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Homo- and hetero-bridged mixed-valence dinuclear complexes which contain the fragment '$Rh(C_6F_5)_3$'

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Abstract

The reaction of the anionic mononuclear rhodium complex $[Rh(C_6F_5)_3Cl(Hpz)]^-$ (Hpz = pyrazole, $C_3H_4N_2$) with methoxo or acetylacetonate complexes of Rh or Ir led to the heterodinuclear anionic compounds $[(C_6F_5)_3Rh(\mu\text{-}Cl)(\mu\text{-}pz)M(L_2)]$ [M = Rh, L_2 = cyclo-octa-1,5-diene, COD (**1**), tetrafluorobenzobarrelene, TFB (**2**) or $(CO)_2$ (**4**); M = Ir, L_2 = COD (**3**)]. The complex $[Rh(C_6F_5)_3(Hbim)]^-$ (**5**) has been prepared by treating $[Rh(C_6F_5)_3(acac)]^-$ with H_2bim (acac = acetylacetonate; H_2bim = 2,2′-biimidazole). Complex **5** also reacts with Rh or Ir methoxo, or with Pd acetylacetonate, complexes affording the heterodinuclear complexes $[(C_6F_5)_3Rh(\mu\text{-}bim)M(L_2)]^-$ [M = Rh, L_2 = COD (**6**) or TFB (**7**); M = Ir, L_2 = COD (**8**); M = Pd, L_2 = η^3-C_3H_5 (**9**)]. With $[Rh(acac)(CO)_2]$, complex **5** yields the tetranuclear complex $[\{(C_6F_5)_3Rh(\mu\text{-}bim)Rh(CO)_2\}_2]^{2-}$. Homodinuclear Rh^{III} derivatives $[\{Rh(C_6F_5)_3\}_2(\mu\text{-}L)_2]^{2-}$ [L_2 = OH, pz (**11**); OH, S^{t}Bu (**12**); OH, SPh (**13**); bim (**14**)] have been obtained by substitution of one or both hydroxo groups of the dianion $[\{Rh(C_6F_5)_3(\mu\text{-}OH)\}_2]^{2-}$ by the corresponding ligands. The reaction of $[Rh(C_6F_5)_3(Et_2O)_x]$ with $[PdX_2(COD)]$ produces neutral heterodinuclear compounds $[(C_6F_5)_3Rh(\mu\text{-}X)_2Pd(COD)]$ [X = Cl (**15**); Br (**16**)]. The anionic complexes **1–14** have been isolated as the benzyltriphenylphosphonium ($PBzPh_3^+$) salts.

Keywords: Rhodium; Palladium; Iridium; Heteronuclear bridged species; Homonuclear bridged species; Syntheses

1. Introduction

Dinuclear transition-metal complexes have attracted considerable interest in recent years [1]. Many types of dinuclear complex with bridging ligands have been synthesized and used in studies of electron-transfer processes and metal–metal interactions [2]. Among bridging ligands, azolate-type heterocycles can yield dinuclear homo- or hetero-metallic complexes with interesting properties [3]. One of the synthetic routes to azolate dinuclear complexes is the reaction of mononuclear derivatives containing this acidic ligand with mononuclear compounds containing a proton abstractor such as methoxo or acetylacetonate groups. In this way, homo- or hetero-dinuclear azolate-bridged complexes containing '(*p*-cymene)Ru' [4] or '$(C_5Me_5)M$' (M = Rh [5] or Ir [6]) fragments joined to Rh^I, Rh^{III}, Ir^I or Pd^{II} have been prepared in our laboratory. Since the 'Ru(arene)' and '$M^{III}(C_5Me_5)$' units are isoelectronic with the '$Rh^{III}(C_6F_5)_3$' moiety, we have also researched the ability of this last fragment to form dinuclear compounds. For this purpose, we prepared the anionic homodinuclear complex $[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}Cl)_2]$ [7] by reaction of the homoleptic $[P(CH_2Ph)Ph_3]_2[Rh(C_6F_5)_5]$ [8] with HCl. Cleavage of the chloro bridges in this complex by neutral bidentate ligands [9], or their substitution by other anionic groups, such as halogen, pseudo-halogen or oxygen-donor ligands [10], yielded homodinuclear rhodium(III) compounds.

As a continuation of our work, we have prepared now heterodinuclear and heterobridged complexes containing the '$Rh^{III}(C_6F_5)_3$' moiety. We have used as starting materials either complexes with an acidic proton (N—H), reacting with methoxo or acetylacetonate complexes, or the dihydroxo derivative $[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}OH)_2]$ [10] in which one or both of the hydroxo groups can be substituted by other anionic ligands. Here we describe the synthesis of anionic heterodinuclear, homo- and hetero-bridged compounds in which the fragment '$Rh^{III}(C_6F_5)_3$' is bonded to Rh^I, Ir^I or Pd^{II} moieties, and rhodium(III) homodinu-

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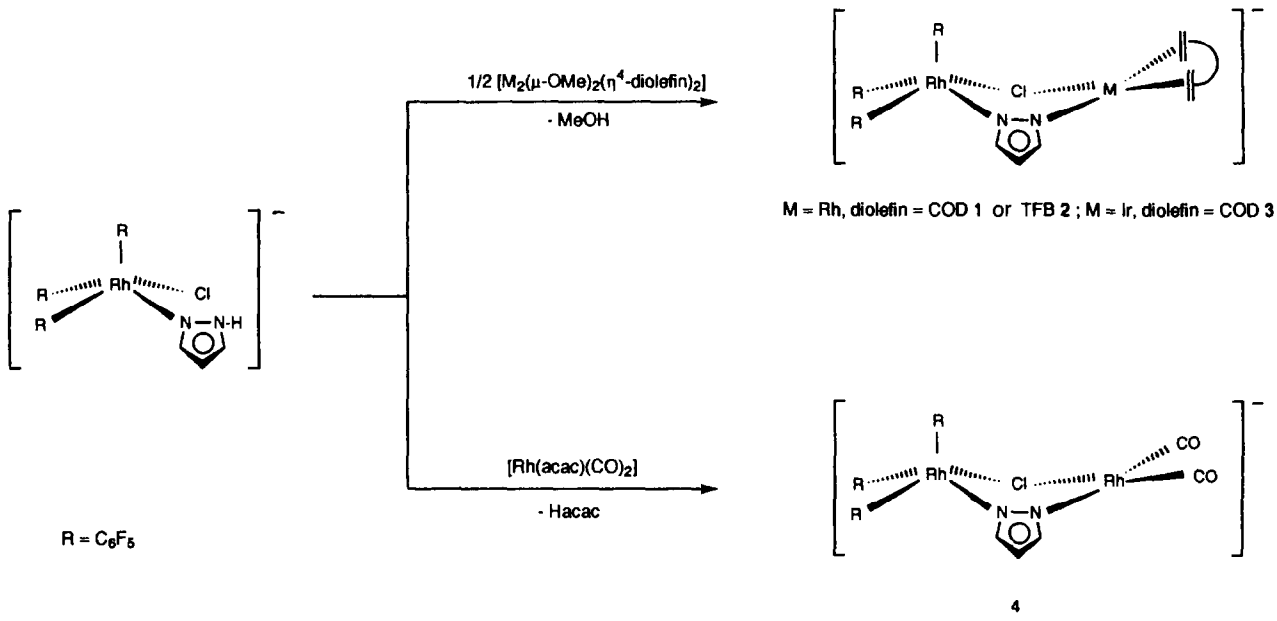


Scheme 1.

clear compounds in which the metal atoms are joined to one another by mixed bridged ligands.

2. Results and discussion

2.1. Dinuclear Rh^{III}—Rh^{I} and Rh^{III}—Ir^{I} (chloro)(pyrazolate)-bridged complexes

The acidic N—H group of the pyrazole ligand in the compound $(PBzPh_3)[Rh(C_6F_5)_3Cl(Hpz)]$ (Hpz = pyrazole, $C_3H_4N_2$) [7] is capable of reacting with the methoxo-bridged rhodium or iridium dimers $[M_2(\mu\text{-}OMe)_2(\eta^4\text{-diolefin})_2]$, or with acetylacetonate complexes, to give heterobridged compounds. For example, the complexes $[PBzPh_3][(C_6F_5)_3Rh(\mu\text{-Cl})(\mu\text{-pz})M(\eta^4\text{-diolefin})]$ [M = Rh, diolefin = cyclo-octa-1,5-diene, COD (**1**) or tetrafluorobenzobarrelene, TFB (**2**); M = Ir, diolefin = COD (**3**)] are formed by addition of a stoichiometric amount of $[PBzPh_3][Rh(C_6F_5)_3Cl(Hpz)]$ to suspensions of the dimers in acetone (Scheme 1). When carbon monoxide is bubbled through dichloromethane solutions of **1** or **2**, the displacement of the diolefin has been observed in solution but only mixtures of com-

Table 1
Analysis, colour, yields and conductance for the new complexes

Compound	Analysis (%) [a]			Colour	Yield (%)	Λ_M (C) [b]
	N	C	H			
$[PBzPh_3][(C_6F_5)_3Rh(\mu\text{-Cl})(\mu\text{-pz})Rh(COD)]$ (**1**)	2.14 (2.20)	52.01 (52.02)	3.20 (2.93)	Yellow	93	104 (9.75×10^{-5})
$[PBzPh_3][(C_6F_5)_3Rh(\mu\text{-Cl})(\mu\text{-pz})Rh(TFB)]$ (**2**)	2.01 (2.02)	50.13 (50.15)	2.69 (2.25)	Orange	77	96 (1.32×10^{-4})
$[PBzPh_3][(C_6F_5)_3Rh(\mu\text{-Cl})(\mu\text{-pz})Ir(COD)]$ (**3**)	1.99 (2.05)	47.19 (47.67)	2.91 (2.74)	Orange	78	96 (1.03×10^{-4})
$[PBzPh_3][(C_6F_5)_3Rh(\mu\text{-Cl})(\mu\text{-pz})Rh(CO)_2]$ (**4**)	2.24 (2.30)	47.57 (47.27)	2.31 (2.06)	Red	56	101 (1.30×10^{-4})
$[PBzPh_3][Rh(C_6F_5)_3(Hbim)]$ (**5**)	4.89 (5.14)	54.22 (53.96)	2.39 (2.49)	Orange	69	92 (4.88×10^{-4})
$[PBzPh_3][(C_6F_5)Rh(\mu\text{-bim})Rh(COD)]$ (**6**)	4.17 (4.31)	52.33 (52.63)	2.86 (2.94)	Yellow	51	105 (2.60×10^{-4})
$[PBzPh_3][(C_6F_5)_3Rh(\mu\text{-bim})Rh(TFB)]$ (**7**)	3.84 (3.95)	51.36 (51.64)	2.56 (2.27)	Orange	68	99 (2.40×10^{-4})
$[PBzPh_3][(C_6F_5)_3Rh(\mu\text{-bim})Ir(COD)]$ (**8**)	3.93 (4.03)	48.97 (49.25)	2.82 (2.75)	Yellow	84	91 (2.74×10^{-4})
$[PBzPh_3][(C_6F_5)_3Rh(\mu\text{-bim})Pd(\eta^3\text{-}C_3H_5)]$ (**9**)	4.50 (4.53)	50.16 (50.49)	2.86 (3.01)	Yellow	65	105 (2.94×10^{-4})
$[PBzPh_3]_2[\{(C_6F_5)_3Rh(\mu\text{-bim})Rh(CO)_2\}_2]$ (**10**)	4.44 (4.48)	48.87 (49.06)	1.81 (2.09)	Orange	48	99 (2.66×10^{-4})
$[PBzPh_3]_2[\{(C_6F_5)_3Rh\}_2(\mu\text{-OH})(\mu\text{-pz})]$ (**11**)	1.34 (1.40)	53.30 (53.47)	2.47 (2.42)	Orange	63	182 (1.69×10^{-4})
$[PBzPh_3]_2[\{(C_6F_5)_3Rh\}_2(\mu\text{-OH})(\mu\text{-}^tBuS)]$ (**12**)	–	53.65 (53.49)	2.93 (2.69)	Red	95	204 (2.30×10^{-4})
$[PBzPh_3]_2[\{(C_6F_5)_3Rh\}_2(\mu\text{-OH})(\mu\text{-SPh})]$ (**13**)	–	54.25 (54.13)	2.73 (2.42)	Red	86	197 (1.56×10^{-4})
$[PBzPh_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-bim})]$ (**14**)	2.82 (2.73)	53.79 (53.84)	2.51 (2.60)	Yellow	81	204 (1.79×10^{-4})
$[(C_6F_5)_3Rh(\mu\text{-Cl})_2Pd(COD)]$ (**15**)	–	35.05 (35.10)	1.48 (1.36)	Orange	73	–
$[(C_6F_5)_3Rh(\mu\text{-Br})_2Pd(COD)]$ (**16**)	–	31.85 (31.91)	1.44 (1.23)	Red	67	–

[a] Calculated values are given in parentheses. [b] $\Lambda_M(\Omega^{-1}\ cm^2\ mol^{-1})$, C (mol dm^{-3}) in acetone.

pounds which cannot be totally identified are isolated from the oily residue. However, the complex $[PBzPh_3][(C_6F_5)_3Rh(\mu\text{-Cl})(\mu\text{-pz})Rh(CO)_2]$ (**4**) is prepared by the reaction of the Rh^I compound $[Rh(acac)(CO)_2]$ with the Rh^{III} complex $[PBzPh_3][Rh(C_6F_5)_3Cl(Hpz)]$ (Scheme 1).

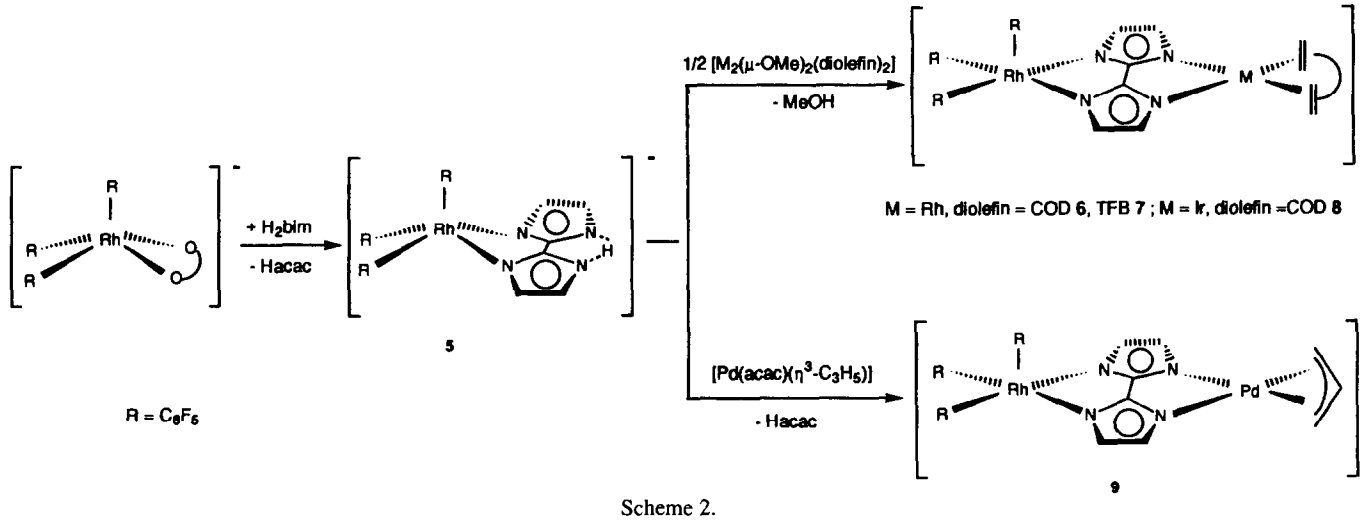
Deprotonation of the pyrazole ligand and formation of the heterobridged dinuclear complexes takes place under very mild conditions (room temperature). The reactions are faster with the methoxo compound than with the acetylacetonato complex, consistent with the basic behaviour of both groups. Under similar conditions, the reactions of $[PBzPh_3][Rh(C_6F_5)_3Cl(Hdmpz)]$ (Hdmpz = 3,5-dimethylpyrazole) with $[Rh_2(\mu\text{-OMe})_2(\eta^4\text{-diolefin})_2]$ did not lead to the expected heterobridged complexes. Instead, redistribution reactions took place to give the known products $[PBzPh_3]_2[\{Rh(C_6F_5)_3(\mu\text{-Cl})\}_2]$ [7] and $[Rh_2(\mu\text{-dmpz})_2(\eta^4\text{-diolefin})_2]$ [11] which were separated by fractional crystallization and identified by analytical and spectroscopic data.

Analytical results (C, H and N), reactions yields, colours and conductivities for the new complexes are listed in Table 1. Complexes **1–4** are stable in air in the solid state but in solution they decompose within a few minutes. They are soluble in common organic solvents but not soluble in hexane. Their conductivities in acetone solution are those expected for electrolytic dinuclear 1 : 1 complexes [12]. The IR spectra of the complexes show the characteristic bands of the pentafluorophenyl group [13] and the phosphonium cation, and no N—H absorption. Compound **4** in dichloromethane solution shows two bands in the carbonyl region, at 2005 and 2090 cm^{-1}, which are expected for a *cis*-dicarbonyl [14]. The ^1H NMR spectra of the complexes are in accordance with the proposed structure. The signals due to the hydrogen atoms of the pyrazolate groups are difficult to assign because they overlap with those of the phosphonium cations. In the related pentacoordinated complexes [8–10] containing the '$Rh(C_6F_5)_3$' unit, the ^{19}F NMR spectra show time-averaged signals at ca. room temperature for the fluorine atoms of the pentafluorophenyl rings. On cooling the samples, the rotation or isomerization processes slow, yielding spectra with distinct signals for all (or most) of the fluorine atoms.

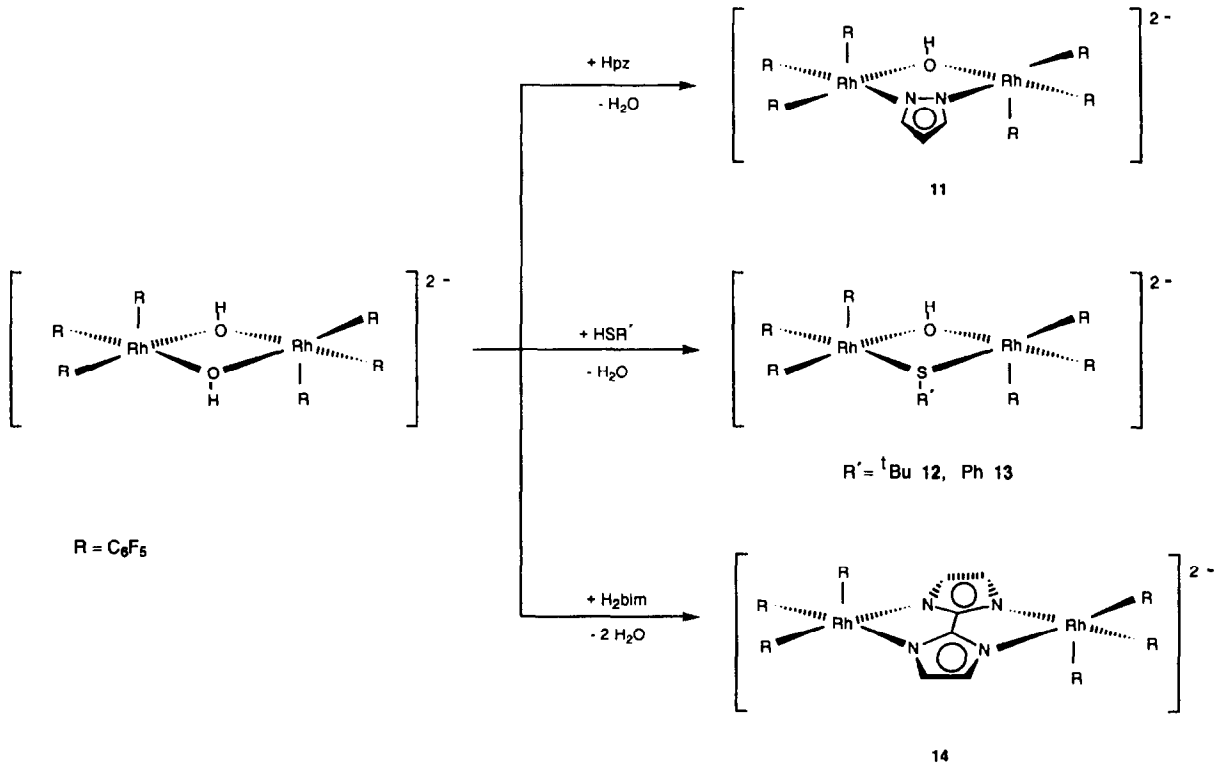
2.2. Dinuclear Rh^{III}—Rh^I, Rh^{III}—Ir^I and Rh^{III}—Pd^{II} bi-imidazolate-bridged complexes

Homo- and hetero-dinuclear complexes with the bi-imidazolate dianion coordinated in a tetradentate manner have been obtained from the anionic complex $[Rh(C_6F_5)_3(Hbim)]^-$ (**5**). This compound is prepared by treatment of $[Rh(C_6F_5)_3(acac)]^-$ with 1 mol of H_2bim. The spectroscopic data are consistent with complex **5** containing bidentate $Hbim^-$ [15]. The broad IR spectrum, from 3000–2300 cm^{-1} indicates an N—H bond remaining in the coordinated monoanion. By reaction of **5** with $[M_2(\mu\text{-OMe})_2(\eta^4\text{-diolefin})_2]$ or $[Pd(acac)(\eta^3\text{-}C_3H_5)]$, the methoxo or acetylacetonato groups are displaced and the dinuclear complexes $[PBzPh_3][(C_6F_5)_3Rh(\mu\text{-bim})M(L_2)]$ [M = Rh, L_2 = COD (**6**) or TFB (**7**); M = Ir, L_2 = COD (**8**); M = Pd, $L_2 = \eta^3\text{-}C_3H_5$ (**9**)] are formed (Scheme 2). The conductivity measurements, analytical, IR, NMR and mass spectra data (Table 1 and Experimental details) are consistent with the formulation of **6–9** as dinuclear complexes with the tetradentate bi-imidazole dianion coordinated to two metal atoms. The IR absorptions of the tetracoordinate bim^{2-} appear at 1410 and 1120 cm^{-1} [16]. The proton NMR spectra show the signals due to the diolefin ligands (**6–8**) or that of the allyl group (**9**).

However, the reaction of **5** with $[Rh(acac)(CO)_2]$ gives complex $[PBzPh_3]_n[\{(C_6F_5)_3Rh(\mu\text{-bim})Rh(CO)_2\}_n]$ (**10**), for which the equivalent conductivity as well as the mass spectrum seem to point to a tetranu-

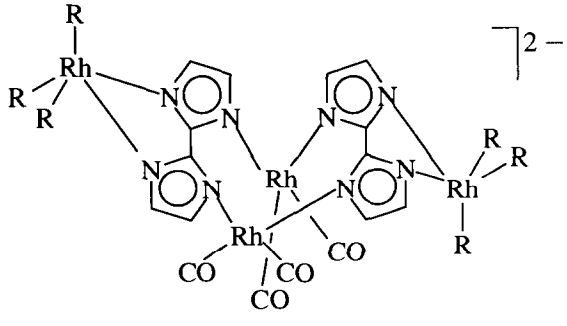


Scheme 2.



Scheme 3.

clear structure ($n = 2$). In the mass spectrum (FAB) of complex **10**, peaks of the $(M + PBzPh_3)^-$ and of the tetranuclear $(M)^-$ anion are evident. The equivalent conductivity at different concentrations (ranging from 10^{-3} to 10^{-5} equiv. l^{-1}) of compound **10** gives a value of A in Onsager's equation of -937, also indicating a 2:1 formulation. Furthermore, the IR spectrum in the solid state or in dichloromethane solution of this complex shows three strong absorptions ν(CO) at 2090, 2065 and 2030 cm^{-1}, which are consistent with the arrangement of the four carbonyl groups as shown below [17].



2.3. Homodinuclear Rh^{III}—Rh^{III} complexes

When the hydroxo-bridged complex $[PBzPh_3]_2[\{Rh(C_6F_5)_3(\mu\text{-}OH)\}_2]$ is treated with azoles such as Hpz or H_2bim, or with thiols, HSR, it yields homodinuclear bridged compounds $[PBzPh_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}OH)(\mu\text{-}L)]$ [L = pz (**11**), S^{t}Bu (**12**) or SPh (**13**)] and $[PBzPh_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-bim})]$ (**14**) (Scheme 3). These reactions imply protonation of the hydroxo groups and replacement by μ-azolato or μ-thiolate groups. When using the pyrazole or the thiols, only one of the hydroxo ligands is displaced, either if the reaction is carried out in 1:1 ratio or with an excess of the donor. For the H_2bim, both hydroxo groups are replaced and the bi-imidazolate dianion is coordinated tetradentally to two rhodium atoms.

2.4. Dinuclear Rh^{III}—Pd^{II} halogen-bridged complexes

Neutral compounds with two halogens *cis* are good precursors for compounds of higher nuclearity [18] and so, when diethyl ether solutions containing the solvated species $[Rh(C_6F_5)_3(Et_2O)_x]$ are added to dichloromethane solutions of $[PdX_2(COD)]$, the neutral dinuclear complexes $[(C_6F_5)_3Rh(\mu\text{-}X)_2Pd(COD)]$ [X = Cl (**15**) or Br (**16**)] are obtained [Eq. (1)]. They were characterized by elemental analysis and spectroscopic data.

$$[Rh(C_6F_5)_3(Et_2O)_x] + [PdX_2(COD)] \rightarrow [(C_6F_5)_3Rh(\mu\text{-}X)_2Pd(COD)] \quad (1)$$

3. Experimental details

3.1. General considerations

All reactions were carried out under dinitrogen at room temperature using Schlenk techniques. Solvents were dried by standard methods and distilled under dinitrogen prior to use. The starting materials, $[Rh_2(\mu\text{-}OMe)_2(\eta^4\text{-diolefin})_2]$, (diolefin = COD or TFB), $[Ir_2(\mu\text{-}OMe)_2(\eta^4\text{-COD})_2]$ [19], $[Rh(acac)(CO)_2]$ [20], $[PBzPh_3][Rh(C_6F_5)_3Cl(Hpz)]$, $[PBzPh_3][Rh(C_6F_5)_3(acac)]$, $[Rh(C_6F_5)_3(OEt_2)_x]$ [7] and $[PBzPh_3]_2[\{Rh(C_6F_5)_3\}_2(\mu\text{-}OH)_2]$ [10] were prepared according to reported methods.

3.2. Physical measurements

IR spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer 783 spectrophotometer using Nujol mulls between polyethylene sheets or in solution in NaCl cells. ^1H and ^{19}F NMR spectra were recorded on a Varian XL-200 spectrometer operating at 200.057 and 188.220 MHz, respectively (in deuterochloroform, $CDCl_3$ or acetone-d_6, HDA, as solvents); chemical shifts are relative to $CFCl_3$ and $SiMe_4$ as external references. Elemental analyses were carried out with a Perkin-Elmer 240C microanalyzer. Mass spectra were measured in a VG Autospec spectrometer operated in the negative mode for anionic species and in the positive mode for neutral complexes. Ions were produced with the standard Cs^+ gun at ca. 30 kV; 3-nitrobenzyl alcohol (NBA) was used as matrix. High-resolution FAB spectra were confirmed by the simulated isotopic pattern distribution.

3.3. Preparation of $[PBzPh_3][(C_6F_5)_3Rh(\mu\text{-}Cl)(\mu\text{-}pz)M(diolefin)]$ [M = Rh, diolefin = COD (1) or TFB (2); M = Ir, diolefin = COD (3)]

To suspensions of the dimer compounds $[M_2(\mu\text{-}OMe)_2(\eta^4\text{-diolefin})_2]$ (M = Rh, diolefin = COD, 34.2 mg, 0.07 mmol; M = Rh, diolefin = TFB, 50.8 mg, 0.07 mmol; M = Ir, diolefin = COD, 46.4 mg, 0.07 mmol) in acetone (10 cm^3), solid $[PBzPh_3][Rh(C_6F_5)_3Cl(Hpz)]$ (150 mg, 0.141 mmol) was added. The initial solids slowly dissolved. After being stirred for 1 h at room temperature, the solvent was pumped off. The oily residues formed were washed with two fractions of hexane (1 cm^3) and stirred in hexane (10 cm^3). The solids obtained were filtered off, washed with hexane and vacuum-dried.

Data for **1**: MS (FAB) *m/e*: 917 (M^-, 15%). ^1H NMR ($CDCl_3$, −50°C) δ: 7.8–6.8 (20H, $PBzPh_3^+$ + 3H, pz); 4.2 (d, $-CH_2Bz$, 2H, $^2J_{P-H}$ = 14.2 Hz + 1H, =CH, COD); 3.9, 3.7, 3.4 (s, 3H, 1:1:1, =CH, COD); 1.7, 1.2, 0.8 (8H, 4:2:2, $-CH_2$, COD) ppm. ^{19}F NMR ($CDCl_3$, −50°C) δ: *o*-F: −113.6 (ft), −118.5 (ft), −123.1 (ft), −123.6 (ft), −127.2 (m), −132.0 (ft) (1:1:1:1:1:1) ppm; *m*-F and *p*-F: complex signal from −162.8 to −167.2 ppm.

Data for **2**: MS (FAB) *m/e*: 1035 (M^-, 66%). ^1H NMR ($CDCl_3$, −50°C) δ: 7.8–7.0 (20H, $PBzPh_3^+$); 6,6 (m, 1H, H^3 or H^5 pz); 6.1 (m, 1H, H^4, pz); 4.9 (m, 2H, −CH, TFB); 3.4, 3.1 (4H, 2:2, =CH, TFB) ppm. ^{19}F NMR ($CDCl_3$, −50°C) δ: *o*-F: −114.5 (fd), −118.8 (fd), −122.1 (ft), −123.3 (ft), −127.4 (m), −131.2 (ft) (1:1:1:1:1:1) ppm; *m*-F and *p*-F: complex signal from −162.8 to −168.6; −147.2 (m, 2F, TFB); −159.9 (d, 2F, TFB, $^3J_{F-F}$ = 19.5 Hz) ppm.

Data for **3**: MS (FAB) *m/e*: 899 [$(M - COD)^-$, 10%]. ^{19}F NMR ($CDCl_3$, −50°C) δ: *o*-F: −113.2 (fd), −116.1 (fd), −119.8 (ft), −123.5 (ft), −127.3 (m) (1:1:1:1:2) ppm; *m*-F and *p*-F: complex signal from −163.2 to −168.5 ppm.

3.4. Preparation of $[PBzPh_3][(C_6F_5)_3Rh(\mu\text{-}Cl)(\mu\text{-}pz)Rh(CO)_2]$ (4)

To a suspension of $[PBzPh_3][Rh(C_6F_5)_3Cl(Hpz)]$ (100 mg, 0.094 mmol) in dry diethyl ether (15 cm^3), $[Rh(acac)(CO)_2]$ (24.3 mg, 0.094 mmol) was added. The red solution was filtered throught kieselgur and taken to dryness by evaporation. The oil residue was washed with hexane (2 × 1 cm^3) and stirred in the same solvent (10 cm^3). The red solid was separated by filtration, washed with hexane and vacuum-dried. IR (dichloromethane solution) ν(CO) (cm^{-1}): 2005, 2090. ^{19}F NMR ($CDCl_3$, −50°C) δ: *o*-F: −120.5 (fd), −126.2 (m), −129.6 (m) (2:2:2) ppm; *m*-F and *p*-F: complex signal from −159.2 to −166.6 ppm.

3.5. Preparation of $[PBzPh_3][Rh(C_6F_5)_3(Hbim)]$ (5)

Solid bi-midazole (12.07 mg, 0.09 mmol) was added to a solution of $[PBzPh_3][Rh(C_6F_5)_3(acac)]$ (0.09 mmol) in THF (15 cm^3). The suspension was heated under reflux with stirring until the solid dissolved and then evaporated to dryness. The orange residue was stirred in 15 cm^3 of hexane, filtered off, washed with hexane and vacuum-dried. MS (FAB) *m/e*: 737 [$(M - H)^-$, 100%]; 604 [$(M - Hbim - H)^-$, 7%]. ^1H NMR (HDA, −60°C) δ: 7.9–7.1 (26H, $PBzPh_3^+$ + 4H, bim); 5.1 (d, $-CH_2Bz$, 2H, $^2J_{P-H}$ = 15.3 Hz); (N–H not seen) ppm. ^{19}F NMR (HDA, 20°C) δ: *o*-F: −123 (m) ppm; *m*-F: −168.4 (m) ppm, *p*-F: −166.5 (m) ppm. ^{19}F NMR (HDA, −60°C) δ: *o*-F: −114.6 (fd), −123.5 (fd), −127.7 (fd) (2:2:2) ppm; *m*-F and *p*-F: complex signal from −163.5 to −167.0 ppm.

3.6. Preparation of [PBzPh$_3$][(C_6F_5)$_3$Rh(μ-bim)M-(L_2)] [M = Rh, L_2 = COD (6) or TFB (7); M = Ir, L_2 = COD (8); M = Pd, L_2 = η^3-C_3H_5 (9)]

The procedures were similar to these for the preparation of complexes **1–3**. The starting materials were [PBzPh$_3$][Rh(C_6F_5)$_3$(acac)] for all and [M$_2$(μ-OMe)$_2$(η^4-diolefin)$_2$] for **6–8** or [Pd(acac)(η^3-C_3H_5)] — prepared in situ from [{Pd(μ-Cl)(η^3-C_3H_5)}$_2$] and [Tl(acac)]. The solids were precipitated from 2-propanol/hexane (1 : 5), separated by filtration, washed with hexane and vacuum-dried.

Data for **6**: MS (FAB) *m/e*: 947 (M^-, 30%); 737 [(M − Rh(COD))$^-$, 100%]. ^{1}H NMR (HDA, −60°C) δ: 7.9–7.1 (22H, $PBzPh_3^+$ + 1H, bim); 6.7, 6.6, 6.4 (3H, bim); 5.1 (d, $-CH_2Bz$, 2H, $^2J_{P-H}$ = 15.3 Hz); 4.3 (m, 2H, =CH, COD); 2.8 (m, 4H, =CH, $-CH_2$, COD); 2.3 (m, 2H, COD) ppm. ^{19}F NMR (HDA, 20°C) δ: *o*-F: −117.7 (m) ppm; *m*-F: −163.3 (m) ppm; *p*-F: −161.5 (ft) ppm. ^{19}F NMR (HDA, −60°C) δ: *o*-F: −114.1 (m), −122.9 (m), −126.2 (m), −128.0 (m) (2 : 2 : 1 : 1) ppm; *m*-F and *p*-F: complex signal from −162.8 to −167.8 ppm.

Data for **7**: MS (FAB) *m/e*: 1065 (M^-, 100%); 737 [(M − Rh(TFB))$^-$, 55%]; 604 [(M − bim − Rh(TFB))$^-$, 10%]. ^{1}H NMR (HDA, −60°C) δ: 7.8–7.0 (22H, $PBzPh_3^+$ + 3H, bim); 6.7 (1H, bim); 5.1 (d, $-CH_2Bz$, 2H, $^2J_{P-H}$ = 15.3 Hz); 3.4 (m, 2H, −CH, TFB); 2.0 (4H, 2 : 2, =CH, TFB) ppm. ^{19}F NMR ($CDCl_3$, 20°C) δ: *o*-F: −117 (m), −124 (m), −130 (m) (2 : 2 : 2) ppm; *m*-F and *p*-F: complex signal from −164 to −168 ppm.

Data for **8**: MS (FAB) *m/e*: 1037 (M^-, 36%); 737 [(M − Ir(COD))$^-$, 80%]; 604 [(M − bim − Ir(COD))$^-$, 20%]. ^{19}F NMR (HDA, −60°C) δ: *o*-F: −114.4 (m), −123.8 (m), −126.6 (m) (2 : 2 : 2) ppm; *m*-F and *p*-F: complex signal from −162.2 to −168.2 ppm.

Data for **9**: MS (FAB) *m/e*: 883 (M^-, 68%); 737 [(M − Pd(η^3-C_3H_5))$^-$, 100%]; 604 [(M − bim − Pd(η^3-C_3H_5))$^-$, 15%]. ^{1}H NMR (HDA, −60°C) δ: 7.9–7.0 (22H, $PBzPh_3^+$ + 4H, bim); 5.5 (m, 1H, −CH, η^3-C_3H_5); 5.1 (d, $-CH_2Bz$, 2H, $^2J_{P-H}$ = 15.3 Hz); 3.5 (m, 4H, $-CH_2$, η^3-C_3H_5) ppm. ^{19}F NMR ($CDCl_3$, −60°C) δ: *o*-F: −115.8 (m), −124.7 (m), −127.3 (m) (2 : 2 : 2) ppm; *m*-F and *p*-F: complex signal from −163.7 to −167.9 ppm.

3.7. Preparation of [PBzPh$_3$]$_2$[{(C_6F_5)$_3$Rh(μ-bim)Rh-(CO)$_2$}$_2$] (10)

The procedure was similar to that for the preparation of complexes **1–3**. The starting materials were [PBzPh$_3$][Rh(C_6F_5)$_3$(acac)] and [Rh(acac)(CO)$_2$]. Solid **10** was precipitated from 2-propanol/hexane (1 : 5), separated by filtration, washed with hexane and vacuum-dried. IR (dichloromethane solution) ν(CO) (cm^{-1}): 2030; 2065; 2090. IR (Nujol mull) ν(CO) (cm^{-1}): 2020, 2055, 2070. MS (FAB) *m/e*: 2143 [(M + PBzPh$_3$)$^-$, 90%]; 1791 (M^-, 15%); 895 (1/2M^-, 100%); 737 [(1/2M − Rh(CO)$_2$)$^-$, 44%]. ^{19}F NMR (HDA, 20°C) δ: *o*-F: −118 (m) ppm; *m*-F: −163.8 (m) ppm; *p*-F: −162.1 (m) ppm. ^{19}F NMR (HDA, −60°C) δ: *o*-F: −113.9 (m), −114.6 (m), −122.9 (m), −123.4 (m), −126.1 (m), −127.1 (m) (2 : 2 : 2 : 2 : 2 : 2) ppm; *m*-F and *p*-F: complex signal from −162.8 to −166.8 ppm.

3.8. Preparation of [PBzPh$_3$][(C_6F_5)$_3$Rh(μ-OH)(μ-pz)Rh(C_6F_5)$_3$] (11)

Solid pyrazole (3.49 mg, 0.05 mmol) was added to a suspension of [PBzPh$_3$]$_2$[{Rh(C_6F_5)$_3$}$_2$(μ-OH)$_2$] (97.5 mg, 0.05 mmol) in diethyl ether (10 cm^3). After 1 h of stirring, the orange solution was concentrated and the oily residue washed with several fractions of hexane (2 cm^3) and stirred in hexane (15 cm^3). The solid was filtered off, washed with hexane and vacuum-dried. MS (FAB) *m/e*: 1645 [(M + PBzPh$_3$)$^-$, 12%]; 1275 [(M − OH)$^-$, 12%]; 1225 [(M − pz)$^-$, 8%]. ^{1}H NMR ($CDCl_3$, 20°C) δ: 6.1 (s, 1H, −OH) ppm. ^{19}F NMR ($CDCl_3$, 20°C) δ: *o*-F: −120.4 (m) ppm; *m*-F: −167.3 (m) ppm; *p*-F: −166.2 (m) ppm. ^{19}F NMR ($CDCl_3$, −50°C) δ: *o*-F: −114.6 (m), −115.1 (m), −122.7 (m), −123.5 (m) (2 : 2 : 4 : 4) ppm; *m*-F: −166.8 (m) ppm; *p*-F: −164.9 (m) ppm.

3.9. Preparation of [PBzPh$_3$][(C_6F_5)$_3$Rh(μ-OH)(μ-X)Rh(C_6F_5)$_3$] [X = ^{t}BuS (12) or PhS (13)]

To a solution of [PBzPh$_3$]$_2$[{Rh(C_6F_5)$_3$}$_2$(μ-OH)$_2$] (97.5 mg, 0.05 mmol) in dichloromethane (10 cm^3) was added the corresponding thiol in excess (0.08 mmol). The red solutions which formed immediately were stirred for 10 min and taken to dryness. The oily residues were washed with two fractions of hexane (2 cm^3) and stirred in hexane (15 cm^3). The solids were filtered off, washed with hexane and vacuum-dried.

Data for **12**: MS (FAB) *m/e*: 1297 [(M − OH)$^-$, 11%]; 1225 [(M − ^{t}BuS)$^-$, 26%]. ^{19}F NMR (HDA, −70°C) δ: *o*-F: −104.6 (m), −118.5 (m), −120.9 (m), −121.3 (m), −124.3 (m) (2 : 2 : 2 : 2 : 4) ppm; *m*-F and *p*-F: complex signal from −163.8 to −168.5 ppm.

Data for **13**: MS (FAB) *m/e*: 1686 [(M + PBzPh$_3$)$^-$, 8%]; 1316 [(M − OH)$^-$, 22%]; 713 [Rh(C_6F_5)$_3$PhS, 75%]. ^{19}F NMR ($CDCl_3$, 20°C) δ: *o*-F: −108.1 (m), −121.0 (m) (4 : 8) ppm; *m*-F: −167.4 (m) ppm; *p*-F: −166.8 (m) ppm.

3.10. Preparation of [PBzPh$_3$]$_2$[{(C_6F_5)$_3$Rh}$_2$(μ-bim)] (14)

Solid bi-imidazole (12.07 mg, 0.09 mmol) was added to a solution of [PBzPh$_3$]$_2$[{Rh(C_6F_5)$_3$}$_2$(μ-OH)$_2$] (0.09 mmol) in THF (15 cm^3). The suspension was heated under reflux with stirring until the solid had dissolved,

and then taken to dryness. The orange residue was stirred in 15 cm^3 of hexane, filtered off, washed with hexane and vacuum-dried. MS (FAB) *m/e*: 1341 (M^-, 11%); 1173 [$(M - C_6F_5)^-$, 10%]; 737 [$(M - Rh(C_6F_5)_3)^-$, 100%]. ^1H NMR (HDA, −60°C) δ: 7.8–7.0 (22H, $PBzPh_3^+$ + 2H, bim); 6.7 (2H, bim); 5.1 (d, $-CH_2Bz$, 2H, $^2J_{P-H}$ = 15.3 Hz) ppm. ^{19}F NMR (HDA, 20°C) δ: *o*-F: −123 (m) ppm; *m*-F: −168.8 (m) ppm; *p*-F: −167.1 (ft) ppm. ^{19}F NMR (HDA, −60°C) δ: *o*-F: −114.4 (m), −123.8 (m), −126.5 (m) (4:4:4) ppm; *m*-F and *p*-F: complex signal from −163 to −168 ppm.

3.11. Preparation of $[(C_6F_5)_3Rh(\mu\text{-}X)_2Pd(COD)]$ [X = Cl (15) or Br (16)]

To solutions of $[PdX_2(COD)]$ (0.1 mmol) (X = Cl, 28.76 mg, X = Br, 37.71 mg) in dichloromethane (10 cm^3) were added solutions of $[Rh(C_6F_5)_3(OEt_2)_x]$ (0.1 mmol) in diethyl ether. After 15 min of stirring the coloured suspensions were concentrated to ca. 1 cm^3. The addition of 10 cm^3 of hexane gave orange solids which were filtered off, washed with hexane and vacuum-dried.

Data for **15**: MS (FAB): not resolved. ^1H NMR (HDA, 20°C) δ: 3.0 (m, 4H, =CH, COD); 2.7 (m, 8H, $-CH_2$, COD) ppm. ^{19}F NMR (HDA, 20°C) δ: *o*-F: −124.7 (fd) ppm; *m*-F: −165.0 (ft) ppm; *p*-F: −161.8 (ft) ppm. ^{19}F NMR (HDA, −80°C) δ: *o*-F: −122.2 (m) ppm; *m*-F: −165.0 (ft) ppm; *p*-F: −162.0 (ft) ppm.

Data for **16**: ^1H NMR (HDA, 20°C) δ: 2.8 (m, 4H, =CH, COD); 2.5 (m, 8H, $-CH_2$, COD) ppm. ^{19}F NMR (HDA, 20°C) δ: *o*-F: −124.8 (fd) ppm; *m*-F: −165.0 (ft) ppm; *p*-F: −161.7 (ft) ppm. ^{19}F NMR (HDA, −80°C) δ: *o*-F: −122.2 (m) ppm; *m*-F: −165.3 (ft) ppm; *p*-F: −162.2 (ft) ppm.

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