)	Cl(1)–Rh(3)–C(67)	99(6)				

* C(67) and C(90) are the midpoints of the diolefinic bonds.

Table 3. Final atomic co-ordinates for compound (22)

Atom	*X/a*	*Y/b*	*Z/c*
Cl(2)	0.351 4(6)	0.135 6(3)	0.482 7(16)
C(14)	0.540 4(34)	0.179 9(27)	0.477 7(50)
O(14)	0.613 1(19)	0.151 8(16)	0.476 8(57)
C(13)	0.501 9(25)	0.267 0(19)	0.475 8(62)
O(13)	0.545 3(22)	0.307 6(13)	0.497 7(46)
Rh(1)	0.431 9(2)	0.212 6(1)	0.476 7(4)
N(1)	0.187 9(19)	0.307 1(8)	0.473 8(37)
N(2)	0.141 4(19)	0.262 2(9)	0.489 1(37)
C(3)	0.215 6(18)	0.226 6(10)	0.482 9(43)
N(4)	0.303 0(13)	0.249 6(8)	0.476 6(33)
C(5)	0.278 0(15)	0.299 6(9)	0.473 1(41)
Rh(2)	−0.003 8(1)	0.248 4(1)	0.514 8(4)
C(12)	0.012 2(17)	0.179 0(15)	0.511 7(56)
O(12)	0.022 2(16)	0.137 4(8)	0.505 1(41)
C(11)	−0.118 2(32)	0.234 5(11)	0.543 9(41)
O(11)	−0.212 0(17)	0.235 7(8)	0.552 1(38)
Cl(1)	−0.029 1(5)	0.334 8(3)	0.520 2(13)
Rh(3)	0.117 9(2)	0.375 3(1)	0.492 9(4)
C(21)	0.244 2(27)	0.556 3(14)	0.603 3(93)
F(21)	0.279 3(17)	0.560 9(8)	0.794 6(45)
C(22)	0.237 8(24)	0.597 4(10)	0.456 9(99)
F(22)	0.278 0(16)	0.641 8(7)	0.543 6(49)
C(23)	0.197 5(23)	0.595 5(15)	0.257 7(84)
F(23)	0.199 5(17)	0.636 0(7)	0.162 4(44)
C(24)	0.160 2(28)	0.549 6(14)	0.208 6(91)
F(24)	0.125 4(18)	0.547 9(9)	0.016 1(50)
C(25)	0.124 4(17)	0.458 9(10)	0.267 8(37)
C(26)	0.055 4(22)	0.444 5(9)	0.388 9(49)
C(27)	0.090 2(17)	0.447 8(9)	0.612 5(42)
C(28)	0.195 6(21)	0.465 4(11)	0.644 9(51)
C(29)	0.242 1(19)	0.420 9(10)	0.521 3(55)
C(30)	0.205 6(19)	0.420 5(9)	0.338 9(53)
C(31)	0.204 0(22)	0.512 4(10)	0.525 3(68)
C(32)	0.161 0(23)	0.509 8(9)	0.340 2(64)
Cl(3)	0.411(6)	0.507(3)	0.168(11)
Cl(4)	0.504(7)	0.480(3)	0.573(11)
C(40)	0.495(15)	0.469(9)	0.316(32)

linear stacks, *e.g.* [$RhCl(CO)_2(Hpz)$] [Rh–Rh 3.452 2(4) Å][23] and [$Rh(acac)(CO)_2$] [Rh–Rh 3.27(6) Å].[24] Interestingly, the latter complex, as well as the analogous iridium derivative, exhibit semiconductor properties.[25,26]

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 NaCl windows. Conductivities were measured in acetone solutions using a Philips 9501/01 conductimeter. Molecular weights were determined with a Perkin-Elmer 115 osmometer using chloroform solutions.

Syntheses.—The reactions were carried out at room temperature. Prior to use, solvents were purified by standard methods. The compounds $[Rh_2(\mu\text{-}Cl)_2(diolefin)_2]$ (diolefin = cod,[27] nbd,[28] tfbb,[29] or tmtfbb[29]), $[Ir_2(\mu\text{-}Cl)_2(cod)_2]$,[30] $[Pd_2(\mu\text{-}Cl)_2(L_2)_2]$ ($L_2 = \eta^3\text{-}C_3H_5$ or $\eta^3\text{-}C_4H_7$),[31] $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$,[32] $[Rh_2(\mu\text{-}N_3)_2(CO)_4]$,[33] and $[AuCl(tht)]$[34] were prepared according to literature methods.

$[Rh_2(\mu\text{-}tz)_2(diolefin)_2]$ (**1**)—(**4**). *Method A*. To a suspension of $[Rh_2(\mu\text{-}Cl)_2(diolefin)_2]$ (diolefin = cod, nbd, tfbb, or tmtfbb) (0.1 mmol) in methanol (20 cm^3) a solution of triazole (14 mg, 0.2 mmol) and KOH–MeOH (0.091 mol dm^{-3}, 2.20 cm^3, 0.2 mmol) in methanol (5 cm^3) was added dropwise. The starting material dissolved during the addition and when the reaction was complete, the yellow products $[Rh_2(\mu\text{-}tz)_2(diolefin)_2]$ precipitated spontaneously from the solution. The resulting suspension was stirred for 30 min. The solvent was pumped off, the residue extracted with dichloromethane (20 cm^3), and then filtered. Concentration of the filtrate to *ca*. 1 cm^3 and addition of hexane (15 cm^3) gave complexes (**1**)—(**4**). They were recovered by filtration, washed with hexane and air-dried.

Method B. To a suspension of $[Rh_2(\mu\text{-}Cl)_2(diolefin)_2]$ (0.1 mmol) in methanol (15 cm^3), a solution of triazole (14 mg, 0.2 mmol) and triethylamine (30 μl, 0.2 mmol) in methanol (5 cm^3) was added dropwise. The yellow complexes $[Rh_2(\mu\text{-}tz)_2(diolefin)_2]$ precipitated spontaneously. The resulting suspension was stirred for 30 min. They were filtered off, washed with methanol–water (2:1, 3 cm^3) and air-dried.

Method C. To a solution of $[Rh(acac)(diolefin)]$ (0.1 mmol) in acetone (15 cm^3), triazole (7 mg, 0.1 mmol) was added. The yellow complexes precipitated spontaneously and were isolated after partial evaporation to *ca*. 3 cm^3, and addition of hexane (10 cm^3). They were filtered off, washed with hexane and air-dried.

$[Rh_2(\mu\text{-}tz)_2(CO)_4]$ (**5**). Carbon monoxide was bubbled through a solution of $[Rh_2(\mu\text{-}tz)_2(cod)_2]$ (**1**) (50 mg, 0.09 mmol) in dichloromethane (20 cm^3) for 15 min. $[Rh_2(\mu\text{-}tz)_2(CO)_4]$ separated immediately almost quantitatively. The suspension was filtered off, washed with hexane and air-dried. This compound can be alternatively prepared starting from $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ or $[Rh(acac)(CO)_2]$, using the synthetic routes described above for complexes (**1**)—(**4**).

trans-$[Rh_2(\mu\text{-}tz)_2(CO)_2(PPh_3)_2]$ (**6**). To a suspension of $[Rh_2(\mu\text{-}tz)_2(CO)_4]$ (**5**) (30 mg, 0.132 mmol) in dichloromethane (20 cm^3), triphenylphosphine (34.6 mg, 0.132 mmol) was added. The resulting yellow solution was stirred for 30 min. Addition of hexane (15 cm^3) to the concentrated solution (1 cm^3) gave a yellow solid, which was filtered off, washed with hexane and air-dried.

$[Ir_2(\mu\text{-}tz)_2(cod)_2]$ (**7**). To a suspension of $[Ir_2(\mu\text{-}Cl)_2(cod)_2]$ (50 mg, 0.074 mmol) in methanol (25 cm^3), kept under an argon atmosphere, a solution of triazole (10.4 mg, 0.15 mmol) and KOH–MeOH (0.091 mol dm^{-3}, 1.65 cm^3, 0.15 mmol) in methanol (6 cm^3) was added dropwise. The starting red suspension changes to dark red at the end of the addition and $[Ir_2(\mu\text{-}tz)_2(cod)_2]$ precipitated spontaneously. The resulting suspension was stirred for 2 h. It was filtered off, washed with cold methanol and vacuum-dried.

$[Ir_2(\mu\text{-}tz)_2(CO)_4]$ (**8**). This complex was prepared as reported for the rhodium analogue (**5**) starting from (**7**).

trans-$[Ir_2(\mu\text{-}tz)_2(CO)_2(PPh_3)_2]$ (**9**). Addition of triphenylphosphine (38.6 mg, 0.147 mmol) to a suspension of $[Ir_2(\mu\text{-}tz)_2(CO)_4]$ (**8**) (43 mg, 0.068 mmol) in dichloromethane (15 cm^3) caused evolution of carbon monoxide. The resulting solution was evaporated to *ca*. 2 cm^3 and hexane (10 cm^3) was added to give a yellow solid which was filtered off, washed with hexane and vacuum-dried.

$[Pd_2(\mu\text{-}tz)_2(L_2)]$ (**10**) and (**11**). To a suspension in methanol (20 cm^3) of $[Pd_2(\mu\text{-}Cl)_2(L_2)_2]$ ($L_2 = \eta^3\text{-}C_3H_5$ or $\eta^3\text{-}C_4H_7$) (0.136 mmol) a solution of triazole (18.8 mg, 0.273 mmol) and KOH–MeOH (0.091 mol dm^{-3}, 3 cm^3, 0.273 mmol) in methanol (7 cm^3) was added dropwise. The starting material dissolved and the resulting solution was stirred for 2 h and vacuum-evaporated until dryness. The residue was extracted with dichloromethane (20 cm^3) and then filtered through $MgSO_4$. Concentration of the filtrate to *ca*. 1 cm^3 and addition of hexane (15 cm^3) gave the complexes as white solids which were filtered off, washed with hexane and air-dried.

$[Rh_4(\mu_3\text{-}tz)_2Cl_2(cod)_4]$ (**12**). To a suspension of $[Rh_2(\mu\text{-}tz)_2(cod)_2]$ (**1**) (33.5 mg, 0.06 mmol) in acetone (20 cm^3), $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ was added. The starting material dissolved and $[Rh_4(\mu_3\text{-}tz)_2Cl_2(cod)_4]$ precipitated spontaneously. The resulting yellow suspension was stirred for 1 h and was isolated after partial evaporation to *ca*. 5 cm^3 and addition of hexane (10 cm^3). It was filtered off, washed with hexane and air-dried.

$[Rh_4(\mu_3\text{-}tz)_2Cl_2(cod)_2(CO)_4]$ (**13**). *Method A*. To a solution of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ (27.2 mg, 0.07 mmol) in dichloromethane (15 cm^3) kept under an argon atmosphere, $[Rh_2(\mu\text{-}tz)_2(cod)_2]$ (**1**) (39 mg, 0.07 mmol) was added. The starting material dissolved immediately. After stirring for 30 min, the solution was filtered through $MgSO_4$ and evaporated under vacuum to *ca*. 1 cm^3; hexane (15 cm^3) was added. The solid which separated was filtered off, washed with hexane, and vacuum-dried.

Method B. The reaction was carried out as above but the starting materials were replaced by $[Rh_2(\mu\text{-}tz)_2(CO)_4]$ (**5**) and $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$.

Method C. To a mixture of $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ (30 mg, 0.0608 mmol) and triazole (8.4 mg, 0.122 mmol) in acetone (20 cm^3), $[Rh(acac)(CO)_2]$ (31.4 mg, 0.122 mmol) was added. The starting material dissolved and after stirring for 30 min, the solution was evaporated under vacuum to *ca*. 1 cm^3, and hexane (15 cm^3) was added. The complex which separated was filtered off, washed with hexane and vacuum-dried.

$[Rh_4(\mu_3\text{-}tz)_2Cl_2(CO)_8]$ (**14**).—*Method A*. To a suspension of $[Rh_2(\mu\text{-}tz)_2(CO)_4]$ (**5**) (40.8 mg, 0.09 mmol) in dichloromethane (20 cm^3) kept under an argon atmosphere, $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ (35 mg, 0.09 mmol) was added. The starting material dissolved immediately. After stirring for 30 min, the solution was filtered off through $MgSO_4$. The filtrate was evaporated under vacuum, and hexane was added. The formed solid was filtered off, washed with hexane and vacuum-dried.

Method B. To a mixture of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ (30 mg, 0.077 mmol) and triazole (10.65 mg, 0.154 mmol) in acetone (25 cm^3), $[Rh(acac)(CO)_2]$ (39.8 mg, 0.154 mmol) was added. The starting material dissolved and after stirring for 30 min, the solution was evaporated under vacuum. Hexane was added to precipitate the orange complex (**14**). The solid was filtered off, washed with hexane and vacuum-dried.

Reaction of $[Rh_4(\mu_3\text{-}tz)_2Cl_2(cod)_4]$ (**12**) *with* CO. *Method* (*i*). Carbon monoxide was bubbled through a suspension of (**12**) (50 mg, 0.047 mmol) in methanol (15 cm^3) for 30 min. The expected product (**14**) separated almost quantitatively. It was filtered off, washed with methanol and hexane, and air-dried.

Method (*ii*) Carbon monoxide was bubbled through a suspension of (**12**) (50 mg, 0.047 mmol) in dichloromethane (15 cm^3) for 30 min to give a pale yellow solution of (**14**). The solution was evaporated under vacuum, and the colour intensified. Hexane was added to complete the precipitation. The precipitated solid $[Rh_4(\mu_3\text{-}tz)_2Cl_2(cod)_2(CO)_4]$ (**13**) was filtered off, washed with hexane, and vacuum-dried [ν(CO) (CH_2Cl_2): 2 090, 2 018 cm^{-1}].

$[Rh_2Ir_2(\mu_3\text{-tz})_2Cl_2(cod)_4]$ (**15**). To a suspension of $[Rh_2(\mu\text{-tz})_2(cod)_2]$ (**1**) (28 mg, 0.05 mmol) in acetone (15 cm^3) kept under an argon atmosphere, $[Ir_2(\mu\text{-Cl})_2(cod)_2]$ (33.6 mg, 0.05 mmol) was added. The starting material gave an orange precipitate. After stirring for 30 min the complex was isolated by partial vacuum-evaporation to *ca.* 1 cm^3 and subsequent addition of diethyl ether (15 cm^3). The solid was filtered off, washed with diethyl ether, and vacuum-dried.

$[Rh_2Pd_2(\mu_3\text{-tz})_2Cl_2(L_2)_2(CO)_4]$ (**16**) and (**17**). *Method A.* To a suspension of $[Pd_2(\mu\text{-tz})_2(L_2)_2]$ [L_2 = η^3-C_3H_5, (**10**), or η^3-C_4H_7, (**11**)] (0.088 mmol) in methanol (20 cm^3), $[Rh_2(\mu\text{-Cl})_2(CO)_4]$ (0.088 mmol) was added. The starting material dissolved and the orange-yellow complexes precipitated spontaneously, in almost quantitative yield.

The compounds were isolated after partial evaporation to *ca.* 10 cm^3 and addition of diethyl ether (15 cm^3). The solids were filtered off, washed with diethyl ether and air-dried.

Method B. To a suspension of $[Rh_2(\mu\text{-tz})_2(CO)_4]$ (40 mg, 0.088 mmol) in dichloromethane (20 cm^3), $[Pd_2(\mu\text{-Cl})_2(L_2)_2]$ (L_2 = η^3-C_3H_5 or η^3-C_4H_7) (0.088 mmol) was added. The starting materials dissolved. The resulting solutions were stirred for 30 min and filtered off through kieselguhr. The solutions were evaporated under vacuum to *ca.* 1 cm^3, and diethyl ether (10 cm^3) was added to complete the precipitation. The solids were filtered off, washed with diethyl ether and air-dried.

Method C. To a mixture of $[Pd_2(\mu\text{-Cl})_2(L_2)_2]$ (L_2 = η^3-C_3H_5 or η^3-C_4H_7) (0.038 mmol) and triazole (0.077 mmol) in methanol (20 cm^3), $[Rh(acac)(CO)_2]$ (0.077 mmol) was added. The starting material dissolved and the complexes precipitated spontaneously. The complexes were filtered off, washed with diethyl ether and air-dried.

$[Rh_2Au_2(\mu_3\text{-tz})_2Cl_2(cod)_2]$ (**18**). To a solution of [AuCl(tht)] (32.2 mg, 0.1 mmol) in dichloromethane (20 cm^3) kept under an argon atmosphere, $[Rh_2(\mu\text{-tz})_2(cod)_2]$ (**1**) (28 mg, 0.05 mmol) was added. The starting material dissolved and the resulting solution was stirred for 30 min. Evaporation of the solvent and addition of diethyl ether (15 cm^3) gave a yellow complex. The solid was filtered off, washed with diethyl ether and vacuum-dried.

$[Rh_4(\mu_3\text{-tz})_2(cod)_4(PPh_3)_2][ClO_4]_2$ (**19**). *Method A.* To a suspension of $[Rh_2(\mu\text{-Cl})_2(cod)_2]$ (30 mg, 0.061 mmol) in acetone (10 cm^3) was added $Ag[ClO_4]$ (25.2 mg, 0.12 mmol). The resulting mixture was stirred, in the absence of light, for 30 min, and the AgCl formed was removed by filtration. Addition to the filtrate of $[Rh_2(\mu\text{-tz})_2(cod)_2]$ (**1**) (34 mg, 0.061 mmol) and triphenylphosphine (32 mg, 0.12 mmol) gave a yellow solution, which was evaporated to *ca.* 1 cm^3. Addition of diethyl ether gave a yellow solid, which was filtered off, washed with diethyl ether and air-dried.

Method B. To a suspension of $[Rh_4(\mu_3\text{-tz})_2Cl_2(cod)_4]$ (**12**) (64 mg, 0.061 mmol) in acetone (25 cm^3) was added $Ag[ClO_4]$ (25.2 mg, 0.12 mmol). The resulting mixture was stirred, in the absence of light, for 30 min and the AgCl formed was removed by filtration. Addition to the filtrate of triphenylphosphine (32 mg, 0.12 mmol) gave a yellow solution, which was evaporated to *ca.* 1 cm^3. Addition of diethyl ether (20 cm^3) gave a solid, which was filtered off, washed with diethyl ether, and air-dried.

$[Rh_2M(\mu_3\text{-tz})(\mu\text{-X})ClL_2(CO)_4]$ [X = Cl, (**20**)—(**22**) *and* (**25**), *or* OH, (**26**)—(**27**)]. *Method A.* To a suspension of $[M_2(\mu\text{-tz})_2(L_2)_2]$ (M = Rh, L_2 = cod, nbd, or tfbb; M = Ir, L_2 = cod; M = Pd, L_2 = η^3-C_3H_5 or η^3-C_4H_7) (0.064 mmol) in acetone (20 cm^3), $[Rh_2(\mu\text{-Cl})_2(CO)_4]$ (0.128 mmol) was added. The red complexes (**20**) and (**22**), dark blue complex (**21**), and dark violet complex (**25**) precipitated spontaneously, whilst the dark blue complexes (**26**) and (**27**) were isolated after partial evaporation of the solvent to *ca.* 1 cm^3, and subsequent addition of diethyl ether (15 cm^3). The solids were filtered off, washed with diethyl ether and air-dried.

Method B. A mixture of $[M(acac)L_2]$ (M = Rh, L_2 = cod, nbd, tfbb; M = Ir, L_2 = cod; M = Pd, L_2 = η^3-C_3H_5 or η^3-C_4H_7) (0.102 mmol), triazole (0.102 mmol), and $[Rh_2(\mu\text{-Cl})_2(CO)_4]$ (0.102 mmol) in acetone (20 cm^3) was stirred for 20 min. The complexes were isolated as above.

Method C. To a suspension of $[Rh_2M_2(\mu_3\text{-tz})_2Cl_2(L_2)_2(CO)_4]$ (M = Rh, L_2 = cod; M = Pd, L_2 = η^3-C_3H_5 or η^3-C_4H_7) (0.05 mmol) in acetone (20 cm^3), $[Rh_2(\mu\text{-Cl})_2(CO)_4]$ (0.05 mmol) was added. The complexes were isolated as above.

$[Rh_3(\mu_3\text{-tz})(\mu\text{-X})Cl(CO)_6]$ [X = Cl, (**23**), *or* OH, (**24**)]. The preparation of these complexes is dependent on the solvent used.

Complex (**23**). To a suspension of $[Rh_2(\mu\text{-tz})_2(CO)_4]$ (**5**) (29 mg, 0.06 mmol) in dried acetone (20 cm^3), $[Rh_2(\mu\text{-Cl})_2(CO)_4]$ (50 mg, 0.128 mmol) was added. The starting material dissolved, and the green complex (**23**) precipitated spontaneously. It was isolated after partial evaporation to *ca.* 10 cm^3 and addition of diethyl ether (10 cm^3). The solid was filtered off, washed with diethyl ether and air-dried.

Complex (**24**). To a suspension of $[Rh_2(\mu\text{-tz})_2(CO)_4]$ (**5**) (29 mg, 0.06 mmol) in a mixture of acetone and water (10:1, 20 cm^3), $[Rh_2(\mu\text{-Cl})_2(CO)_4]$ (50 mg, 0.128 mmol) was added. The starting material dissolved and the violet complex (**24**) precipitated spontaneously. It was isolated as above.

$[Rh_3(\mu_3\text{-tz})(\mu\text{-}N_3)(N_3)(diolefin)(CO)_4]$ [diolefin = nbd, (**28**), *or* tfbb, (**29**)]. To $[Rh_2(\mu\text{-tz})_2(diolefin)_2]$ (diolefin = nbd or tfbb) (0.064 mmol) in acetone (20 cm^3) was added $[Rh_2(\mu\text{-}N_3)_2(CO)_4]$ (0.128 mmol). The red complexes precipitated spontaneously in almost quantitative yield. The solids were filtered off, washed with diethyl ether and air-dried.

Crystal Structure Determination.—Crystal data. $C_{18}H_8Cl_2F_4N_3O_4Rh_3\cdot 0.5CH_2Cl_2$, monoclinic, $M = 828.36$, $a = 13.890\,6(15)$, $b = 26.858\,6(39)$, $c = 6.848\,0(4)$ Å, $\beta = 98.668(11)°$, $U = 2\,525.7(5)$ Å^3, space group $P2_1/c$, $D_c = 2.178$ g cm^{-3}, $Z = 4$, $F(000) = 1\,580$, $\lambda(Cu\text{-}K_\alpha) = 1.541\,78$ Å, $\mu = 196.5$ cm^{-1} (no absorption correction applied).

The compound incorporates two molecules of solvent, CH_2Cl_2, per unit cell. A plate like sample of dimensions 0.27 × 0.12 × 0.03 mm was used for the analysis on a Philips PW 1100 diffractometer, with Cu-K_α radiation, graphite monochromator, $\omega/2\theta$ scans, bisecting geometry, and scan width 1.5°. The stability was checked every 90 min, with no observed decay. The cell parameters were obtained from a least-squares fit of the angular position of 41 reflections with θ up to 45°.

The structure was solved from the Patterson function and refined by least-squares methods[35,36] on F_o. Of the 2 934 independent data, 2 103 were considered observed [$I > 3\sigma(I)$]. Refinement converged at $R = 0.108$, and $R' = 0.127$. Weights were chosen empirically so as to give no trends in $\langle w\Delta^2F\rangle$ *vs.* $\langle|F_o|\rangle$ or $\langle\sin\theta/\lambda\rangle$, through the use of functions of the type $w = K/f(F_o)g(\sin\theta/\lambda)$, K ensuring that $\langle w\Delta^2F\rangle \sim 1$. The final difference synthesis showed no peaks greater than 2 e Å^{-3}, the largest near the Rh atoms. Final atomic co-ordinates are given in Table 3 for the non-hydrogen atoms, according to the numbering scheme in Figure 1.

Acknowledgements

We thank the Comisión Asesora de Investigación Científica y Técnica (Spain) for financial support and Professor S. García-Blanco for facilities.

References

1 (*a*) R. Usón, L. A. Oro, M. A. Ciriano, M. T. Pinillos, A. Tiripicchio, and M. Tiripicchio Camellini, *J. Organomet. Chem.*, 1981, **205**, 247;

(*b*) R. Usón, L. A. Oro, M. A. Ciriano, D. Carmona, A. Tiripicchio, and M. Tiripicchio Camellini, *ibid.*, 1982, **224**, 69.

2 G. Banditelli, A. L. Bandini, F. Bonati, and G. Minghetti, *J. Organomet. Chem.*, 1981, **218**, 229.

3 (*a*) K. A. Beveridge, G. W. Bushnell, K. R. Dixon, D. T. Eadie, S. R. Stobart, J. L. Atwood, and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1982, **104**, 920; (*b*) A. W. Coleman, D. T. Eadie, S. R. Stobart, M. J. Zaworotko, and J. L. Atwood, *ibid.*, p. 922; (*c*) K. A. Beveridge, G. W. Buschnell, S. R. Stobart, J. L. Atwood, and M. J. Zaworotko, *Organometallics*, 1983, **2**, 1447.

4 J. Powell, A. Kuksis, S. C. Nyburg, and W. W. Ng, *Inorg. Chim. Acta*, 1982, **64**, L211.

5 A. Tiripicchio, F. J. Lahoz, L. A. Oro, and M. T. Pinillos, *J. Chem. Soc., Chem. Commun.*, 1984, 936.

6 L. A. Oro, M. T. Pinillos, A. Tiripicchio, and M. Tiripicchio Camellini, *Inorg. Chim. Acta*, 1985, **99**, L13.

7 J. L. Atwood, K. A. Beveridge, G. W. Bushnell, K. R. Dixon, D. T. Eadie, S. R. Stobart, and M. J. Zaworotko, *Inorg. Chem.*, 1984, **23**, 4050 and refs. therein.

8 F. Barceló, P. Lahuerta, M. A. Ubeda, C. Foces-Foces, F. H. Cano, and M. Martínez-Ripoll, *J. Chem. Soc., Chem. Commun.*, 1985, 43.

9 L. A. Oro, D. Carmona, P. L. Pérez, M. Esteban, A. Tiripicchio, and M. Tiripicchio Camellini, *J. Chem. Soc., Dalton Trans.*, 1985, 973.

10 J. L. Marshall, S. R. Stobart, and H. B. Gray, *J. Am. Chem. Soc.*, 1984, **106**, 3027.

11 R. Usón, L. A. Oro, M. A. Ciriano, M. T. Pinillos, and J. A. Cabeza, *J. Organomet. Chem.*, 1981, **221**, 249.

12 R. Usón, L. A. Oro, J. Gimeno, M. A. Ciriano, J. A. Cabeza, A. Tiripicchio, and M. Tiripicchio Camellini, *J. Chem. Soc., Dalton Trans.*, 1983, 323; R. Usón, J. Gimeno, L. A. Oro, J. M. Martínez de Ilarduya, J. A. Cabeza, A. Tiripicchio, and M. Tiripicchio Camellini, *ibid.*, p. 1729.

13 R. Usón, L. A. Oro, and J. A. Cabeza, *J. Organomet. Chem.*, 1983, **247**, 205.

14 F. Bonati and H. C. Clark, *Can. J. Chem.*, 1978, **56**, 2513; E. C. Alyea, S. A. Dias, and F. Bonati, *Transition Met. Chem.*, 1981, **6**, 24.

15 L. A. Oro, M. T. Pinillos, and C. Tejel, *J. Organomet. Chem.*, 1985, **280**, 261.

16 S. Morton and J. F. Nixon, *J. Organomet. Chem.*, 1985, **282**, 123.

17 L. A. Oro, M. T. Pinillos, C. Tejel, C. Foces-Foces, and F. H. Cano, *J. Chem. Soc., Chem. Commun.*, 1984, 1687.

18 L. A. Oro, D. Carmona, and J. Reedijk, *Inorg. Chim. Acta*, 1983, **71**, 115 and refs. therein.

19 A. Tiripicchio, F. J. Lahoz, L. A. Oro, M. T. Pinillos, and C. Tejel, *Inorg. Chim. Acta*, 1985, **100**, L5.

20 J. P. Farr, M. M. Olmstead, F. E. Wood, and A. L. Balch, *J. Am. Chem. Soc.*, 1983, **105**, 792.

21 W. C. Deese, D. A. Johnson, and A. W. Cordes, *Inorg. Chem.*, 1981, **20**, 1519.

22 L. A. Oro, D. Carmona, J. Reyes, C. Foces-Foces, and F. H. Cano, *J. Chem. Soc., Dalton Trans.*, 1986, 31.

23 M. J. Decker, D. O. K. Fjeldsted, S. R. Stobart, and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1983, 1525.

24 N. A. Bailey, E. Coates, G. B. Robertson, F. Bonati, and R. Ugo, *Chem. Commun.*, 1967, 1041.

25 C. G. Pitt, L. K. Monteith, L. F. Ballard, J. P. Collman, J. C. Morrow, W. R. Roper, and D. Ulkü, *J. Am. Chem. Soc.*, 1966, **88**, 4286.

26 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.

27 G. Giordano and R. H. Crabtree, *Inorg. Synth.*, 1979, **19**, 218.

28 E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 1959, 3178.

29 D. M. Roe and A. G. Massey, *J. Organomet. Chem.*, 1971, **28**, 273.

30 L. J. Herde, J. C. Lambert, and C. V. Senoff, *Inorg. Synth.*, 1979, **15**, 8.

31 J. Tatsuno, T. Yoshida, and N. Seiotsuka, *Inorg. Synth.*, 1979, **19**, 220.

32 J. Powell and B. L. Shaw, *J. Chem. Soc. A*, 1968, 211.

33 L. Busetto, A. Palazzi, and R. Ros, *Inorg. Chem.*, 1970, **9**, 2792.

34 E. A. Allen and W. Wilkinson, *Spectrochim. Acta, Part A*, 1972, **28**, 2257.

35 J. M. Stewart, P. A. Machin, C. W. Dickinson, H. L. Ammon, H. Heck, and H. Flack, 'The *X*-RAY System,' Technical report TR-446, Computer Science Center, University of Maryland, 1976.

36 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

Received 18*th June* 1985; *Paper* 5/1023