Pentamethylcyclopentadienyl-rhodium and -iridium Complexes. Part 21.[1] Neutral and Cationic β-Diketonato-, η^3-Allylic, and NN''-Triazenido-Complexes: the *X*-Ray Crystal Structure of the Binuclear Complex $[Rh_2(C_5Me_5)_2(acac)_2][BF_4]_2$

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The synthesis and properties of the β-diketonato-complexes $[M(\eta^5\text{-}C_5Me_5)X(R^1COCHCOR^2)]$ [M = Rh, X = Cl, $R^1 = R^2 = Me$, $R^1 = R^2 = CF_3$, $R^1 = Me$, $R^2 = Pr^n$, $R^1 = Me$, $R^2 = OEt$, or $R^1 = Me$, $R^2 = CF_3$; M = Rh, $R^1 = R^2 = Me$, X = Br, I, N_3, or OAc (acetate); and M = Ir, X = Cl, $R^1 = R^2 = Me$, or $R^1 = R^2 = CF_3$] obtained from $[M_2(\eta^5\text{-}C_5Me_5)_2Cl_4]$ [M = Rh (1a) or Ir (1b)] and $Na[R^1COCHCOR^2]$ are reported. Iridium forms a stable complex $[Ir(\eta^5\text{-}C_5Me_5)(acac)_2]$ in which the two acac (MeCOCHCOMe) groups are *OO'*- and *C*-bonded respectively; no exchange is detectable on the ^1H n.m.r. time scale. The complex $[Rh(\eta^5\text{-}C_5Me_5)Cl(acac)]$ undergoes substitution when treated with *N*-bromo- or *N*-iodo-succinimide to give $[Rh(\eta^5\text{-}C_5MC_5)Cl(MeCOCYCOMe)]$ (Y = Br or I). Reaction of $[Rh(\eta^5\text{-}C_5Me_5)Cl(MeCOCHCOR^2)]$ with AgX gives binuclear $[Rh_2(\eta^5\text{-}C_5Me_5)_2(MeCOCHCOR^2)_2][X]_2$ (R^2 = Me, Pr^n, or OEt; X = PF_6 or BF_4). The complex $[Rh_2(\eta^5\text{-}C_5Me_5)_2(acac)_2][BF_4]_2$ (14a) has been shown by *X*-ray crystallography to contain two bridging acac ligands, *OO'*-bonded to one rhodium and *C*-bonded to the other. A major contributor to the structure of the acac ligand is the β-diketone form, although a delocalised β-diketonate form also plays an important role. The $\eta^5\text{-}C_5Me_5$ ring in (14a) is distorted towards an 'ene-enyl' structure, the shortest $C\overset{\cdots}{-}C$ ('ene') bond being *trans* to the Rh–C(acac) σ-bond. Reaction of $[Rh_2(\eta^5\text{-}C_5Me_5)_2(acac)_2][PF_6]_2$ with L gives $[Rh(\eta^5\text{-}C_5Me_5)L(acac)][PF_6]$ [L = PPh_3, $P(OEt)_3$, Bu^tNC, py, NH_2Me, or $NHMe_2$]; similarly prepared are $[Rh(\eta^5\text{-}C_5Me_5)L(CF_3COCHCOCF_3)][PF_6]$ (L = MeCN or PPh_3). Reaction of (1a) with RNHN=NR and base or $Ag[N_3R_2]$ gives the *NN''*-bonded triazenido-complexes $[Rh(\eta^5\text{-}C_5Me_5)Cl(N_3R_2)]$ (R = Ph, *p*-MeC_5H_4, or *p*-ClC_5H_4); the *NN'*-bonded acetamidinato-complex $[Rh(\eta^5\text{-}C_5Me_5)Cl(PhNCMeNPh)]$ is prepared similarly. On reaction with L in the presence of $Ag[PF_6]$ these give $[Rh(\eta^5\text{-}C_5Me_5)L(RNXNR)][PF_6]$ [X = N, R = Ph, L = MeCN or $P(OMe)_3$; X = CMe, R = Ph, L = MeCN or PPh_3. The azido-complex $[Rh_2(\eta^5\text{-}C_5Me_5)_2(N_3)_4]$ forms adducts $[Rh_2(\eta^5\text{-}C_5Me_5)(N_3)_4(RNHN{=}NR)]$ with RNHN=NR (R = Ph or *p*-MeC_6H_4). The η^3-1-methylallyl complex $[Rh(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}1\text{-}MeC_3H_4)Cl]$ also forms the cationic complexes $[Rh(\eta^5\text{-}C_5Me_5)(\eta^3\text{-}1\text{-}MeC_3H_4)L][PF_6]$ [L = MeCN, $P(OMe)_3$, PPh_3, or NH_2Et] on reaction with L in the presence of $Ag[PF_6]$.

IN previous papers of this series we have discussed metathetical reactions of di-μ-chloro-bis[chloro(η^5-pentamethylcyclopentadienyl)rhodium] (1a) and its iridium analogue (1b) in which the labile chlorines have been replaced by halide,[2] carboxylate,[3] hydroxide,[3] hydride,[4] or pseudo-halide (N_3, NCO, or NCS) ligands.[5] We have also extensively examined reactions in which the chlorines were replaced by a wide variety of hydrocarbon ligands.[6] In continuation of these studies we now report on neutral and cationic β-diketonato-complexes and the structurally related triazenido-complexes as well as on some new cationic η^3-allylic complexes.

RESULTS AND DISCUSSION

β-Diketonato-complexes.—Reaction of (1a) with the β-diketones $MeCOCH_2COMe$ (acacH),† $CF_3COCH_2COCF_3$ (hfacH),† $MeCOCH_2COPr$, $MeCOCH_2CO_2Et$, or $MeCOCH_2COCF_3$ (tfacH),† and of (1b) with acacH or hfacH in acetone (or dichloromethane), in the presence of sodium carbonate gave the β-diketonato-complexes (2)—(6) (Scheme) which were characterised on the basis of elemental analysis and spectroscopically (Table 1). The rhodium-bonded chlorine in (2a) could also be replaced by bromide, iodide, azide (on reaction with the appropriate sodium salt), or acetate [on reaction with AgOAc (OAc = acetate)].

The delocalised ('aromatic') nature of the Rh(acac) in (2a) is shown by the substitution reactions[7] with *N*-bromo- and *N*-iodo-succinimide to give (11) and (12) respectively.

Under more vigorous conditions the remaining chlorine in the iridium acac complex (2b) was also replaced by acac to form the bis-acac complex (13). The ^1H n.m.r. spectrum (Table 1) showed the presence of two types of acac ligand, one *OO'*-bonded and the other *C*-bonded [through C(γ)] to the metal.[8] The ^1H n.m.r. spectrum in *o*-dichlorobenzene did not vary over the temperature range 35—120 °C, showing that the two types of acac ligand did not exchange; decomposition occurred at higher temperatures. The ^1H n.m.r. spectrum of a solution in benzene indicated that an analogous bis-acac rhodium complex was formed under similar conditions but it decomposed rapidly to give unidentified products when attempts were made to isolate it [^1H n.m.r. (C_6H_6): δ 1.25 (s, C_5Me_5), 1.86 (s, *OO'*-acac Me), 2.03 (s, *C*-acac Me), 4.41 [d, J(H–Rh) = 3 Hz, *C*-acac H], and 5.03 p.p.m. (s, *OO'*-acac H)]. Attempts to form bis-hfac complexes of Rh or Ir were unsuccessful.

When the β-diketonato-complexes (2a), (4), or (5) were treated with silver hexafluorophosphate (or tetrafluoroborate) in dichloromethane, chloride was removed and the binuclear cationic complexes (14)—(16) were obtained. An *X*-ray crystal-structure determination was carried out on $[Rh_2(\eta^5\text{-}C_5Me_5)_2(acac)_2][BF_4]_2$ (14a). This showed that the acac ligands bridge the two $Rh(C_5Me_5)$ units by *OO'*-bonding to one rhodium and

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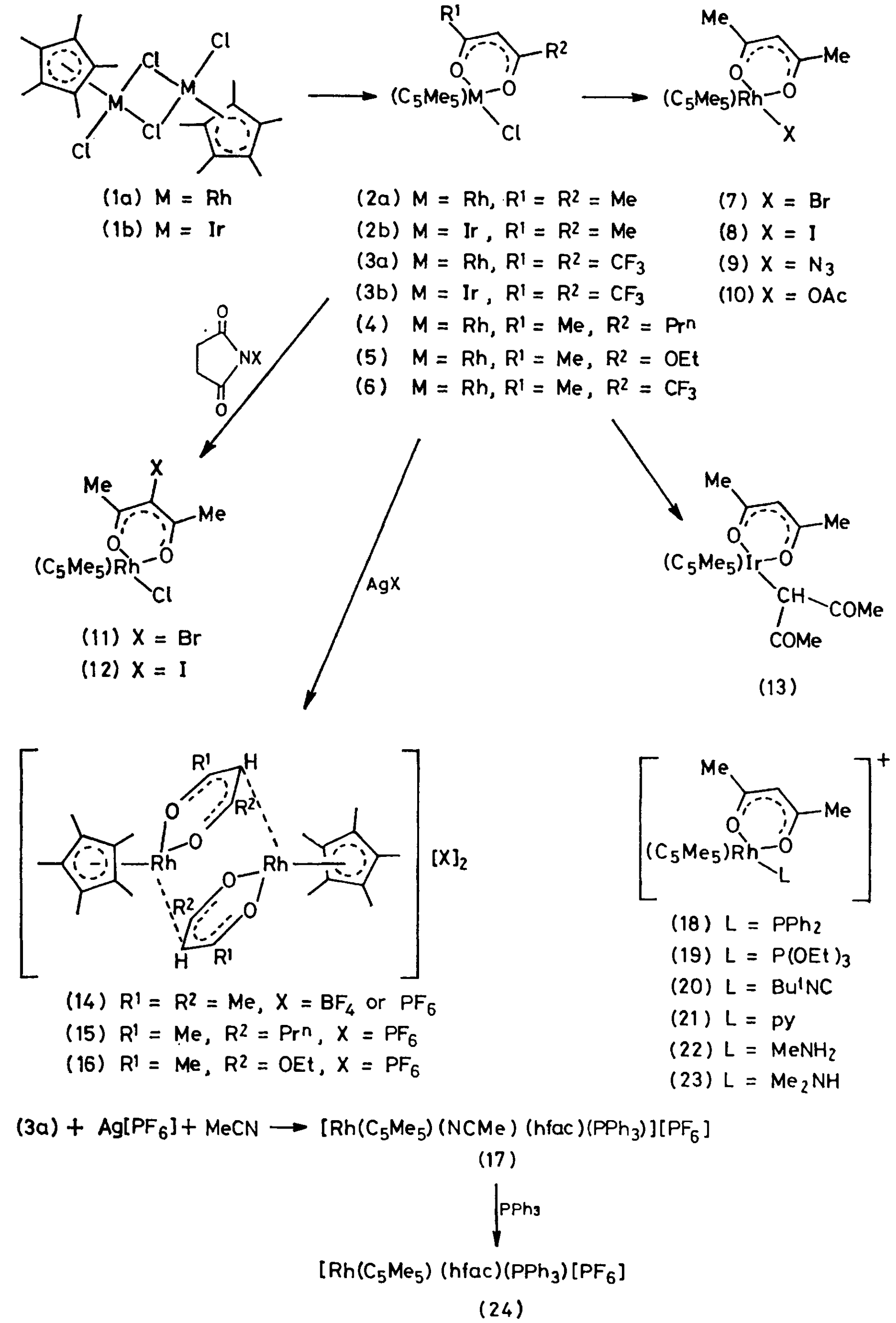
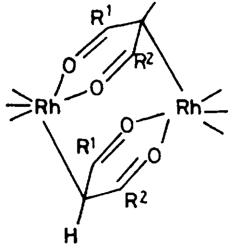
† The contractions acacH, hfacH, and tfacH are used to denote acetylacetone (pentane-2,4-dione), hexafluoroacetylacetone (1,1,1,5,5,5-hexafluoropentane-2,4-dione), and 1,1,1-trifluoroacetylacetone (1,1,1-trifluoropentane-2,4-dione) respectively.

C-bonding [*via* C(γ)] to the other (Figure 1, Table 5). This type of structure, where a β-diketonate ligand bridges two metals, is well known and has been established in, for example, $[Pt_2Me_6(acac)_2]$.[9]

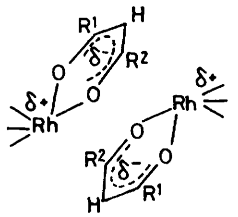


SCHEME (24)

The other binuclear complexes are similarly formulated by analogy; a notable characteristic of these complexes is the appearance of a strong band [ν(CO)] at 1 620 cm^{-1} in the i.r. spectrum. No carbonyl bands at frequencies higher than 1 590 cm^{-1} are present in the spectra of either complexes (2)—(6) or of the cationic adducts (18)—(23) and this suggests that in these binuclear complexes an important contributor to the bonding is the β-diketone form (A). This is confirmed by the Rh–O bond lengths in complex (14a) [2.103 and 2.101(4) Å] which are substantially longer (0.110, 27σ) than in $[Rh(acac)_3]$ and also by the C(1)–C(2) and C(2)–C(3) bond lengths [1.449 and 1.446(8) Å] which are longer (0.064 Å, 8σ) than in $[Rh(acac)_3]$.[10] However, the C–O distances [1.252 and 1.260(7) Å] in (14a) are longer (0.041 Å, 6σ) than those found in normal organic ketones [1.215(5) Å];[11] furthermore, the rhodium to carbon distance, Rh–C(2′) = 2.287(6) Å, is long for a Rh–C(sp^3) σ-bond, which usually falls in the range 2.04—2.08 Å.[12] Clearly, therefore a delocalised β-diketonate structure, which may be written as the dipolar form (B), is also important in describing the overall bonding.

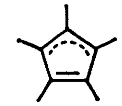


(A)



(B)

One further feature of the X-ray structure of complex (14a) deserves comment since the low R factor has allowed precise determination also of the C–C distances in the η^5-C_5Me_5 ring. These (Figure 2) show a variation consistent with a degree of localisation into an ' ene-enyl ' form (C). This type of localisation has been



(C)

observed before [13] in cyclopentadienyl complexes where there is no cylindrical symmetry about the metal, and has been suggested to arise from an unequal population of the η^5-C_5R_5 e_1 orbitals.[14] However, in contrast to the cases discussed previously,[14] the C⋯C⋯C

TABLE 1

Microanalytical and ^1H n.m.r. spectroscopic data for the β-diketonato-complexes

		Yield	Analysis (%) [a]					^1H N.m.r. (δ/p.p.m.) in C^2HCl_3				
	Complex	(%)	C	H	Cl	Other	M [a]	C_5Me_5	$R^1COC\mathit{H}COR^2$	R^1	R^2	Other
(2a)	$[Rh(C_5Me_5)Cl(acac)]$	94	48.4 (48.3)	5.9 (5.9)	9.4 (9.5)		421 (373)	1.61	5.07	2.00	2.00	
(2b)	$[Ir(C_5Me_5)Cl(acac)]$	65	38.9 (39.0)	4.9 (4.8)	6.8 (7.7)			1.59	5.19	1.19	1.91	
(3a)	$[Rh(C_6Me_5(Cl(hfac)]$	85	38.2 (37.5)	3.5 (3.4)		F 23.8 (23.7)	515 (481)	1.64	5.82		(^{19}F n.m.r., −75.4 [b])	
(3b)	$[Ir(C_5Me_5)Cl(hfac)]$	60	32.3 (31.6)	2. (2.8)		F 19.8 (20.0)		1.59	5.91		(^{19}F n.m.r., −76.0 [b])	
(4)	$[Rh(C_5Me_5)Cl(MeCOCHCOPr^n)]$	94	51.0 (50.9)	6.7 (6.5)	8.7 (8.9)		416 (401)	1.62	5.10	2.00	0.92 (t, Me, J = 7 Hz) 2.21 (m, CH_2CH_2)	
(5)	$[Rh(C_5Me_5)Cl(MeCOCHCO_2Et)]$	89	47.5 (47.7)	6.1 (6.0)	8.6 (8.8)		392 (403)	1.64	4.58	1.97		1.25 (t, Me J = 7 Hz) 4.18 (m, CH_2)
(6)	$[Rh(C_5Me_5)Cl(tfac)]$	78	42.4 (42.2)	4.5 (4.5)	7.5 (8.3)		442 (427)	1.64	5.51	2.14		(^{19}F n.m.r., −75.2 [b])
(7)	$[Rh(C_6Me_5)Br(acac)]$	81	43.2 (43.2)	5.5 (5.3)		Br 19.3 (19.2)	432 (417)	1.66	5.10	1.96	1.96	
(8)	$[Rh(C_5Me_5)I(acac)]$	70	38.9 (38.8)	4.8 (4.7)		I 26.9 (27.4)	499 (464)	1.70	5.18	1.99	1.99	
(9)	$[Rh(C_5Me_5)(N_3)(acac)]$	94	48.1 (47.5)	6.0 (5.8)		N 11.3 (11.1)	388 (379)	1.60	5.09	1.99	1.99	
(10)	$[Rh(C_5Me_5)(OAc)(acac)]$	81	51.6 (51.5)	6.1 (6.3)			340 (396)	1.63	5.10	1.97	1.97	OAc, 2.04
(11)	$[Rh(C_5Me_5)Cl(MeCOCBrCOMe)]$	61	40.1 (39.9)	4.5 (4.7)	7.7 (7.9)	Br 17.3 (17.7)	470 (452)	1.67		2.29	2.29	
(12)	$[Rh(C_5Me_5)Cl(MeCOCICOMe)]$	46	36.6 (36.1)	4.2 (4.2)	7.4 (7.1)	I 26.5 (25.5)	470 (499)	1.72		2.20	2.20	
(13)	$[Ir(C_5Me_5)(acac)\{CH(COMe)_2\}]$	55	45.8 (45.7)	5.5 (5.6)				1.41	5.20	1.85	1.85	4.74 [Ir–CH(COMe)$_2$], 1.86 [Ir–CH(COMe)$_2$]
(14a)	$[Rh(C_5Me_5)_2(acac)_2][BF_4]_2$	90	42.5 (42.5)	5.2 (5.2)			(301 [c]	1.59	5.67	1.84	1.84	
(14b)	$[Rh(C_5Me_5)_2(acac)_2][PF_6]_2$ [d]	91	37.7 (37.3)	4.8 (4.6)			291 [c]	1.54	n.o.	n.o.	n.o.	
(15)	$[Rh_2(C_5Me_5)_2(MeCOCHCOPr^n)_2]$-$[PF_6]_2$ [d]	86	40.1 (40.0)	5.1 (5.1)			291 [c]	1.56	5.46	2.24	0.99 (t, J = 6 Hz, Me) 2.45 (br m, CH_2CH_2)	
(16)	$[Rh_2(C_5Me_5)(MeCOCHCO_2Et)_2][PF_6]_2$	88	37.7 (37.5)	4.8 (4.7)			275 [c]	1.69	5.27	2.37	1.39 (t, J = 7 Hz, Me) 4.40 (br m, CH_2)	
(17)	$[Rh(C_5Me_5)(NCMe)(hfac)][PF_6]_2$	42	32.5 (32.3)	3.0 (3.0)		N 2.3 (2.2)		1.79	6.11			2.35 (MeCN)
(18)	$[Rh(C_5Me_5)(acac)(PPh_3)][PF_6]$	98	53.4 (53.2)	5.1 (5.0)			129 [c]	1.29 (d) [J (H–P) = 4 Hz]	4.75	1.76	1.76	7.5 (br m, Ph)
(19)	$[Rh(C_5Me_5)(acac)\{P(OEt)_3\}][PF_6]$	76	39.0 (38.9)	5.5 (5.7)			146 [c]	1.57 (d) [J (H–P) = 6 Hz)	5.30	1.98	1.98	1.29 (t, J = 6 Hz, Me) 4.01 [quintet, J (H–H) = J-(H–P) = 7 Hz, CH_2]
(20)	$[Rh(C_5Me_5)(acac)(CNBu^t)][PF_6]$	86	42.5 (42.5)	5.8 (5.5)		N 2.3 (2.5)	139 [c]	1.65	5.21	1.98	1.98	1.54 (s, br)
(21)	$[Rh(C_5Me_5)(acac)(py)][PF_6]$	90	43.1 (42.8)	5.1 (4.8)		N 2.6 (2.7)	144 [c]	1.50	4.98	1.94	1.94	7.54 (m), 7.9 (m), 8.33 (br d, J = 5 Hz) (all py)
(22)	$[Rh(C_5Me_5)(acac)(NH_2Me)][PF_6]$	87	37.3 (37.4)	5.5 (5.3)		N 2.6 (2.7)	144 [c]	1.57	5.20	1.99	1.99	2.25 (br t, J = 6 Hz, MeNH) 2.70 (br, NH_2)
(23)	$[Rh(C_5Me_5)(acac)(NHMe_2)][PF_6]$	69	38.9 (38.7)	5.8 (5.5)		N 2.8 (2.7)		1.58	5.27	1.99	1.99	2.36 (br d, J = 6 Hz, Me_2N) 3.18 (br NH)
(24)	$[Rh(C_5Me_5)(hfac)(PPh_3)][PF_6)$	42	46.0 (46.5)	3.4 (3.6)				1.72 [J (H–P) = 3 Hz]	5.70			7.3 (br m, Ph)

[a] Calculated values are given in parentheses. [b] With respect to $CFCl_3$. [c] Molar conductivities (Λ/S cm^2 mol^{-1}) measured in acetonitrile solution at *ca.* 0.5 × 10^{-3} mol dm^{-3} concentration. [d] ^1H N.m.r. run in $C^2H_2Cl_2$ solution; n.o. = not observed.

bonds making up the 'enyl' part of the ring in complex (14a) are *not trans* to π-bonding ligands and in complex (14a) the shortest $\mathrm{C}\underset{\cdots}{-}\mathrm{C}$ bond (the 'ene' part) is *trans* to the Rh–C(2') σ-bond. We note that a similar type of localisation also appears to be present in [Rh(η-C_5H_5)(σ-C_2F_5)I(CO)],[15] and although the quality of the data there did not allow this to be determined unambiguously, the σ-C_2F_5 group again appeared to be *trans* to the shortest ring C–C bond. We therefore suggest that this asymmetry in the bonding, due to unequal occupation of the e_1 orbitals of the C_5R_5 ring, can arise from the *trans*-influence of a σ-bonded carbon as well as from the asymmetric distribution of other π-bonded ligands. Other types of asymmetric bonding have also been noted for Rh–C_5R_5 complexes.[16]

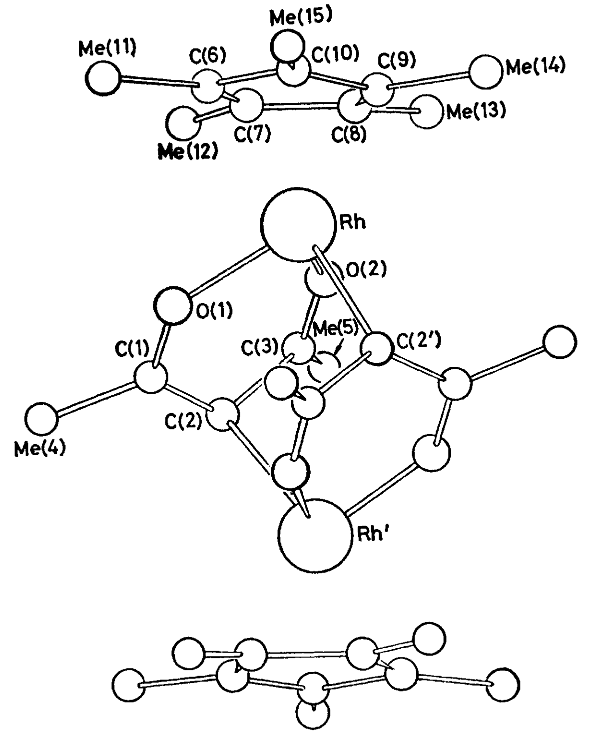


FIGURE 1 View of the cationic part of [Rh_2(η^5-C_5Me_5)$_2$(acac)$_2$][BF_4]$_2$ (14a), hydrogen atoms being omitted

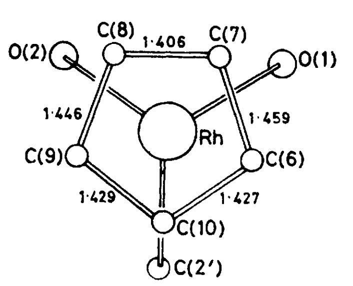


FIGURE 2 Projection on to the η^5-C_5Me_5 ring in [Rh_2(η_5-C_5Me_5)$_2$(acac)$_2$][BF_4]$_2$ (14a) showing the orientations of the Rh–C(2'), Rh–O(1), and Rh–O(2) bonds. Methyl groups are omitted for clarity

Although acetonitrile cannot break the dimer (14) other ligands will do so to give, for example, the mononuclear cationic complexes (18)—(23).[17] Phosphines, phosphites, isocyanides, and secondary as well as primary amines will cleave the dimer; however, neither tertiary amines (NMe_3 or NEt_3), nor diphenylacetylene nor azobenzene will form adducts of this type. Reaction of (14) with an excess of triphenyl phosphite gave the previously reported *o*-metallated complex $[\overline{\mathrm{Rh}(C_5Me_5)\{P(O\text{-}o\text{-}C_6}H_4)(OPh)_2\}\{P(OPh)_3\}][PF_6]$.[18]

TABLE 2

Microanalytical and ^1H n.m.r. spectroscopic data for triazenido- and acetamidinato-complexes

	Complex	Yield (%)	Analysis (%) [a] C	H	N	Cl	M [a]	^1H N.m.r. (δ/p.p.m.) in C^2HCl_3 C_5Me_5	Other
(25a)	[Rh(C_5Me_5)Cl(N_3Ph_2)]	86	56.1 (56.2)	5.4 (5.3)	9.2 (9.0)	7.9 (7.6)	448 (470)	1.79	7.25 (m, Ph)
(25b)	[Rh(C_5Me_5)Cl{N_3(C_6H_4Me-*p*)$_2$}]	89	57.9 (57.9)	5.9 (5.8)	8.4 (8.4)	7.1 (7.1)	488 (498)	1.74	2.26 (Me), 7.14 (aryl)
(25c)	[Rh(C_5Me_5)Cl{N_3(C_6H_4Cl-*p*)$_2$}]	79	48.7 (49.0)	4.2 (4.3)	7.6 (7.8)	19.9 (19.8)	609 (539)	1.76	7.16, 7.24 (dd, J = 8 Hz, aryl)
(26a)	[Rh(C_5Me_5)(NCMe)(N_3Ph_2)][PF_6]	80	46.0 (46.4)	4.4 (4.7)	9.1 (9.0)			1.80	2.11 (MeCN), 7.19 (br m, aryl)
(26b)	[Rh(C_5Me_5)(N_3Ph_2){P(OMe)$_3$}][PF_6]	74	43.0 (42.7)	4.9 (4.8)	6.0 (6.0)			1.69 (J = 5 Hz) [b]	3.70 [d, J (H–P) = 11 Hz, MeO], 7.2 (br m, aryl)
(28)	[Rh(C_5Me_2){N_3(C_6H_4Cl-*p*-)$_2$}(N_3)]	71	48.5 (48.4)	4.3 (4.2)	14.7 (15.4)	12.5 (13.0)		1.75	7.14, 7.25 (dd, J = 8 Hz, aryl)
(30a)	[Rh_2(C_5Me_5)$_2$(N_3)$_4$(N_3Ph_2H)]	91	45.4 (45.7)	4.9 (4.9)	24.9 (25.0)			1.67	7.36 (m, aryl)
(30b)	[Rh_2(C_5Me_5)$_2$(N_3)$_4${N_3(C_6H_4Me-*p*)$_2$H}]	92	46.9 (47.0)	5.4 (5.2)	24.2 (24.2)			1.65	2.33 (Me), 7.12, 7.28 (dd,) J = 8 Hz)
(31)	[Rh(C_5Me_5)Cl(PhNCMeNPh)]	81	59.5 (59.7)	6.0 (5.8)	6.0 (5.8)	7.3 (7.4)	496 (483)	1.57	1.84 (Me), 7.09 (m, Ph)
(32)	[Rh(C_5Me_5)(NCMe)(PhNCMeNPh)][PF_6]	67	47.7 (48.3)	5.0 (5.0)	6.8 (6.8)			1.61	1.95 (Me), 2.42 (MeCN), 7.21 (m, Ph)
(33)	[Rh(C_5Me_5)(PhNCMeNPh)(PPh_3)][PF_6]	82	58.6 (59.0)	5.0 (5.0)	3.1 (3.3)		115 [c]	1.23 (J = 4 Hz) [b]	1.65 (Me), 7.07 (br m, Ph)

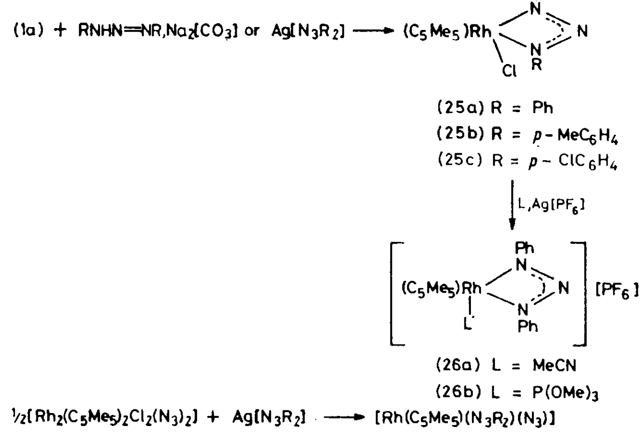
[a] Calculated values are given in parentheses. [b] J(H–P). [c] Molar conductivity (Δ/S cm^2 mol^{-1}) measured in acetonitrile solution at *ca* 5×10^{-3} mol dm^{-3} concentration.

The hfac complex (3a) on treatment with Ag[PF_6] in acetonitrile did not give the corresponding binuclear complex but gave the acetonitrile adduct (17), which could be converted into the triphenylphosphine adduct (24) on reaction with PPh_3. Evidence was also obtained for the formation of $[Rh(C_5Me_5)(tfac)(NCMe)][PF_6]$ in solution [^1H n.m.r. (C^2HCl_3): δ 1.64 (C_5Me_5), 2.12 (MeCN), 2.21 (tfac Me), and 5.61 p.p.m. (tfac H)] but attempts to isolate this material failed.

These results show clearly that the strength of binding of the weak acetonitrile ligand to Rh is substantially enhanced when a more electron-withdrawing ligand is present (*e.g.* hfac). However, none of these complexes is particularly inert and the β-diketonate is usually quite easily displaced by an excess of ligand; for example, complex (2a) reacted with 1,2-bis(diphenylphosphino)ethane in the presence of $[NH_4][PF_6]$ to give $[Rh(C_5Me_5)Cl(Ph_2PCH_2CH_2PPh_2)][PF_6]$.

NN''-1,3-*Diaryltriazenido-complexes*.—In the presence of sodium carbonate the rhodium dichloride dimer (1a) reacted with 1,3-diaryltriazenes (RNHN=NR, R = Ph or *p*-MeC_6H_4) to give the triazenido complexes (25) (Table 2). These complexes could also be obtained by reaction of (1a) with $Ag[RN_3R]$ (R = *p*-chlorophenyl). Only one RN_3R could be introduced by either of these means. In agreement with other workers,[19] we propose that the triazenide ligand is NN'' bonded to give a delocalised planar RhN_3 unit.

The remaining chlorine in (25a) could be replaced by a neutral ligand [MeCN or $P(OMe)_3$] in the presence of $Ag[PF_6]$ to give the cationic complexes (26a). Di-μ-azido-bis[chloro(pentamethylcyclopentadienyl)rhodium] [5] (27) also reacted with $Ag[N_3R_2]$ (R = *p*-ClC_6H_4) to give the azido(triazenido)-complex (28).



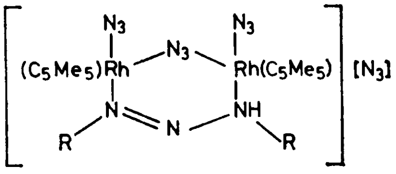
(25a) R = Ph
(25b) R = *p*-MeC_6H_4
(25c) R = *p*-ClC_6H_4

(26a) L = MeCN
(26b) L = $P(OMe)_3$

(27)

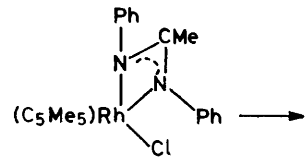
(28) R = *p*-ClC_6H_4

Although no reaction occurred between (1a) and free triazenes, RNHN=NR (R = Ph or *p*-tolyl), the tetra-azido complex (29) [5] readily reacted with R_2N_3H in acetone to give the binuclear tetra-azido(triazene) complexes $[Rh_2(C_5Me_5)_2(N_3)_4(N_3R_2H)]$, [R = Ph (30a) or *p*-$MeC_6H_4$ (30b)]. The ^1H and ^{13}C n.m.r. spectra suggested the presence of only one type of *p*-tolyl and one type of C_5Me_5 group even at low temperatures. The solution i.r. spectrum showed bands at 2 028 and 2 052 cm^{-1} indicating the presence of both terminal and bridging azide ligands.[5] In the solid (Nujol mull) the i.r. spectrum of (30b) showed $\nu(N_3)$ bands at 2 028 and 2 047 cm^{-1}, corresponding to the solution spectra, as well as an extra band at 2 010 cm^{-1}, which could be due to ionic N_3^-, and ν(NH) at 3 130 cm^{-1}. The spectroscopic data for (30a) were similar. The structures of these complexes are not known but one possibility is that they are ionic with the triazene H moving rapidly between two equivalent sites.

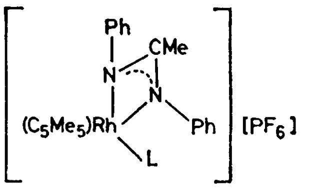


(30)

NN'-*Diphenylacetamidinato-complexes*.—The *NN'*-diphenylacetamidinate ligand [20] is very similar to the diaryltriazenes discussed above and complex (31) was obtained by reaction of (1a) and PhN=CMeNHPh in the presence of base; this complex reacted with $Ag[PF_6]$ in acetonitrile to give (32) which, with PPh_3, gave (33) (Table 2). Again, the diphenylacetamidinate ligand is presumed to bond *NN'* to the rhodium.

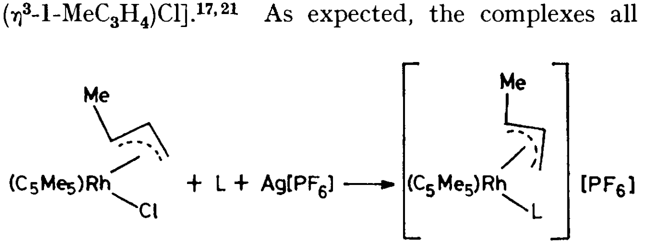


(31)



(32) L = MeCN
(33) L = PPh_3

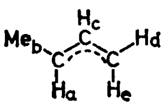
Cationic η^3-1-*Methylallylic Complexes*.—In order to compare the cationic complexes of the bidentate β-diketonate, triazenide, and acetamidinate ligands with those containing an η^3-allylic group, complexes (34a)—(34d) were also prepared from the known $[Rh(C_5Me_5)(\eta^3\text{-}1\text{-}MeC_3H_4)Cl]$.[17, 21] As expected, the complexes all showed similar properties (Table 3). Only one isomer could be detected for (34a)—(34d); this is probably because steric factors favour the isomer with the allylic C(2) carbon pointing away from the C_5Me_5 ligand.



(34a) L = MeCN
(34b) L = $P(OMe)_3$
(34c) L = PPh_3
(34d) L = $EtNH_2$

TABLE 3

Microanalytical and ^1H n.m.r. spectroscopic data for the η^3-allylic complexes



Complex	Yield (%)	Analysis (%) [a]			Λ [b]	^1H N.m.r. spectra in C^2HCl_3 (δ/p.p.m.) [c]						
		C	H	N		C_5Me_5	H_a	Me_b	H_c	H_d	H_e	Others
(34) $[Rh(C_5Me_5)(MeC_3H_4)L][PF_6]$												
(a; L = MeCN)	85	40.2 (40.1)	5.3 (5.3)	2.9 (2.9)	184	1.77	3.23 (m)	1.68 (d) [J (Me_b–H_a) = 6]	4.06 (m)	3.38 (d) [J (H_d–H_c) = 7]	2.58 (d) [J (H_e–H_c) = 11]	2.50 (MeCN)
[b; L = $P(OMe)_3$]	93	36.5 (36.3)	5.5 (5.5)		145	1.71 {5}	3.04 (br)	1.41 (d) [6]	3.85 (m)	2.78 (d) [7]	2.24 (dd) [11]{11}	3.50 [d, {10}, $P(OMe)_3$]
(c; L = PPh_3)	81	55.1 (54.9)	5.2 (5.3)		138	1.54 (d) {5}	2.50 (m)	1.60 (d) [6]	4.02 (m)	3.05 (d) [7]	1.84 (dd) [12]{12}	7.5 (br m, Ph)
(d; L = NH_2Et)	82	39.9 (39.8)	5.9 (6.0)	2.9 (2.9)		1.73	2.60 (m)	1.63 (d) [6]	4.00 (m)	3.31 (d) [7]	2.05 (d) [11]	1.13 (t, [8], CH_2*Me*) 2.55 (q, [8], *CH_2*Me) 2.10 (br, NH_2)

[a] Calculated values are given in parentheses. [b] Molar conductivities Λ/S cm^2 mol^{-1}) measured in acetonitrile solution at *ca.* 0.5×10^{-3} mol dm^{-3} concentration. [c] Values of J(H–H) and J(H–P) (both in Hz) are given in square brackets and braces respectively.

EXPERIMENTAL

Microanalyses were carried out by the University of Sheffield Microanalytical Laboratory. ^1H N.m.r. spectra were determined on Perkin-Elmer R-12B (60 MHz), R-34 (220 MHz), or Varian HA-100 spectrometers using $SiMe_4$ as internal standard. Microanalytical and ^1H n.m.r. data are collected in Tables 1—3. ^{13}C and ^{31}P n.m.r. spectra were determined on a JEOL PFT-100 n.m.r. spectrometer using $SiMe_4$ as internal reference (for ^{13}C) and H_3PO_4 as external reference (for ^{31}P) respectively. Molecular weights were determined osmometrically in chloroform and molar conductivities were measured in acetonitrile with a Philips conductivity bridge. I.r. spectra were determined on a PE-180 spectrometer. All reactions were carried out under an atmosphere of nitrogen but the compounds were not usually air-sensitive. Representative preparations are detailed below.

$[Rh(C_5Me_5)Cl(acac)]$ (2a).—A suspension of $[Rh_2(C_5Me_5)_2Cl_4]$ (1.00 g, 1.62 mmol) and Na(acac) (0.39 g, 3.24 mmol) in acetone (80 cm^3) was stirred for 15 h while the colour changed from red to orange. The solvent was then removed *in vacuo*, the residue was dissolved in dichloromethane (25 cm^3), and the solution was filtered to remove NaCl. The product crystallised from this solution as orange-red crystals (1.13 g) on addition of di-isopropyl ether. ^{13}C N.m.r. (C^2HCl_3): δ 8.4 (s, C_5*Me*$_5$), 28.2 (s, acac Me), 91.9 [d, J(C–Rh) = 9.2 Hz, *C*$_5$Me$_5$], 98.2 (acac *C*H), and 186.3 p.p.m. (s, acac CO).

Complexes (2b), (3a), and (3b) [crystallised from acetone–light petroleum (b.p. 30—60 °C)] as well as (4)—(6) (crystallised from diethyl ether–hexane) were obtained by analogous routes. ^{13}C N.m.r. of (4) (C^2HCl_3): δ 8.4 (C_5*Me*$_5$), 13.9 (C_2H_4*C*H$_3$), 20.2 (CH_2*C*H$_2$Me), 42.8 (*C*H$_2$C$_2$H$_5$), 28.3 (*Me*CO), 91.9 [d, J(C–Rh) = 9.2 Hz], 98.0 (CH), 186.3 (CO), and 189.1 p.p.m. (CO). Complex (3a) was also prepared (85%) by reaction of (1a) and Tl(hfac).

$[Rh(C_5Me_5)I(acac)]$ (8).—A suspension of (2a) (0.20 g, 0.54 mmol) and NaI (0.81 g, 5.4 mmol) in acetone (40 cm^3) was stirred for 6 h, while the colour changed from bright red to dark purple. The precipitate was then filtered off and discarded and the solvent removed *in vacuo*. The product was obtained from the residue, as dark red crystals (0.10 g, 40%), by crystallisation from dichloromethane–n-hexane. The yield for this reaction was low due to the formation of $[Rh_2(C_5Me_5)_2I_4]$. It was found that displacement of the (acac) ligand was inhibited by the addition of a ten-fold excess of $Na_2[CO_3]$ to the reaction mixture, thereby increasing the yield of complex (8) to 70%. The analogous complexes (7), (9) [ν(N_3) at 2 014 cm^{-1}], and (10) were obtained by the same method.

$[Rh(C_5Me_5)Cl\{MeCOC(Br)COMe\}]$ (11).—A solution of (2a) (0.20 g, 0.54 mmol) and *N*-bromosuccinimide (0.10 g, 0.54 mmol) in dichloromethane (30 cm^3) was stirred for 6 h. The solvent was then removed *in vacuo* and the residue was washed with diethyl ether (3 × 10 cm^3) to remove succinimide. The product was crystallised from acetone–n-hexane to afford rust-coloured microcrystals (0.15 g). Complex (12) was prepared as maroon crystals by the analogous reaction of (2a) and *N*-iodosuccinimide.

$[Ir(C_5Me_5)$(*OO'*-acac)(*C*-acac)] (13).—A suspension of complex (1b) (0.25 g, 0.32 mmol), anhydrous $Na_2[CO_3]$ (0.15 g), and pentane-2,4-dione (0.3 cm^3, 3 mmol) in acetone (30 cm^3) was stirred (30 h, 25 °C). The solvent was removed *in vacuo* and the residue crystallised from acetone–light petroleum (b.p. 30—60 °C) to give yellow crystals of (13) (0.18 g).

$[Rh_2(C_5Me_5)_2(acac)_2][PF_6]_2$ (14b).—A suspension of (2a) (0.60 g, 1.61 mmol) and $Ag[PF_6]$ (0.41 g, 1.61 mmol) in dichloromethane (40 cm^3) was stirred for 1 h. A white solid was precipitated which was filtered off and the solvent was removed *in vacuo*. The product, a bright orange powder (0.71 g), was obtained from the residue by crystallisation from dichloromethane–di-isopropyl ether.

Complexes (14a), (15), and (16) were obtained by reaction of (2a), (4), and (5) with $Ag[BF_4]$, $Ag[PF_6]$, and $Tl[PF_6]$ respectively. ^{13}C N.m.r. of (15) ($C^2H_2Cl_2$): δ 8.9 (C_5*Me*$_5$), 13.9 (C_2H_5*C*H$_3$), 18.9 (CH_2*C*H$_2$Me), 44.4 (*C*H$_2$C$_2$H$_5$), 31.1 (*Me*CO), 97.1 [d, J(C–Rh) = 9.2 Hz, *C*$_5$Me$_5$], 193.4 (CO), and 199.1 p.p.m. (CO).

$[Rh(C_5Me_5)(NCMe)(hfac)][PF_6]$ (17).—A solution of $[Rh(C_5Me_5)Cl(hfac)]$ (0.20 g, 0.42 mmol) and $Ag[PF_6]$ (0.11 g, 0.42 mmol) in acetonitrile (30 cm^3) was stirred for 3 h; during this time a white solid precipitated. The precipitate was filtered off and the solvent was removed *in vacuo*. The product was obtained as yellow microcrystals (0.11 g) from acetonitrile–di-isopropyl ether [ν(CN) at 2 339 cm^{-1}]. When a larger amount (0.84 mmol) of $Ag[PF_6]$ was used the product (79%) was $[Rh(C_5Me_5)(NCMe)_3][PF_6]_2$.

$[Rh(C_5Me_5)(acac)(PPh_3)][PF_6]$ (18).—A suspension of $[Rh_2(C_5Me_5)_2(acac)_2][PF_6]_2$ (0.20 g, 0.20 mmol) and PPh_3

(0.11 g, 0.41 mmol) in acetone (30 cm^3) was stirred for 3 h; the solid dissolved to give a clear orange solution. The solvent was removed *in vacuo* and the product was obtained as orange crystals (0.3 g) from dichloromethane–di-isopropyl ether. ^{31}P-{H} N.m.r. (C^2HCl_3): δ 30.4 [d, J(P–Rh) = 146.5 Hz, PPh_3] and −144.1 p.p.m. [septet, J(P–F) = 708.8 Hz, PF_6].

Complexes (19) {^{31}P-{H} n.m.r. (C^2HCl_3): δ 114.6 [d, J(P–Rh) = 234.4 Hz, $P(OEt)_3$] and −144.1 p.p.m. [septet, J(P–F) = 710.4 Hz, PF_6^-]}, (20) [ν(NC) at 2 212 cm^{-1}], and (21)—(23) were prepared analogously.

$[Rh(C_5Me_5)(hfac)(PPh_3)][PF_6]$ (24).—A solution of $[Rh(C_5Me_5)(NCMe)(hfac)][PF_6]$ (0.20 g, 0.32 mmol) and PPh_3 (0.08 g, 0.32 mmol) in dichloromethane (20 cm^3) was stirred for 3 h. The solvent was then removed *in vacuo* and the product, an orange powder (0.11 g), was obtained from the residue by crystallisation from dichloromethane–di-isopropyl ether.

$[Rh(C_5Me_5)Cl(N_3R_2)]$ (25a, 25b) *and* (31).—A suspension of $[Rh_2(C_5Me_5)_2Cl_4]$, (0.40 g, 0.65 mmol), $PhN_3(H)Ph$ (0.26 g, 1.29 mmol) and $Na_2[CO_3]$ (1.00 g) in acetone (60 cm^3) was stirred for 15 h. The solvent was removed *in vacuo* and the product was dissolved in dichloromethane (10 cm^3). The solution was then filtered to remove NaCl and $Na_2[CO_3]$ and the product was crystallised to afford pale red crystals (0.52 g) on addition of di-isopropyl ether. The complexes (25b; R = p-MeC_6H_4) and $[Rh(C_5Me_5)Cl(PhNCMeNPh)]$ (31) were prepared analogously.

$[Rh(C_5Me_5)Cl\{N_3(C_6H_4Cl\text{-}p)_2\}]$ (25c).—A suspension of $[Rh_2(C_5Me_5)_2Cl_4]$ (0.20 g, 0.32 mmol) and $Ag[ClC_6H_4N_3C_6H_4Cl]$ (0.24 g, 0.65 mmol) in acetone (30 cm^3) was stirred for 2 h. The solution was then filtered to remove AgCl and the solvent was removed *in vacuo*. The product was crystallised from dichloromethane–di-isopropyl ether to afford red microcrystals (0.28 g). The complex $[Rh(C_5Me_5)\{N_3(C_6H_4Cl\text{-}p)_2\}(N_3)]$ (28) [$\nu(N_3)$ at 2 018 cm^{-1}] was obtained analogously from $[Rh_2(C_5Me_5)_2Cl_2(N_3)_2]$ and $Ag[N_3R_2]$.

$[Rh(C_5Me_5)(NCMe)(PhN_3Ph)][PF_6]$ (26a).—A suspension of $[Rh(C_5Me_5)Cl(\eta^2\text{-}PhN_3Ph)]$ (0.20 g, 0.43 mmol) and $Ag[PF_6]$ (0.11 g, 0.43 mmol) in acetonitrile (20 cm^3) was stirred for 1 h. The solution was then filtered to remove AgCl and the solvent was removed *in vacuo*. The orange product was crystallised from acetonitrile–di-n-butyl ether to afford an orange powder (0.21 g). The complex $[Rh(C_5Me_5)(NCMe)(PhNCMeNPh)][PF_6]$ (32) was prepared by the same method.

$[Rh(C_5Me_5)(PhN_3Ph)\{P(OMe)_3\}][PF_6]$ (26b).—A suspension of $[Rh(C_5Me_5)Cl(PhN_3Ph)]$ (0.20 g, 0.43 mmol), $Ag[PF_6]$ (0.11 g, 0.43 mmol), and $P(OMe)_3$ (0.05 g, 0.43 mmol) in acetone (20 cm^3) was stirred for 3 h. The colour changed from dark red to orange. The solution was then filtered to remove AgCl and the solvent was removed *in vacuo*. The product was crystallised from dichloromethane–di-isopropyl ether to afford golden brown crystals (0.22 g). Complex (33), $[Rh(C_5Me_5)(PhNCMeNPh)(PPh_3)][PF_6]$, was obtained analogously.

$[Rh_2(C_5Me_5)_2(N_3)_4\{\mu\text{-}PhN_3(H)Ph\}]$ (30a).—A solution of $[Rh_2(C_5Me_5)_2(N_3)_4]$ (0.20 g, 0.31 mmol) and PhNHN=NPh (0.12 g, 0.62 mmol) in acetone (30 cm^3) was stirred for 6 h. A red solid precipitated which was filtered off, washed with diethyl ether (3 × 10 cm^3) to remove excess of PhNHN=NPh, and crystallised from dichloromethane–n-hexane to afford bright red crystals (0.24 g) [$\nu(N_3)$ at 2 028, 2 052 cm^{-1} ($CHCl_3$ solution); 2 006, 2 015, and 2 051 cm^{-1} (Nujol)].

Complex (30b), $[Rh_2(C_5Me_5)_2(N_3)_4]$, was prepared analogously [$\nu(N_3)$ at 2 028, 2 052 ($CHCl_3$ solution); 2 010, 2 028, and 2 047 cm^{-1} (Nujol)]. ^{13}C N.m.r. ($C^2H_2Cl_2$): δ 7.8 (s, C_5Me_5), 20.9 (s, C_6H_4Me), 93.0 [d, J(C–Rh) = 9.2 Hz, C_5Me_5], 117.6, 129.7, and 134.6 p.p.m. (C_6H_4Me).

$[Rh(C_5Me_5)(\eta^3\text{-}MeC_3H_4)L][PF_6]$ (34).—These complexes were prepared from $[Rh(C_5Me_5)(\eta^3\text{-}MeC_3H_4)Cl]$ by the methods described for complexes (17) and (26b); the complexes were crystallised from dichloromethane–di-isopropyl ether [(34b), (34c)] or acetone–di-isopropyl ether [(34b), (34c)].

X-*Ray Crystal-structure Determination of* $[Rh_2(C_5Me_5)_2(acac)_2][BF_4]_2$ (14a).—A crystal of complex (14a) was obtained from a sample made as described above and crystallised from dichloromethane–di-isopropyl ether.

Crystal data. $C_{30}H_{44}O_4Rh_2 \cdot 2BF_4^-$, M = 848.10, Monoclinic, a = 12.320(5), b = 16.951(7), c = 8.417(5) Å, β = 98.17(1)°, U = 1 739.9 Å^3, D_c = 1.618 g cm^{-3}, Z = 2, space group $P2_1/n$ (non-standard setting of no. 14 C_{2h}^5) from systematic absences, crystal size 0.018 × 0.018 × 0.024 cm, μ = 10.04 cm^{-1}, Mo-K_α radiation, λ = 0.710 69 Å. Cell constants were determined from a least-squares fit to the setting angles of 83 reflections centred manually.

Three-dimensional X-ray data ($6.5 < 2\theta \leqslant 50°$) were collected, with the crystal mounted along the c axis using a Stoe STADI-2 diffractometer, by the stationary counter–moving crystal method. Scans of variable width were measured with a background count at each extremity of the scan. 2 384 Independent reflections were collected with $I_{obs.} \geqslant 3\sigma(I_{obs.})$ and Lorentz and polarisation corrections were applied to the data. No allowance was made for absorption or extinction. The structure was solved using Patterson and Fourier methods; each dimer contains a crystallographic centre of symmetry and two acetylacetonate ligands bridge the two rhodium atoms (Figure 1).

TABLE 4

Atomic co-ordinates (× 10^4; × 10^5 for Rh) for complex (14a)

Atom	x	y	z
Rh	117 250(3)	102 747(3)	7 763(5)
F(01)	15 557(6)	12 071(4)	2 061(7)
F(02)	15 144(4)	11 230(3)	3 891(7)
F(03)	16 851(3)	11 693(3)	4 090(6)
F(04)	15 502(5)	12 512(3)	4 526(7)
O(01)	9 088(3)	9 482(2)	1 540(5)
O(02)	9 579(3)	9 146(2)	−1 647(5)
C(01)	10 044(5)	9 212(3)	1 905(7)
C(02)	10 836(4)	9 092(3)	809(7)
C(03)	10 466(5)	8 922(3)	−864(7)
C(04)	10 383(6)	8 985(4)	3 633(7)
C(05)	11 195(5)	8 410(4)	−1 752(9)
C(06)	13 356(4)	10 142(3)	216(7)
C(07)	13 127(4)	10 982(4)	361(7)
C(08)	12 903(5)	11 122(4)	1 929(7)
C(09)	12 989(4)	10 383(1)	2 796(7)
C(10)	13 309(4)	9 791(4)	1 746(7)
C(11)	13 673(5)	9 755(5)	−1 255(8)
C(12)	13 152(6)	11 578(4)	−963(9)
C(13)	12 598(6)	11 908(4)	2 588(10)
C(14)	12 893(6)	10 292(5)	4 559(7)
C(15)	13 612(5)	8 941(4)	2 176(9)
B	15 752(7)	11 887(5)	3 651(11)

The structure has refined using block-diagonal least squares to an R of 0.034, with anisotropic thermal parameters for all non-hydrogen atoms.

Atomic scattering factors were taken from ref. 22. Calculations were performed on the Sheffield University ICL

1906S computer using programs from the Sheffield *X*-ray System. Atomic co-ordinates are given in Table 4 and important bond lengths and bond angles in Table 5. Tables of observed and calculated structure factors, thermal parameters, and complete bond-length and bond-angle data for the structure are listed as Supplementary Publication No. SUP 22392 (33 pp.).*

TABLE 5

Bond lengths (Å) and bond angles (°) in $[Rh_2(C_5Me_5)_2(acac)_2][BF_4]_2$ (14a) with estimated standard deviations in parentheses

Rh–O(1)	2.103(4)	C(6)–C(7)	1.459(8)
Rh–O(2)	2.101(4)	C(7)–C(8)	1.406(8)
Rh–C(2′)	2.287(6)	C(8)–C(9)	1.446(8)
Rh–C(6)	2.140(6)	C(9)–C(10)	1.429(8)
Rh–C(7)	2.171(6)	C(10)–C(6)	1.427(8)
Rh–C(8)	2.170(6)	C(6)–Me(11)	1.502(9)
Rh–C(9)	2.144(6)	C(7)–Me(12)	1.509(10)
Rh–C(10)	2.166(6)	C(8)–Me(13)	1.512(10)
C(1)–O(1)	1.260(7)	C(9)–Me(14)	1.513(9)
C(3)–O(2)	1.252(7)	C(10)–Me(15)	1.519(9)
C(1)–Me(4)	1.505(9)		
C(3)–Me(5)	1.520(9)		
C(1)–C(2)	1.449(8)		
C(2)–C(3)	1.446(8)		
C(2′)–Rh–O(1)	91.0(2)	C(6)–C(7)–C(8)	108.0(5)
C(2′)–Rh–O(2)	90.8(2)	C(7)–C(8)–C(9)	108.5(5)
O(1)–Rh–O(2)	86.8(2)	C(8)–C(9)–C(10)	107.6(5)
C(1)–C(2)–C(3)	120.0(5)	C(9)–C(10)–C(6)	108.4(5)
C(1)–C(2)–Rh′	104.6(4)	C(10)–C(6)–C(7)	107.4(5)
C(3)–C(2)–Rh′	104.4(4)		

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