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SYNTHESIS AND REACTIVITY OF MONO- AND HETERO-NUCLEAR RHODIUM(I) OR IRIDIUM(I) COMPLEXES WITH 2-(2′-PYRIDYL)BENZIMIDAZOLE

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Summary

Rhodium(I) and iridium(I) complexes of the formulae M(PyBzIm)(diolefin), [M(HPyBzIm)(diolefin)]ClO_4, (diolefin)M(μ-PyBzIm)AuCl, [(diolefin)M(μ-PyBzIm)AuL]ClO_4 (L = PPh_3 or $P(OMe)_3$), [(diolefin)M(μ-PyBzIm)$AgPPh_3$]ClO_4 and [Ag{M(μ-PyBzIm)(diolefin)}$_2$]ClO_4 (diolefin = COD or NBD) are described. The related carbonyl derivatives M(PyBzIm)(CO)Y, [Rh(HPyBzIm)(CO)Y]ClO_4 (Y = CO or PPh_3), $(CO)_2$M(μ-PyBzIm)AuCl, [$(CO)_2$Rh(μ-PyBzIm)Au$P(OMe)_3$]ClO_4, [Ag{M(μ-PyBzIm)$(CO)_2$}$_2$]ClO_4 and [Au{Rh(μ-PyBzIm)$(CO)_2$}$_2$]ClO_4 have been obtained by reaction of diolefin derivatives with carbon monoxide and triphenylphosphine.

Introduction

Increasing attention is being given to polynuclear transition metal compounds because of interest in possible effects derived from the mutual influence of neighbouring metal centres. Thus, the formation of polymetallic azolate complexes of rhodium and iridium was recently studied by our group [1–9], as well as in other laboratories [10–15]. In this field we have now focussed our attention on the ligand 2-(2′-pyridyl)benzimidazole, which has the appropriate features to behave as a bidentate chelating ligand towards rhodium(I) and iridium(I), with one nitrogen atom still capable of forming bonds to other metal centres.

In the present paper we describe the synthesis, properties and reactions of diolefin rhodium(I) or iridium(I) complexes of 2-(2′-pyridyl)benzimidazole (HPyBzIm), and its anion 2-(2′-pyridyl)benzimidazolate, $(PyBzIm)^-$, along with the preparation of several heteronuclear rhodium-gold, rhodium-silver, iridium-gold or iridium-silver complexes, as well as of some related carbonyl derivatives.

2-(2′-Pyridyl)benzimidazole has been widely used in the synthesis of complexes of the types $[M(HPyBzIm)_n]X_m$ and $M(PyBzIm)_m$ containing a large number of transition metals in different oxidation states [16–24], but to the best of our

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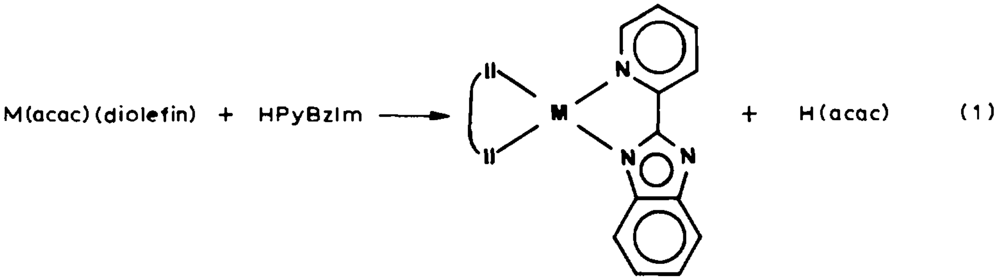
knowledge only two papers have been published in which this ligand is part of an organometallic complex such as $[M(\eta^5\text{-}C_5H_5)_2(HPyBzIm)](PF_6)_x$ ($x = 2$, M = Mo or W; $x = 1$, M = Ti) [25], $[M(\eta^5\text{-}C_5H_5)(PyBzIm)]PF_6$ (M = Mo or W) [25] and HgPh(PyBzIm) [26].

Results and discussion

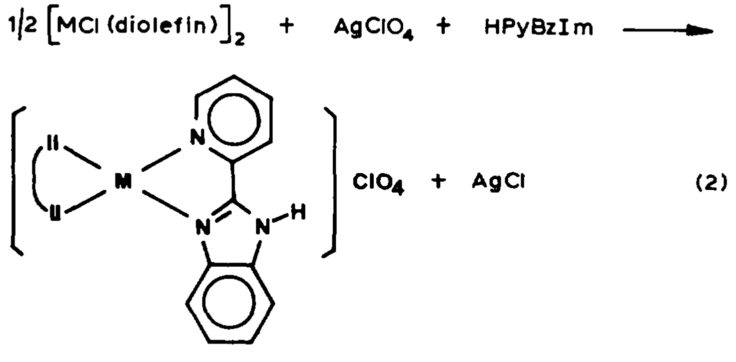
Mononuclear complexes

Complexes of the type M(acac)(diolefin) react with HPyBzIm in dichoromethane to give the neutral complexes M(PyBzIm)(diolefin) (I–III). The deeply coloured solids are insoluble in water and in weakly polar solvents (eq. 1):



(M = Rh, diolefin = COD (I), NBD (II);
M = Ir, diolefin = COD (III))

On the other hand, the dimeric complexes $[MCl(diolefin)]_2$ react with HPyBzIm, in the presence of $AgClO_4$, to give the cationic complexes [M(HPyBzIm)(diolefin)]-ClO_4 (IV–VI) (eq. 2):



(M = Rh, diolefin = COD (IV), NBD (V);
M = Ir, diolefin = COD (VI))

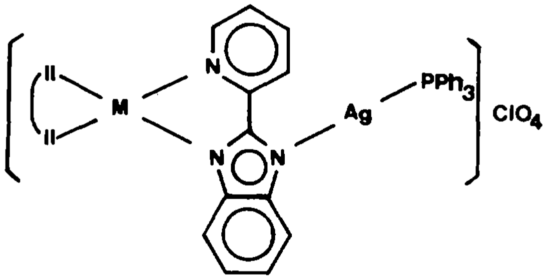
The acidic character of the amine nitrogen of HPyBzIm increases considerably upon complexation [25], and with triethylamine the cationic complexes can thus be readily deprotonated to give the neutral complexes, which in the presence of perchloric acid can be reprotonated, as represented in eq. 3.

$$[M(HPyBzIm)(diolefin)]ClO_4 \underset{HClO_4}{\overset{Et_3N}{\rightleftharpoons}} M(PyBzIm)(diolefin) \qquad (3)$$

Bubbling of carbon monoxide through dichloromethane solutions of these complexes leads to displacement of the coordinated diolefin and to formation of the *cis*-dicarbonyl derivatives $\mathrm{M(PyBzIm)(CO)_2}$ (VII, M = Rh or VIII, M = Ir) and $\mathrm{[Rh(HPyBzIm)(CO)_2]ClO_4}$ (IX). Their IR spectra, in dichloromethane solution, show two strong ν(CO) absorption bands, characteristic of a *cis*-arrangement of the two CO groups (VII: 2083, 2020; VIII: 2076, 1998; IX: 2090, 2042 $\mathrm{cm^{-1}}$), whilst in the solid state (Nujol mulls) their IR spectra are more complex in the carbonyl region (see Table 1). The complex $\mathrm{[Ir(HPyBzIm)(CO)_2]ClO_4}$ was detected in solution (ν(CO) ($\mathrm{CH_2Cl_2}$): 2081s and 2007s $\mathrm{cm^{-1}}$), but could not be isolated as an analytically pure solid.

Complexes VII and IX react with triphenylphosphine (in 1/1 molar ratio) to give the rhodium(I) monocarbonyl derivatives $\mathrm{Rh(PyBzIm)(CO)(PPh_3)}$ (X) and $\mathrm{[Rh(HPyBzIm)(CO)(PPh_3)]ClO_4}$ (XI) (ν(CO) ($\mathrm{CH_2Cl_2}$) X: 1983s; XI: 2004s $\mathrm{cm^{-1}}$). Similar reactions with analogous iridium derivatives were unsuscessful.

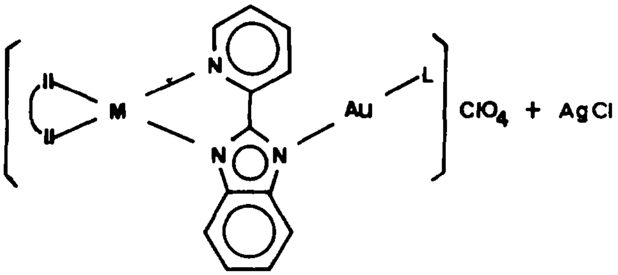
$$\mathrm{M(PyBzIm)(diolefin)} + \mathrm{AgClO_4} + \mathrm{PPh_3} \longrightarrow$$



(4)

(M = Rh, diolefin = COD (XII), NBD (XIII);
M = Ir, diolefin = COD (XIV))

$$\mathrm{M(PyBzIm)(diolefin)} + \mathrm{AuClL} + \mathrm{AgClO_4} \longrightarrow$$



(5)

(M = Rh, L = $\mathrm{PPh_3}$, diolefin = COD (XV), NBD (XVI);
M = Ir, L = $\mathrm{PPh_3}$, diolefin = COD (XVII);
M = Rh, L = $\mathrm{P(OMe)_3}$, diolefin = COD (XVIII), NBD (XIX);
M = Ir, L = $\mathrm{P(OMe)_3}$, diolefin = COD (XX))

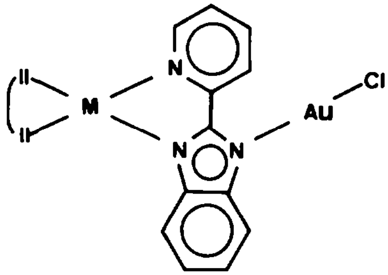
Heterobinuclear complexes

In complexes of the type M(PyBzIm)(diolefin) the metal atom is to some extent kinetically inert, while the heterocyclic ligand still has one basic function available to serve as a donor group. Thus, complexes I–III react with $AgClO_4$, in the presence of triphenylphosphine, or with AuClL ($L = PPh_3$ or $P(OMe)_3$) and $AgClO_4$ to give heterobinuclear complexes, according to eqs. 4 and 5.

Attempts to prepare complexes containing the $AgP(OMe)_3$ moiety by use of trimethylphosphite were unsuccessful.

The uncoordinated nitrogen in complexes I–III is capable of displacing the coordinated tetrahydrothiophen of AuCl(tht) to yield neutral complexes of the general formula (diolefin)M(μ-PyBzIm)AuCl (XXII–XXIV) (eq. 6).

M(PyBzIm)(diolefin) + AuCl(tht) →



\+ tht (6)

(M = Rh, diolefin = COD (XXII), NBD (XXIII);
M = Ir, diolefin = COD (XXIV))

Complexes XVIII, XIX, and XXII–XXIV react in dichloromethane with carbon monoxide at atmospheric pressure to give the slightly soluble XXI ($\nu(CO)(CH_2Cl_2)$: 2099s and 2037s cm^{-1}) or the highly insoluble XXV, XXVI *cis*-dicarbonyl derivatives, as may be seen from eqs. 7 and 8

$$[(diolefin)Rh(\mu\text{-}PyBzIm)AuP(OMe)_3]ClO_4 + 2CO \rightarrow$$

$$[(CO)_2Rh(\mu\text{-}PyBzIm)AuP(OMe)_3]ClO_4 + diolefin \quad (7)$$
$$(XXI)$$

$$(diolefin)M(\mu\text{-}PyBzIm)AuCl + 2CO \rightarrow (CO)_2M(\mu\text{-}PyBzIm)AuCl + diolefin \quad (8)$$
$$(M = Rh\ (XXV),\ Ir\ (XXVI))$$

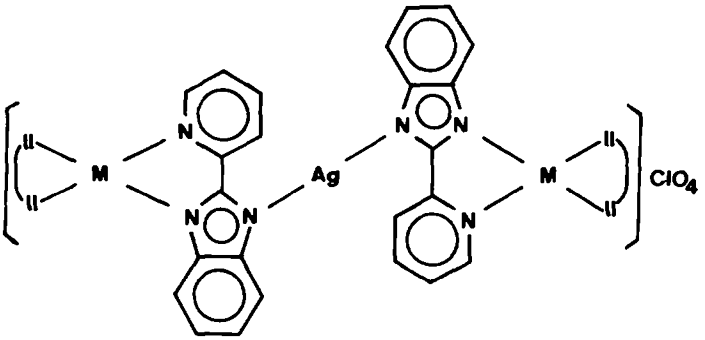
With $[(COD)Ir(\mu\text{-}PyBzIm)AuP(OMe)_3]ClO_4$ the same treatment gave products which could not be identified.

Heterotrinuclear complexes

Complexes M(PyBzIm)(diolefin) react with $AgClO_4$ in 2/1 molar ratio to give the highly insoluble silver diamine derivatives XXVII–XXIX (eq. 9).

The analogous heterotrinuclear gold(I) derivatives could not be obtained pure, either by treatment of I–III with AuCl(tht) and $AgClO_4$, or by reacting (diolefin)M(μ-PyBzIm)AuCl with I–III and $AgClO_4$. In the first case decomposition to metallic gold took place, while in the second the formed AgCl could not be

$2\ Rh(PyBzIm)(diolefin) + AgClO_4 \longrightarrow$



(M = Rh, diolefin = COD (XXVII), NBD (XXVIII);
M = Ir, diolefin = COD (XXIX))

separated from the expected complexes because of the low solubility of the latter.

Bubbling of carbon monoxide through dichloromethane solutions or suspensions of the heterobinucelar triphenylphosphine derivatives XII–XVI gave rise to rearrangement reactions, similar to those which have previously been described for heteronuclear rhodium(I)-gold(I) complexes [3,7] (eqs. 10 and 11)

$$2[(diolefin)M(\mu\text{-}PyBzIm)AgPPh_3]ClO_4 + 4CO \rightarrow [Ag\{M(\mu\text{-}PyBzIm)(CO)_2\}_2]ClO_4 + Ag(OClO_3)(PPh_3)_2 \qquad (10)$$

(M = Rh (XXX), Ir (XXXI))

$$2[(diolefin)Rh(\mu\text{-}PyBzIm)AuPPh_3]ClO_4 + 4CO \rightarrow \underset{(XXXII)}{[Au\{Rh(\mu\text{-}PyBzIm)(CO)_2\}_2]ClO_4} + [Au(PPh_3)_2]ClO_4 \qquad (11)$$

Very dark blue-green, highly insoluble heterotrinucleartetracarbonyl derivatives (XXX–XXXII) were isolated from the reaction mixture in 32–47%. Silver- or gold-bis(triphenylphosphine)perchlorate complexes can be spectroscopically identified in the filtrate, which, however, are contaminated by unidentified monocarbonyls. If the reaction is carried out with $[(COD)Ir(\mu\text{-}PyBzIm)AuPPh_3]ClO_4$ a *cis*-dicarbonyl species can be detected in the solution ($\nu(CO)(CH_2Cl_2)$: 2086s and 2003s cm^{-1}) but the isolated solid did not give satisfactory analyses.

Although $[Au(PPh_3)_2]ClO_4$ has previously been described and characterized [27], silver complexes containing the $Ag(PPh_3)_2$ moiety have been little studied [28]. If the perchlorate anion is present, the IR spectrum of the isolated compound (Nujol mull) shows the perchlorate group to be coordinated, two strong bands in the 630–620 cm^{-1} region and several complex absorptions in the 1200–1000 cm^{-1} region being observed [29,30]. In dichloromethane solution the perchlorate anion is uncoordinated (ν(Cl–O): 1100s,vbr and 623s cm^{-1}) and the complex is therefore linear [31].

Complexes XXX–XXXI can also directly be prepared in high yield by starting from $[Ag\{M(\mu\text{-}PyBzIm)(diolefin)\}_2]ClO_4$ and displacing the coordinated diolefin with carbon monoxide.

(Continued on p. 112)

TABLE 1

ANALYTICAL AND PHYSICAL DATA FOR THE NEW COMPLEXES

Compound		Analyses (Found (calcd.)(%))			Colour	Λ_m [a] (ohm^{-1} cm^2 mol^{-1})	Yield (%)	Selected IR bands [c] (cm^{-1})
		C	H	N				
Rh(PyBzIm)(COD)	(I)	59.01 (59.27)	4.80 (4.97)	10.23 (10.37)	yellow	–	95	–
Rh(PyBzIm)(NBD)	(II)	58.66 (58.63)	4.33 (4.14)	10.91 (10.79)	yellow-orange	–	97	–
Ir(PyBzIm)(COD)	(III)	48.97 (48.57)	4.21 (4.08)	8.40 (8.50)	red	–	84	–
[Rh(HPyBzIm)(COD)]ClO_4	(IV)	47.44 (47.50)	4.18 (4.19)	8.73 (8.31)	deep-orange	144	96	3100s,vbr [d]
[Rh(HPyBzIm)(NBD)]ClO_4	(V)	46.17 (46.60)	3.50 (3.50)	8.80 (8.58)	red-orange	148	94	3120s,vbr [d]
[Ir(HPyBzIm)(COD)]ClO_4	(VI)	40.39 (40.37)	3.56 (3.39)	6.75 (7.06)	dark-violet	136	88	3030s,vbr [d]
Rh(PyBzIm)$(CO)_2$	(VII)	46.99 (47.62)	2.35 (2.28)	12.10 (11.90)	maroon	–	91	2092s,2063s,2036m,2010s, 1972m [e]
Ir(PyBzIm)$(CO)_2$	(VIII)	37.63 (38.00)	1.96 (1.82)	9.38 (9.50)	green	–	98	2072s,2046m,2018s,2009s, 1990m [e]
[Rh(HPyBzIm)$(CO)_2$]ClO_4	(IX)	37.04 (37.07)	2.11 (2.00)	9.46 (9.26)	cream	131	92	2110s,2050s,2028m [e] 3090s,vbr [d]
Rh(PyBzIm)(CO)(PPh_3)	(X)	63.56 (63.40)	4.00 (3.95)	7.19 (7.15)	yellow	–	94	1962s [e]
[Rh(HPyBzIm)(CO)(PPh_3)]ClO_4	(XI)	54.56 (54.14)	3.96 (3.52)	5.87 (6.11)	yellow	124	81	1985s [e] 3060m,br [d]
[(COD)Rh(μ-PyBzIm)$AgPPh_3$]ClO_4	(XII)	52.64 (52.17)	4.45 (4.15)	4.91 (4.80)	orange	[b]	95	–
[(NBD)Rh(μ-PyBzIm)$AgPPh_3$]ClO_4	(XIII)	51.23 (51.75)	3.83 (3.76)	5.09 (4.89)	orange	[b]	95	–
[(COD)Ir(μ-PyBzIm)$AgPPh_3$]ClO_4	(XIV)	47.66 (47.34)	3.84 (3.66)	4.47 (4.36)	red-brown	136	94	–
[(COD)Rh(μ-PyBzIm)$AuPPh_3$]ClO_4	(XV)	47.51 (47.35)	3.77 (3.66)	4.11 4.36)	orange	136	95	–

[(NBD)Rh(μ-PyBzIm)AuPPh$_3$]ClO$_4$	(XVI)	46.46	3.44	4.31	orange	136	94	–
		(46.88)	(3.30)	(4.43)				
[(COD)Ir(μ-PyBzIm)AuPPh$_3$]ClO$_4$	(XVII)	43.64	3.67	4.12	red-brown	128	97	–
		(43.34)	(3.35)	(3.99)				
[(COD)Rh(μ-PyBzIm)AuP(OMe)$_3$]ClO$_4$	(XVIII)	33.64	3.86	5.12	orange	151	95	–
		(33.45)	(3.54)	(5.09)				
[(NBD)Rh(μ-PyBzIm)AuP(OMe)$_3$]ClO$_4$	(XIX)	32.15	3.11	5.21	orange	158	95	–
		(32.63)	(3.11)	(5.19)				
[(COD)Ir(μ-PyBzIm)AuP(OMe)$_3$]ClO$_4$	(XX)	30.23	3.26	4.86	red-brown	142	91	–
		(30.18)	(3.19)	(4.59)				
[(CO)$_2$Rh(μ-PyBzIm)AuP(OMe)$_3$]ClO$_4$	(XXI)	26.89	2.40	5.17	olive-green	^{b}	94	2108s,2091m,2046s,
		(26.39)	(2.21)	(5.43)				2038m ^{e}
(COD)Rh(μ-PyBzIm)AuCl	(XXII)	37.13	3.10	6.53	orange	^{b}	95	360m ^{f}
		(37.67)	(3.16)	(6.59)				
(NBD)Rh(μ-PyBzIm)AuCl	(XXIII)	37.11	2.96	6.69	red-orange	^{b}	79	358m ^{f}
		(36.71)	(2.59)	(6.76)				
(COD)Ir(μ-PyBzIm)AuCl	(XXIV)	32.53	2.73	5.76	red-brown	^{b}	87	356w ^{f}
		(33.04)	(2.77)	(5.78)				
(CO)$_2$Rh(μ-PyBzIm)AuCl	(XXV)	28.68	1.34	7.22	deep-red	^{b}	79	2091s,2069m,2040s,2023s,
		(28.72)	(1.38)	(7.18)				1990m ^{e},352m,341sh ^{f}
(CO)$_2$Ir(μ-PyBzIm)AuCl	(XXVI)	25.03	1.66	5.97	dark-green	^{b}	90	2076s,2055m,2021m,1998s,
		(24.92)	(1.19)	(6.23)				1974m ^{e},352m,340sh ^{f}
[Ag(Rh(μ-PyBzIm)(COD))$_2$]ClO$_4$	(XXVII)	46.65	3.77	8.31	yellow-orange	^{b}	95	–
		(47.20)	(3.96)	(8.26)				
[Ag(Rh(μ-PyBzIm)(NBD))$_2$]ClO$_4$	(XXVIII)	45.47	3.29	8.67	yellow-orange	^{b}	97	–
		(46.30)	(3.27)	(8.62)				
[Ag(Ir(μ-PyBzIm)(COD))$_2$]ClO$_4$	(XXIX)	39.88	3.44	6.93	deep-red	^{b}	92	–
		(40.15)	(3.37)	(7.02)				
[Ag(Rh(μ-PyBzIm)(CO)$_2$)$_2$]ClO$_4$	(XXX)	36.59	1.87	9.18	dark-green	^{b}	97	2109s,br,2039s,br ^{e}
		(36.81)	(1.77)	(9.20)				
[Ag(Ir(μ-PyBzIm)(CO)$_2$)$_2$]ClO$_4$	(XXXI)	30.55	1.77	7.40	dark-green	^{b}	93	2079s,br,2016s,br ^{e}
		(30.79)	(1.48)	(7.69)				
[Au(Rh(μ-PyBzIm)(CO)$_2$)$_2$]ClO$_4$	(XXXII)	33.08	1.84	7.60	dark-green	^{b}	47	2100s,br,2032s,br ^{e}
		(33.54)	(1.61)	(8.38)				

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[a] Ca. 4×10^{-4} *M* acetone solutions. [b] Insoluble. [c] Nujol mulls. [d] ν(NH). [e] ν(CO). [f] ν(Au–Cl).

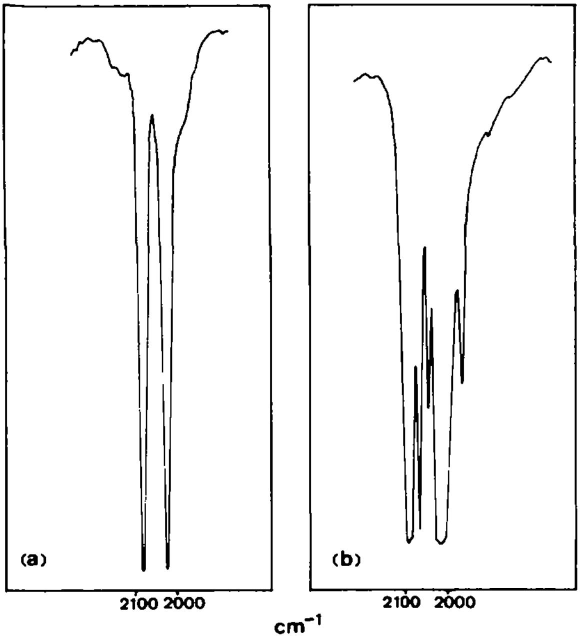

Fig. 1. IR spectra of Rh(PyBzIm)(CO)$_2$: (a) dichloromethane solution; (b) Nujol mull.

General properties

All the complexes described in this paper are air-stable solids, which decompose above 150°C. Their IR spectra show bands characteristic of the heterocyclic ligand, similar to those described for related complexes [18,19]. The complexes containing the neutral ligand HPyBzIm show absorptions assignable to the N–H bond (ν(NH) at ca. 3200–2900vbr cm^{-1} and δ(N–H) at ca. 1592w cm^{-1}). The ionic character of the cationic derivatives is confirmed by the presence of two strong absorption bands at ca. 1090br and 623 cm^{-1}, characteristic of the perchlorate group (Td) [29,30] and by their conductivities in acetone solution (Table 1) [32].

In the solid state all the described *cis*-dicarbonyl derivatives show very complex IR spectra, with broad or multiple bands (see Table 1 and Fig. 1). These spectra and the deep colours of the complexes along with their high insolubility point to the existence of intermolecular metal-metal interactions [32].

Experimental

C, H and N analyses were carried out with a Perkin–Elmer 240-B microanalyzer. IR spectra were recorded on a Perkin–Elmer 599 spectrophotometer over the range 4000–200 cm^{-1}, using Nujol mulls between polyethylene sheets, potassium bromide pellets or dichloromethane solutions between sodium chloride windows, and calibrated with polyethylene. Conductivities were measured at 20°C in ca. 4×10^{-4} *M* acetone solutions using a Philips 9501/01 conductimeter. Melting points were determined in the air on a Büchi apparatus.

[RhCl(COD)]$_2$ [34], [RhCl(NBD)]$_2$ [35], [IrCl(COD)]$_2$ [36], Rh(acac)(COD) [37], Rh(acac)(NBD) [37], Ir(acac)(COD) [38], AuCl(tht) [39] and HPyBzIm [17] were prepared as described elsewhere. $AuClPPh_3$ and $AuClP(OMe)_3$ were prepared by displacing tetrahydrothiophen from AuCl(tht) with the stoichiometric amount of the phosphorous donor ligand. All the heteronuclear complexes and the reactions involving iridium compounds were carried out under argon with deoxygenated solvents.

Since the preparations of all the complexes were very similar only typical procedures are described. Either hexane or ether could be used to precipitate the products.

Preparation of Rh(PyBzIm)(COD). General methods for the synthesis of I–III

(i) Rh(acac)(COD) (400 mg, 1.29 mmol), HPyBzIm (252 mg, 1.29 mmol) and 30 ml of dichloromethane were stirred for 2 h and filtered. The orange-yellow filtrate was vacuum-concentrated until formation of a yellow precipitate was observed. Ether was added and the crystals were filtered off, washed with ether, and vacuum-dried. Yield 495 mg (95%).

(ii) Addition of 18 μl of Et_3N to an orange-coloured suspension of $[Rh(HPyBzIm)(COD)]ClO_4$ (47 mg, 0.09 mmol) in 10 ml of methanol caused immediate dissolution of the complex. After 15 min stirring, the yellow solution was vacuum-concentrated to ca. 2 ml and kept for 3 h at −10°C. The yellow precipitate was filtered off, washed with 2 × 2 ml of cold methanol and ether and vacuum-dried. Yield: 15.4 mg (41%). Its IR spectrum was identical to that of the sample obtained by the first method.

Preparation of [Rh(HPyBzIm)(COD)]ClO$_4$. General methods for the synthesis of IV–VI

(i) A mixture of $[RhCl(COD)]_2$ (125 mg, 0.25 mmol), HPyBzIm (99 mg, 0.50 mmol), $AgClO_4$ (105.0 mg, 0.50 mmol) and 25 ml of acetone was stirred for 30 min. The AgCl was filtered off and the filtrate was vacuum-evaporated to dryness. The residue was extracted with 10 ml of dichloromethane and 5 ml of hexane were added. Vacuum-concentration led to the formation of orange crystals, which were filtered off, washed with ether and vacuum-dried. Yield: 246 mg (96%).

(ii) Aqueous $HClO_4$ (50 μl, 60%) was added to a yellow suspension of Rh(PyBzIm)(COD) (80 mg, 0.2 mmol) in 10 ml of methanol. The suspension, immediately turned orange and was stirred for 15 min. Vacuum-concentration to ca. 2 ml and addition of ether gave rise to the formation of a solid, which was filtered off, washed with cold methanol and then ether, and vacuum-dried over P_2O_5. Yield: 33 mg (33%). Its IR spectrum is identical to that of the sample prepared by the first method.

Preparation of Ir(PyBzIm)(CO)$_2$. General method for the synthesis of VII–IX and XXI

Dry carbon monoxide was bubbled for 20 min through a red solution of Ir(PyBzIm)(COD) (25 mg, 0.05 mmol) in 10 ml of dichloromethane. The resulting dark-brown solution had a green solid in suspension. Addition of 5 ml of hexane and vacuum-concentration led to the complete precipitation of the green complex, which was filtered off, washed with hexane and vacuum-dried.

Preparation of Rh(PyBzIm)(CO)(PPh$_3$). General method for the synthesis of X and XI

Addition of PPh_3 (41 mg, 0.16 mmol) to the red solution of $Rh(PyBzIm)(CO)_2$

(55 mg, 0.15 mmol) in 5 ml of dichloromethane caused a colour change to yellow and release of bubbles (CO). After 2 h stirring (12 h for complex XI) 5 ml of hexane were added. Vacuum-concentration led to the formation of a yellow solid, which was filtered off, washed with hexane and vacuum-dried.

Preparation of $[(NBD)Rh(\mu\text{-}PyBzIm)AgPPh_3]ClO_4$*. General method for the synthesis of XII–XIV*

Addition of $AgClO_4$ (26.6 mg, 0.13 mmol) in 5 ml of acetone to a solution of PPh_3 (33.7 mg, 0.13 mmol) and Rh(PyBzIm)(NBD) (50 mg, 0.13 mmol) in 15 ml of dichloromethane caused immediate precipitation of an orange solid. After 30 min stirring the suspension was evaporated to dryness. Ether was added and the solid was filtered off, washed with ether, and vacuum-dried.

Preparation of $[(COD)Rh(\mu\text{-}PyBzIm)AuP(OMe)_3]ClO_4$*. General method for the synthesis of XV–XX*

$AgClO_4$ (72.7 mg, 0.35 mmol) in 8 ml of acetone was added to a solution of $AuClP(OMe)_3$ (125 mg, 0.35 mmol) and Rh(PyBzIm)(COD) (142 mg, 0.35 mmol) in 20 ml of dichloromethane. After 30 min stirring the AgCl was filtered off and the bright-orange filtrate was vacuum-evaporated to dryness to give an oily residue. Addition of 2 ml of dichloromethane and 10 ml of ether led to precipitation of orange crystals, which were filtered off, washed with ether, and vacuum-dried.

Preparation of (COD)Ir(μ-PyBzIm)AuCl. General method for the synthesis of XXII–XXIV

Addition of AuCl(tht) (48.6 mg, 0.15 mmol) to a solution of Ir(PyBzIm)(COD) (75 mg, 0.15 mmol) in 15 ml of dichloromethane led to immediate precipitation of red-brown crystals. After 30 min stirring, 10 ml of ether were added, and the solid was filtered off, washed with ether until the smell of tetrahydrothiophen could no longer be perceived, and vacuum-dried.

Preparation of $(CO)_2Ir(\mu\text{-}PyBzIm)AuCl$*. General method for the synthesis of XXV and XXVI*

Bubbling of dry carbon monoxide (for 20 min) through a suspension of (COD)Ir(μ-PyBzIm)AuCl (70 mg, 0.096 mmol) in 20 ml of dichloromethane gave a precipitate of a dark-green, almost black, solid. The suspension was vacuum-concentrated to ca. 4 ml and 10 ml of ether were added. The formed solid was filtered off, washed with ether, and vacuum-dried.

Preparation of $[Ag\{Rh(\mu\text{-}PyBzIm)(NBD)\}_2]ClO_4$*. General method for the synthesis of XXVII–XXIX*

Addition of $AgClO_4$ (24.5 mg, 0.12 mmol) in 8 ml of acetone to a solution of Rh(PyBzIm)(NBD) (91 mg, 0.24 mmol) in 15 ml of dichloromethane gave orange-yellow crystals. After 20 min stirring and vacuum-concentration to ca. 2 ml, 10 ml of ether were added, and the formed solid was filtered off, washed with ether, and vacuum-dried.

Preparation of $[Ag\{Ir(\mu\text{-}PyBzIm)(CO)_2\}_2]ClO_4$*. General method for the synthesis of XXX and XXXI*

Bubbling of dry carbon monoxide (for 20 min) through a suspension of [Ag{Ir(μ-

PyBzIm)(COD))$_2$]ClO$_4$ (52 mg, 0.05 mmol) in 15 ml of dichloromethane immediately gave a dark-green solid; 10 ml of ether were added and the solid was filtered off, washed with ether, and vacuum-dried.

Reaction of $[(COD)Rh(\mu\text{-}PyBzIm)AuPPh_3]ClO_4$ *with carbon monoxide*

Bubbling of dry carbon monoxide (for 1 h) through a solution of [(COD)Rh(μ-PyBzIm)AuPPh$_3$]ClO$_4$ (310 mg, 0.32 mmol) in 20 ml of dichloromethane gave a dark-green solid. The mixture was kept for 2 h at − 10°C, then the solid was filtered off, washed with cold dichloromethane, and vacuum-dried. It was identified as [Au(Rh(μ-PyBzIm)(CO)$_2$)$_2$]ClO$_4$. The orange-red filtrate was vacuum-concentrated to ca. 2 ml and ether was added to precipitate a brown solid, which was twice recrystallized from dichloromethane/ether to give a pale-yellow solid. It was identified as a mixture of [Au(PPh$_3$)$_2$]ClO$_4$ (characterized by its IR spectrum) and monocarbonyl derivatives which were not further studied. Complexes XII–XIV and XVI underwent similar reactions.

Preparation of $Ag(OClO_3)(PPh_3)_2$

PPh$_3$ (100 mg, 0.38 mmol) was added to a solution of AgClO$_4$ (39.5 mg, 0.19 mmol) in 20 ml of acetone. Stirring for 30 min in the absence of light and vacuum-evaporation to dryness gave a colourless oil, which was dissolved in ca. 2 ml of dichloromethane. Addition of 10 ml of ether gave white crystals, which were filtered off, washed with ether, and vauum-dried. Yield: 135 mg (97%). Analysis: Found: C, 59.40; H, 4.36. $C_{36}H_{30}AgClO_4P_2$ calcd.: C, 59.10; H, 4.13%.

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