Synthesis and structure of N-heterocyclic carbene complexes of rhodium and iridium derived from an imidazolium-linked cyclophane ☆

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Abstract

This paper describes the synthesis, spectroscopic and structural characterisation, and electrochemical behaviour of some rhodium and iridium complexes of the form $LM(X_1)(X_2)^+$, where L is a chelating bis(carbene) derived from an imidazolium-linked *ortho*-cyclophane. The complexes where $X_1/X_2 = 1,5$-cycooctadiene or norbornadiene were prepared from the imidazolium-linked cyclophane and the appropriate metal source. In these complexes, the M–L bonding was quite robust, but the diene could be displaced by CO to give the dicarbonyl complexes $LM(CO)_2^+$, from which one or both carbonyl ligands could be displaced by monodentate or bidentate phosphines, respectively. Structural studies revealed only minor variations in the cyclophane unit upon exchange of the ancillary ligands, in each case the rhodium complex being isomorphous with its iridium analogue. In cyclovoltammetric studies of $LRh(dppe)^+$, reversible Rh(I/II) and Rh(II/III) redox couples were observed. The other rhodium complexes displayed more complex electrochemical behaviours and did not undergo simple reversible redox reactions.
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Keywords: Heterocyclic carbene complexes; Imidazolium-linked cyclophanes; Rh complexes; Ir complexes; Electrochemistry

1. Introduction

Metal complexes of N-heterocyclic carbenes were first reported independently by Wanzlick and Schönherr [1] and Öfele [2] in 1968. Subsequently, Lappert et al. [3–9] reported many N-heterocyclic carbene complexes of a variety of transition metals. Since the isolation of stable free N-heterocyclic carbenes (NHCs) by Arduengo et al. in 1991 [10], however, there has been an upsurge of interest in the study of NHCs and their metal complexes, particularly those derived from imidazolium salts. NHCs exhibit ligand characteristics similar to

those of electron-rich phosphines [11], and crystallographic and theoretical studies suggest that NHCs are primarily σ-donors [11].

We are interested in N-heterocyclic carbene complexes derived from azolium salts in which the azolium units are parts of a larger macrocycle. Shi and Thummel [12] reported the first such complex, a rhodium bis(NHC) complex where the NHCs were derived from benzimidazolium units linked by two trimethylene chains. More recently, we have described chelate nickel and palladium complexes (e.g., **1**) [13,14] and dinuclear gold complexes (e.g., **2**) [15] of bidentate NHCs derived from azolium-linked cyclophanes, and Garrison et al. [16] have reported dinuclear silver NHC complexes derived from imidazolium-linked cyclophanes. Perhaps because of the rigidity imposed by the cyclophane

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skeletons, palladium complexes such as **1** showed remarkable stability, and gave impressive results when used as catalysts for Heck reactions. These interesting results prompted us to investigate cyclophane–NHC complexes of other catalytically important metals.
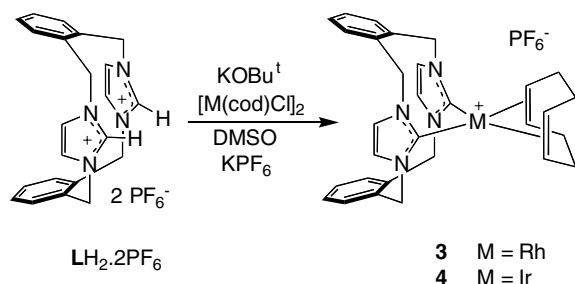

1   **2**
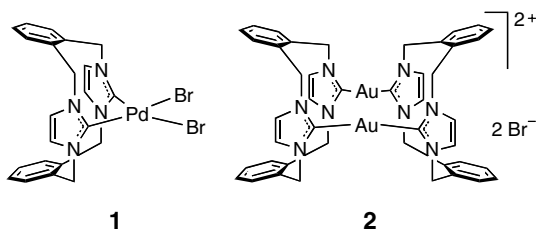
Many complexes of rhodium and iridium containing one carbene ligand [17–19], and several examples of chelating bis-carbene complexes of rhodium and iridium [12,20–23] have been reported. In this paper, we describe the synthesis, structural characterisation, electrochemistry, and spectral properties of a selection of cationic rhodium and iridium NHC complexes derived from an imidazolium-linked *ortho*-cyclophane.

2. Results and discussion

2.1. Synthesis of compounds

The cyclooctadiene adducts $LRh(cod) \cdot PF_6$ (**3**) and $LIr(cod) \cdot PF_6$ (**4**) were prepared by treating solutions of $[M(cod)Cl]_2$ and the *ortho*-cyclophane salt $(LH_2 \cdot 2PF_6)$ with potassium *tert*-butoxide (Scheme 1). The norbornadiene rhodium adduct $LRh(nbd) \cdot PF_6$ (**5**) can be obtained similarly by the reaction of di-μ-chlorobis(η^4-norbornadiene)dirhodium with $LH_2 \cdot 2Br$ and potassium *tert*-butoxide. The complexes were conveniently isolated as their hexafluorophosphate salts, which were purified by chromatography where necessary. The rhodium–cod adduct was also obtained as its bromide salt, $LRh(cod) \cdot Br$ (**6**), albeit in lower yield, from the reaction of $LH_2 \cdot 2Br$, $[Rh(cod)Cl]_2$, and NaOAc at 98 °C for 72 h. The cyclophane–NHC complexes are stable to a number of reagents including hydrogen, hydrazine, triethyl phosphite, refluxing acetonitrile and refluxing pyridine.

When solutions of the cyclooctadiene compounds in dichloromethane were treated with carbon monoxide at atmospheric pressure, the cyclooctadiene was slowly displaced (ca. 2 h for Ir, overnight for Rh) to give the dicarbonyls **7** and **8** (Scheme 2). In contrast, similar bis(carbene)(η^4-1,5-cyclooctadiene)rhodium complexes react much more rapidly with carbon monoxide [22] (ca. 10 min), highlighting the resistance of **3** towards ligand displacement.

Reaction of the dicarbonyls **7** and **8** with bidentate ligands resulted in displacement of both carbonyl groups. Bis(1,2-diphenylphosphino)ethane rapidly displaced both carbonyls at room temperature to give the chelate species **9** and **10**. The rhodium dicarbonyl **7** also reacted with norbornadiene in refluxing acetonitrile to give the norbornadiene adduct **5**.

The reaction of the dicarbonyls **7** and **8** with unidentate ligands resulted in displacement of only one carbonyl, even when large excesses of ligands were used. Triphenylphosphine reacted with the rhodium dicarbonyl **7** within minutes at room temperature, to give the monophosphine compound **11**. In CD_3CN solution, **7** was rapidly (<5 min by ^1H NMR) converted to an equilibrium mixture of $LRh(CO)_2 \cdot PF_6$ and a complex tentatively assigned as the solvolysis product $LRh(CO)(CD_3CN) \cdot PF_6$, in approximately 95:5 ratio (by ^1H NMR). If this solution was purged with nitrogen for 5 min, further loss of carbon monoxide occurred, giving a mixture containing $LRh(CO)_2 \cdot PF_6$ and $LRh(CO)(CD_3CN) \cdot PF_6$ in approximately 70:30 ratio, and after 3 h of purging with nitrogen, the ratio became 20:80. Under similar conditions, the iridium dicarbonyl **8** was unreactive towards CD_3CN. In acetonitrile solution, **7** was converted to $LRh(CO)(CD_3CN) \cdot PF_6$ quantitatively (NMR) using excess *N*-methylmorpholine *N*-oxide, but the material was not sufficiently stable to be isolated.

The rhodium dicarbonyl did not react with olefins at room temperature, but the addition of excess *N*-methylmorpholine *N*-oxide to an acetone-d_6 solution of the dicarbonyl and *N*-butylmaleimide (nbm) resulted in displacement of one carbonyl, forming what is thought to
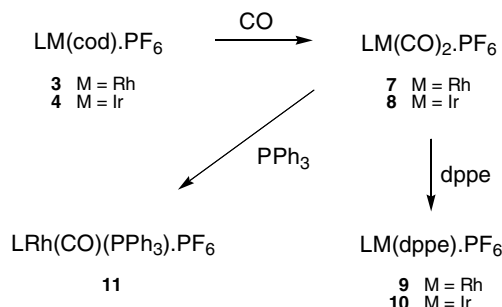
Scheme 1.

Scheme 2.

be a mono-alkene complex. This material is tentatively assigned the structure LRh(CO)(nbm) · PF$_6$, on the basis of its ^{1}H NMR spectrum (see below), which shows a signal attributed to a coordinated alkene at δ 4.93 (J_{Rh-C} = 1.8 Hz). Attempted preparation of the analogous cyclopentene rhodium complex using a similar procedure gave a mixture of unidentified products.

2.2. Spectroscopic properties of the complexes

The ^{1}H NMR spectra showed signals characteristic of a rigid *ortho*-cyclophane unit chelating a metal centre [13]. The benzylic protons of the cyclophane unit appear as a pair of doublets near δ 5.2 and δ 6.6 (*exo* and *endo* protons, respectively) for "symmetrical" complexes (those that have a plane of symmetry orthogonal to the coordination plane), e.g., Fig. 1(a). For the "unsymmetrical" complexes **11** and LRh(CO)(nbm) · PF$_6$, the benzylic protons appear as two pairs of doublets, e.g., Fig. 1(b). All spectra showed the additional signals expected for the other coordinating group(s).

The ^{13}C NMR spectra for the complexes (e.g., Fig. 2) showed a characteristic carbene signal between δ 172.1 and δ 188.2 for Rh–C or δ 168.2 and δ 181.7 for Ir–C; the chemical shift of the carbene carbon in an iridium complex was always upfield of that for the analogous rhodium complex. Interestingly, amongst the Rh complexes **3**, **7**, and **9**, the [103]Rh–[13]C coupling constant increased as the Rh–C distance decreased (**7**, 2.056(12) Å/44.1 Hz; **9**, 2.050(2) Å/46.8 Hz; **3**, 2.024(3) Å/52.7 Hz. Distances from X-ray studies, see below).

The infrared spectrum of the rhodium complex **7** showed asymmetric and symmetric carbonyl stretches at 2085 and 2025 cm^{-1}, respectively, while the iridium complex **8** displayed analogous stretches at 2075 and 2008 cm^{-1}. In each case, the asymmetric and symmetric stretches were of similar intensity, as expected for com-
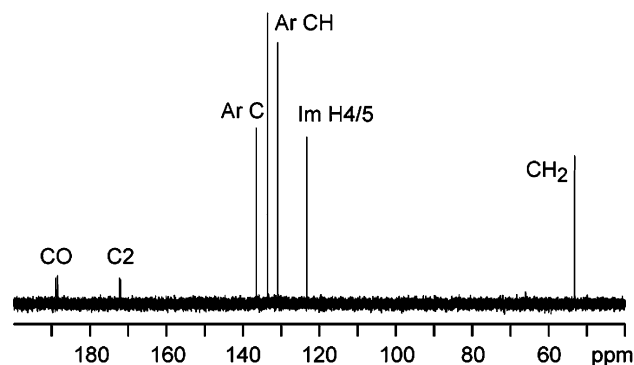

Fig. 2. ^{13}C NMR spectrum (125.77 MHz, acetone-d$_6$) of LRh(CO)$_2$ · PF$_6$ **7**.

plexes containing two mutually *cis*-carbonyl groups. The stretches for the iridium species are of lower frequency, indicating a higher degree of back-bonding. This result is consistent with average bond lengths determined from X-ray studies (Rh–C(O) 1.897 Å versus Ir–C(O) 1.875 Å and (Rh)C≡O 1.126 Å versus (Ir)C≡O 1.143 Å; see below), and also correlates well with the chemical properties of the carbonyls – the iridium species is less reactive towards carbonyl displacement reactions and would thus be predicted to have stronger M–C bonds. The infrared spectrum of the mono-carbonyl complex **11** showed only one carbonyl stretch, at 1985 cm^{-1}. This stretch is at significantly lower frequency than those seen for the dicarbonyl complex **7**, as expected for a situation where one carbonyl has been replaced by a more electron-donating ligand, resulting in greater backbonding for the remaining carbonyl group.

2.3. Electrochemistry

The compounds studied showed a variety of electrochemical responses when subjected to cyclic
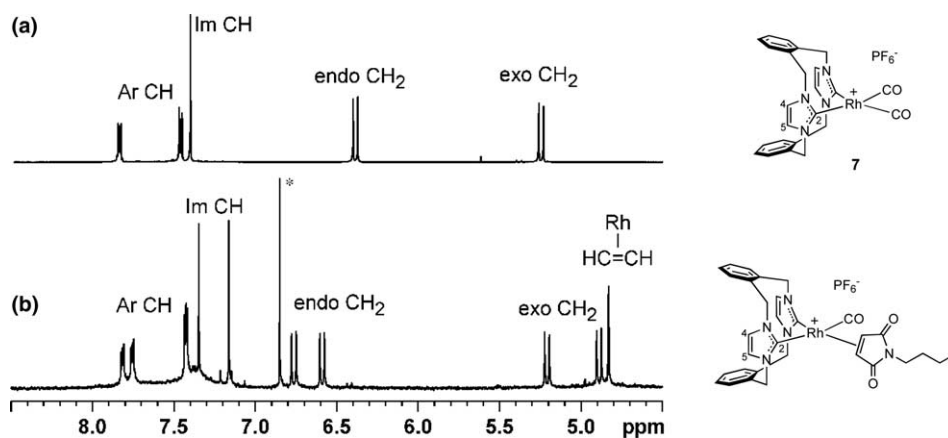

Fig. 1. ^{1}H NMR spectra for acetone-d$_6$ solutions of (a) **7** and (b) the product tentatively assigned as LRh(CO)(nbm) · PF$_6$ (downfield region only). Excess *N*-butylmaleimide is marked with an asterisk.

voltammetry in CH_3CN with 0.1 M Bu_4NClO_4 as supporting electrolyte. The dppe complex **9** showed two reversible oxidations near 0.49 and 0.86 V, presumably arising from $Rh(I) \rightarrow Rh(II) \rightarrow Rh(III)$ (Fig. 3(a)). The cyclic voltammograms of the other rhodium complexes **3**, **5**, and **7** (Fig. 3(b)–(d)) were more complex, consistent with processes involving exchange of the non-carbene ligands (Scheme 3). The rhodium diene complexes **3** and **5** (Fig. 3(b) and (c)) both displayed irreversible oxidation waves near 1 V, and a partially reversible redox couple at 0.13 V. In each case, the redox couple near 0.13 V was only detected after cycling past the irreversible oxidation wave. We interpret these results in terms of (i) an oxidation process (ca. 1 V) that converts the Rh(I) complexes **3** and **5** to the corresponding Rh(II) complexes, which in turn undergo rapid solvolysis to $LRh(CH_3CN)_n^{2+}$, and (ii) a (partially) reversible reduction of $LRh(CH_3CN)_n^{2+}$ to $LRh(CH_3CN)_n^+$ (ca. 0.13 V). For **7**, the cyclic voltammogram was even more complicated, showing two irreversible oxidation waves (0.8 and 1.35 V, Fig. 3(d)), which we attribute to oxidation of $LRh(CO)(CH_3CN)^+$ and $LRh(CO)_2^+$, respectively. Consistent with these assignments, prolonged purging of the solution with nitrogen prior to cyclic voltammetry resulted in decrease in the signal at 1.35 V. Cycling past

either oxidation wave gave rise to the partially reversible redox couple at 0.13 V.

In cyclovoltammmetric studies of **3** in nitromethane, a wave at 1.0 V was attributed to the oxidation of $LRh(cod)^+$ to $LRh(cod)^{2+}$. In this solvent, however, this oxidation was partially reversible, with a corresponding small reduction wave seen at 0.89 V. On continuation of the cycle, an additional reduction wave was observed at 0.09 V, but this wave had no matching oxidation wave. We tentatively assign the wave at 0.09 V to $LRh(CH_3NO_2)_n^{2+} \rightarrow LRh(CH_3NO_2)_n^+$, in which case the latter species presumably undergoes rapid decomposition due to the poorer coordinating ability of CH_3NO_2 compared to CH_3CN.

2.4. X-ray studies

The results of the single crystal X-ray studies (Fig. 4; Tables 1–4) are consistent in all cases, in terms of stoichiometry and connectivity, with the formulation of the complexes as ionic arrays with $[LMX_{1,2}]^+$ cations, accompanied by non-interacting counterions (PF_6^-, Br^-, BPh_4^-) and, in some cases, solvent molecules. M is Rh or Ir and the ancillary ligand(s) X a pair of unidentates (CO, PPh_3) or a bidentate (cod, $(Ph_2PCH_2)_2$). In those examples where the pair of ancillary donors are equivalent, the putative cation symmetry is 2*mm*, as in the dicarbonyl complexes. In the cod and dppe complexes this symmetry is degraded to 2 by virtue of the chirality imposed by the conformation of the bidentate ancillary ligand (all complexes crystallize in racemic space groups). The metal–carbene carbon distances vary little throughout the array of species. A number of isomorphous systems have been studied for both M = Rh, Ir. Differences between counterpart bonding distances involving these metals are generally less than 0.01 Å, with those involving Ir perhaps marginally the shorter. The distances are shortest for X = cod and longest for X = CO, those for X = P donor in between, indicative of slight differences in *trans* effects among this array of 'soft' ligands. The distances to the ancillary ligands themselves are also within the usual norms, e.g., $((H_2C(3,5\text{-}Me_2pz)_2)Rh(CO)_2 \cdot BF_4$, Rh–CO = 1.86 Å [24]; $(Me_2im)_2Rh(cod) \cdot Cl$, Rh–cod = 2.18–2.20 Å [19]; $(dppe)_2Rh \cdot Cl$, Rh–P = 2.31 Å [25]). The dicarbene ligand conformations are generally similar, both C_6 aromatic rings being directed 'outwards', away from the metal centre in all cases. In the cod ligand, the usual chirality imposes an inequivalence between the carbons of each olefinic pair, but the effects of this in terms of bonding parameters and other interactions are quite minor. The conformation of the diphosphine ligand in its complex is also chiral, again with minimal consequences. The form of the cyclophane ligand (and also the cod in its complexes) appears to offer scope for the formation of inclusion complexes, either of the anion or
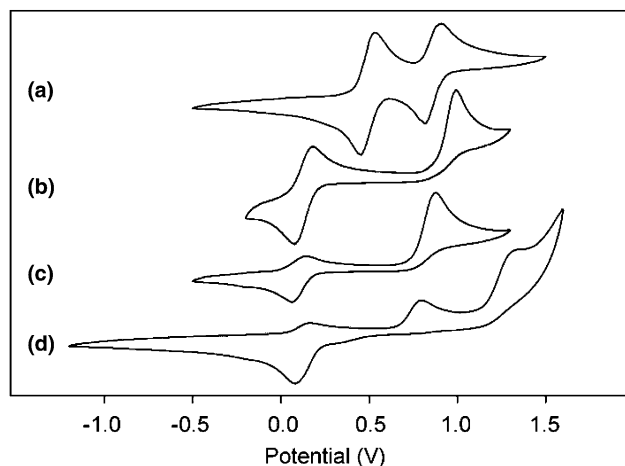
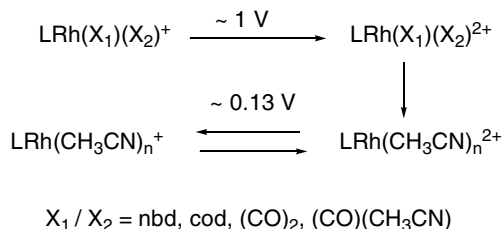Fig. 3. Cyclic voltammograms of (a) **9**, (b) **3**, (c) **5** and (d) **7**. Electrolyte, 0.1 M tetrabutylammonium perchlorate in CH_3CN; Pt working electrode; referenced to ferrocene (0.47 V), scan rate 500 mV s^{-1}.

$$LRh(X_1)(X_2)^+ \xrightarrow{\sim 1\ V} LRh(X_1)(X_2)^{2+}$$

$$\sim 0.13\ V$$

$$LRh(CH_3CN)_n^+ \rightleftarrows LRh(CH_3CN)_n^{2+}$$

$$X_1 / X_2 = \text{nbd, cod, } (CO)_2, (CO)(CH_3CN)$$

Scheme 3.
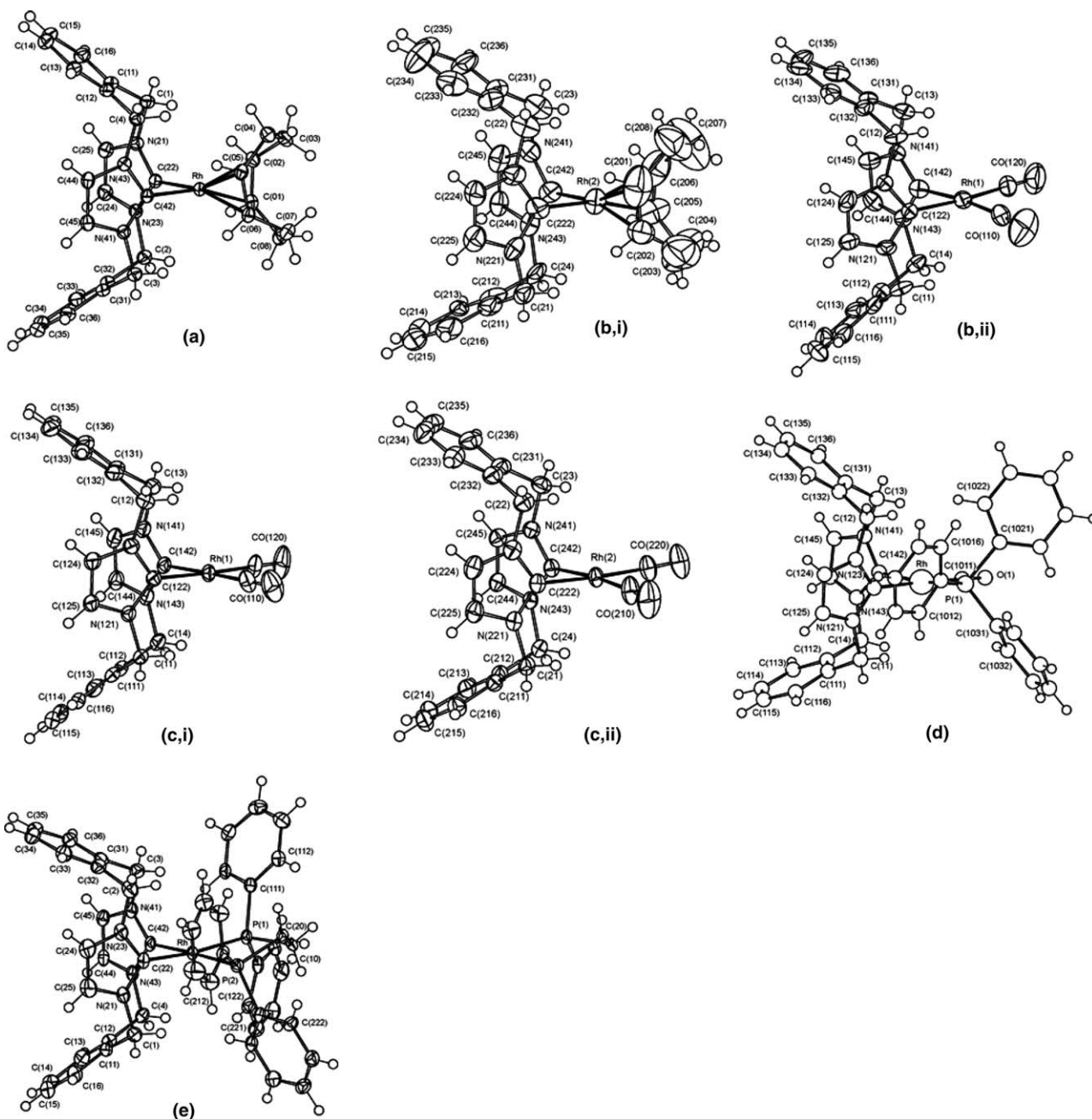
Fig. 4. Single cation projections of: (a) $[LRh(cod)]^+$ in the PF_6^- salt **3** (the Ir complex **4** is isomorphous); (b) (i) $[LRh(cod)]^+$ and (ii) $[LRh(CO)_2]^+$ of the PF_6^- cocrystal (**3**, **7**); (c) (i,ii) $[LRh(CO)_2]^+$ (cations 1,2) in the PF_6^- salt **7** (the Ir complex **8** is isomorphous); (d) $[LRh(CO)(PPh_3)]^+$ in the BPh_4^- salt (cation 1) **11a**; (e) $[LRh(Ph_2PCH_2)_2]^+$ in the PF_6^- salt **9** (the Ir complex **10** is isomorphous).

solvent, or even 'self-inclusion', but this is found only very peripherally. Of particular interest is the isomorphism found with $[LM(CO)_2](PF_6) \cdot 3/4CH_3NO_2$. With two formula units in the asymmetric unit, there are two independent cations, and it has been found possible to cocrystallize the M = Rh adduct with its cod counterpart, in such a manner that one of the two cations is replaced by the cod complex. The material was formed as micaceous flakes not conducive to a precise determination; the M = Ir counterpart and systems with mixed metals have not been studied.

3. Experimental

3.1. General

Electrochemical experiments were performed using a MacLab 4e Potentiostat with a platinum working electrode in 0.1 M Bu_4NClO_4 supporting electrolyte at a scan rate of 500 mV s^{-1}. The solvent was either CH_3CN or CH_3NO_2, and potentials were referenced using a silver/silver chloride reference electrode (ferrocene = 0.47 V). Infrared spectra were recorded from KBr disks using

Table 1
The metal environments, [LM(cod)]$^+$

Species	[LRh(cod)]$^{+a}$	[LRh(cod)]$^{+b}$	[LRh(cod)]$^{+c}$	[LIr(cod)]$^{+d}$
Bond distances (Å)				
M–C(22)	2.022(8)	2.04(1)	2.020(2)	2.020(3)
M–C(42)	2.017(8)	2.04(2)	2.028(2)	2.026(3)
M–C(0n)	2.195(8)–2.252(8)	2.14(2)–2.23(3)	2.195(2)–2.224(2)	2.184(3)–2.201(4)
(Mean)	2.21(2)	2.20(4)	2.208(13)	2.188(9)
Bond angles (°)				
C(22)–M–C(42)	82.1(3)	84.4(6)	83.11(7)	81.7(1)
C(m2)–M–C(0n)				
('cis')	93.7(3)–98.5(3)	91.9(7)–96.4(8)	93.05(7)–98.42(7)	94.2(1)–96.7(1)
(Mean)	95.4(3)	94(2)	95(2)	94.9(12)
('trans')	155.4(2)–168.0(2)	159.8(7)–166.0(7)	157.83(7)–165.89(7)	159.8(1)–163.7(1)
(Mean)	161(6)	162(3)	162(3)	161(2)
C(01)–M–C(02)	36.6(3)	35.7(9)	36.65(7)	36.5(1)
C(05)–M–C(06)	36.8(3)	34.2(8)	36.27(7)	36.9(1)
C(01)–M–C(06)	81.4(3)	80.5(7)	81.06(7)	80.3(1)
C(02)–M–C(05)	81.5(3)	83.4(3)	81.32(7)	80.9(1)
C(01)–M–C(05)	97.4(3)	94.1(7)	96.71(7)	93.2(1)
C(02)–M–C(06)	87.9(3)	90.4(8)	87.82(7)	90.8(1)
cod Torsion angles (°)				
C(08)–C(01)–C(02)–C(03)	2(1)	−2(4)	3.1(3)	1.4(6)
C(04)–C(05)–C(06)–C(07)	5(1)	0(4)	5.1(3)	2.4(7)
C(02)–C(03)–C(04)–C(05)	38(1)	24(4)	37.4(3)	15.6(7)
C(06)–C(07)–C(08)–C(01)	35(1)	24(4)	34.7(2)	15.2(6)
C(07)–C(08)–C(01)–C(02)	42(1)	52(4)	42.0(3)	58.2(6)
C(01)–C(02)–C(03)–C(04)	−93(1)	−83(3)	−94.3(2)	−79.4(6)
C(03)–C(04)–C(05)–C(06)	39(1)	54(4)	38.7(3)	56.7(7)
C(05)–C(06)–C(07)–C(08)	−92(1)	−84(4)	−93.4(2)	−80.1(6)

[a] In the bromide **6** (torsion angle signs reversed).
[b] In the PF$_6^-$ cocrystal (**3/7**).
[c] In the PF$_6^-$ salt **3**.
[d] In the PF$_6^-$ salt **4**.

Table 2
The metal environments, [LMX$_{1,2}$]$^+$

Species	[LRh(CO)$_2$]$^{+a}$	[LRh;Ir(CO)$_2$] (mols 1,2)^b	[LRh(PPh$_3$)(CO)]$^{+c}$	[LRh;Ir(PPh$_2$CH$_2$)$_2$]$^{+d}$
X$_{1,2}$	C(10,20)	C(10,20)	P,CO	P(2,1)
Bond distances (Å)				
M–C(22)	2.04(1)	2.050(3), 2.055(2); *2.056(10), 2.056(9)*	2.05(2)	2.049(4); *2.032(6)*
M–C(42)	2.04(1)	2.053(2), 2.068(3); *2.069(2), 2.070(9)*	2.04(2)	2.052(4); *2.042(5)*
M–X$_1$	1.87(1)	1.889(3), 1.902(3); *1.886(9), 1.88(1)*	2.316(5)	2.243(1); *2.245(1)*
M–X$_2$	1.89(1)	1.896(4), 1.900(4); *1.878(12), 1.85(1)*	1.84(2)	2.265(1); *2.263(1)*
Bond angles (°)				
C(22)–M–C(42)	81.1(6)	81.1(1), 81.6(1); *81.2(4), 81.2(4)*	82.1(5)	83.6(2); *83.8(2)*
C(22)–M–X$_1$	96.0(6)	96.5(1), 91.2(1); *96.1(4), 91.7(4)*	91.5(12)	95.1(1); *95.1(2)*
C(42)–M–X$_2$	91.5(6)	92.0(1), 95.0(1); *92.7(4), 95.9(4)*	93.0(10)	97.7(1); *97.0(1)*
C(22)–M–X$_2$	172.5(6)	173.0(1), 175.8(2); *173.9(4), 176.1(4)*	173.4(13)	173.3(1); *173.4(2)*
C(42)–M–X$_1$	174.3(6)	177.5(1), 171.9(1); *177.3(5), 172.3(5)*	172.7(20)	177.7(1); *177.2(2)*
X$_1$–M–X$_2$	91.6(7)	90.5(2), 92.4(2); *89.9(5), 91.4(5)*	93(2)	84.34(4); *84.26(5)*

[a] In the PF$_6^-$ cocrystal (**3/7**).
[b] In **7** and **8**.
[c] The mean of the three individual values.
[d] In **9** and **10**.

a Digilab Excalibur FTS 3000 spectrometer. Nuclear magnetic resonance spectra were recorded using Bruker Avance 500 (500.13 MHz for ^{1}H, 125.8 MHz for ^{13}C, 202.5 MHz for ^{31}P) or Avance 600 (600.13 MHz for ^{1}H, 150.9 MHz for ^{13}C) spectrometers. ^{1}H and ^{13}C spectral assignments were made with the aid of DEPT, HSQC, HMBC and NOESY spectra. Microanalyses were performed by the Microanalytical Laboratory at the Australian National University, Canberra. Syntheses of compounds were performed under nitrogen, with

Table 3
Ligand conformational descriptors
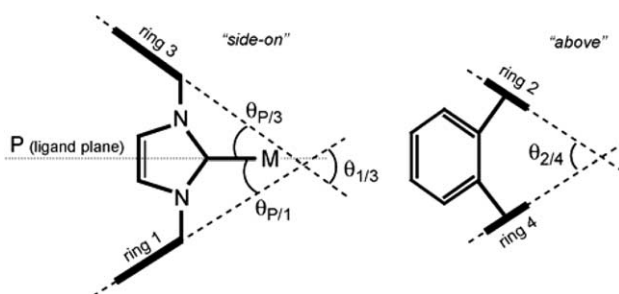
Cation (salt)	$\theta_{P/1}, \theta_{P/3}$	$\theta_{1/3}$	$\theta_{2/4}$	δ_2, δ_4
$[LRh(CO)_2]^+$ (PF_6^-; **3/7**)	40.3(5), 32.4(5)	72.1(5)	72.9(7)	0.23(3), 0.04(2)
$[LRh(CO)_2]^+$ (PF_6^-; **7**)				
mol. 1	38.1 (1), 34.6(1)	71.9(1)	71.3(1)	0.250(5), 0.083(5)
mol. 2	29.3(1), 30.3(1)	59.6(1)	69.0(1)	0.136(5), 0.319(5)
$[LIr(CO)_2]^+$ (PF_6^-; **8**)				
mol. 1	37.9(3), 35.2(3)	72.3(3)	70.9(4)	0.27(1), 0.09(2)
mol. 2	28.2(3), 30.7(4)	58.9(4)	69.5(4)	0.12(2), 0.31(2)
$[LRh(CO)(PPh_3)]^+$				
mol. 1	–	59.6(3)	79.8(4)	0.01(2), 0.09(2)
mol. 2	–	61.3(3)	74.0(4)	0.10(1), 0.17(2)
mol. 3	–	67.0(3)	70.4(4)	0.11(2), 0.30(2)
$[LRh(PPh_2CH_2)_2]^+$ (PF_6^-; **9**)	34.8(1), 27.1(1)	60.1(2)	74.1(2)	0.229(8), 0.101(7)
$[LIr(PPh_2CH_2)_2]^+$ (PF_6^-; **10**)	34.1(2), 27.5(2)	59.9(2)	74.7(2)	0.22(1), 0.09(1)
$[LRh(cod)]^+$ (Br^-; **6**)	–	68.2(3)	70.6(3)	0.25(1), 0.14(1)
$[LRh(cod)]^+$ (PF_6^-; **3/7**)	–	54.7(6)	72.2(6)	0.06(3), 0.10(3)
$[LRh(cod)]^+$ (PF_6^-; **3**)	–	70.51(7)	70.40(8)	0.096(3), 0.157(3)
$[LIr(cod)]^+$ (PF_6^-; **4**)	–	69.8(1)	70.6(1)	0.140(6), 0.156(6)

'P' is the coordination plane of the four donor atoms. Interplanar dihedral angles, θ, are given in °. δ (Å) are the metal atom deviations from the C_3N_2 planes.

workups being performed in air. Di-μ-chlorobis(η^4-1,5-cyclooctadiene)dirhodium [26], di-μ-chlorobis(η^4-norbornadiene)dirhodium [27], di-μ-chlorobis(η^4-1,5-cyclooctadiene)diiridium [28] and the *ortho*-cyclophane salts $LH_2 \cdot 2PF_6$ and $LH_2 \cdot 2Br$ [13] were prepared using literature methods.

3.2. Synthesis of compounds

3.2.1. LRh(cod) · PF₆ (3)

A suspension of potassium *tert*-butoxide (160 mg, 1.4 mmol) in DMSO (4 mL) was added to a solution of di-μ-chlorobis(η^4-1,5-cyclooctadiene)dirhodium (93 mg, 0.19 mmol) and $LH_2 \cdot 2PF_6$ (250 mg, 0.40 mmol) in DMSO (4 mL) and the mixture was stirred for 1 h. The solution was poured into water, the mixture was filtered, and the solid was washed with water (3 × 10 mL), dried in vacuo and recrystallised from dichloromethane/di-isopropyl ether to give the product as a yellow powder (0.23 g, 87%).

^{1}H NMR (500.13 MHz, acetone-d_6): δ 7.77–7.82 (m, 4H, Ar H), 7.38–7.44 (m, 4H, Ar H), 7.26 (s, 4H, Im H), 6.76 (d, J = 14.1 Hz, 4H, *endo* NCHH), 5.23 (d, J = 14.1 Hz, 4H, *exo* NCHH), 4.83–4.90 (m, 4H, cod CH), 2.65–2.8 (m, 4H, cod CH₂), 2.32–2.43 (m, 4H, cod CH₂).

^{13}C NMR (125.8 MHz, acetone-d_6): δ 182.57 (d, $J_{Rh–C}$ = 52.7 Hz, NCN), 137.02 (Ar C), 133.34, 130.45 (Ar CH), 122.03 (Im CH), 90.86 (d, $J_{Rh–C}$ = 7.7 Hz, cod CH), 52.78 (NCH₂), 31.29 (cod CH₂).

Anal. Calc. for $C_{30}H_{32}F_6N_4PRh$: C, 51.74; H, 4.63; N, 8.04. Found: C, 51.97; H, 4.64; N, 8.12%.

Crystals suitable for X-ray diffraction studies were grown by diffusion of vapours between diethyl ether and a solution of the complex in acetonitrile.

3.2.2. LIr(cod) · PF₆ (4)

A solution of potassium *tert*-butoxide (50 mg, 440 μmol) in DMSO (2 mL) was added to a solution of $LH_2 \cdot 2PF_6$ (80 mg, 127 μmol) and di-μ-chlorobis(η^4-1,5-cyclooctadiene)diiridium (39 mg, 58 mmol) in DMSO (2 mL) and the mixture was stirred for 2 h. The mixture was poured into water (25 mL) and the aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined organic extracts were washed with water (1 × 10 mL) and dried (MgSO₄) and the solvent was removed in vacuo. The residue

Table 4
Crystal/refinement data, [LMX$_{(1,2)}$](anion) · nS

M/X$_{1,2}$ anion/nS	Rh/cod Br/2MeOH[a] (6)	Rh/cod PF$_6$/2MeCN (3)	Ir/cod PF$_6$/2MeCN[b] (4)	Rh$_2$/(cod/(CO)$_2$) (PF$_6$)$_2$/MeNO$_2$[c] (3/7)	Rh/(CO)$_2$ PF$_6$/3/4MeNO$_2$ (7)	Ir/(CO)$_2$ PF$_6$/3/4MeNO$_2$ (8)	Rh/(CO)(PPh$_3$) BPh$_4$/2/3Me$_2$CO[d] (11a)	Rh/(PPh$_2$CH$_2$)$_2$ PF$_6$ (9)	Ir/(PPh$_2$CH$_2$)$_2$ PF$_6$ (10)
Formula	C$_{32}$H$_{40}$BrN$_4$O$_2$Rh	C$_{34}$H$_{38}$F$_6$N$_6$PRh	C$_{34}$H$_{38}$F$_6$IrN$_6$P	C$_{55}$H$_{55}$F$_{12}$N$_9$O$_4$P$_2$Rh$_2$	C$_{24.75}$H$_{22.25}$F$_6$N$_{4.75}$O$_{3.5}$PRh	C$_{24.75}$H$_{22.25}$F$_6$IrN$_{4.75}$O$_{3.5}$P	C$_{67}$H$_{59}$BN$_4$O$_{5/3}$PRh	C$_{48}$H$_{44}$F$_6$N$_4$P$_3$Rh	C$_{48}$H$_{44}$F$_6$IrN$_4$P$_3$
M_r (Da)	695.5	778.6	867.9	1401.8	690.1	779.4	1091.6	986.7	1076.0
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$Pbca$ (No. 61)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$Pbca$ (No. 61)	$Pbca$ (No. 61)
a (Å)	16.849(3)	14.5051(9)	14.4454(7)	12.293(5)	11.9845(7)	11.987 (2)	61.84(2)	18.102(2)	18.103(2)
b (Å)	15.155(3)	14.843(1)	15.2049(7)	12.444(5)	12.3547(7)	12.342(2)	11.590(3)	18.956(2)	18.948(2)
c (Å)	23.064(4)	15.583(1)	15.7605(7)	20.747(8)	21.344(1)	21.328(3)	23.036(6)	24.800(3)	24.734(2)
α (°)				104.131(6)	98.785(2)	98.773(2)			
β (°)		93.319(2)	95.133(1)	97.422(7)	104.391(2)	104.465 (2)	90.807(3)		
γ (°)				107.418(6)	106.679(2)	106.779(2)			
V (Å^3)	5889	3349	3448	2866	2846	2838	16508	8510	8484
D_{calc} (g cm^{-3})	1.56$_9$	1.54$_4$	1.67$_2$	1.62$_4$	1.61$_1$	1.82$_4$	1.31$_8$	1.54$_0$	1.68$_5$
Z	8	4	4	2	4	4	12	8	8
μ_{Mo} (mm^{-1})	1.97	0.63	4.0	0.73	0.73	4.8	0.39	0.58	3.3
Specimen (mm)	0.40 × 0.30 × 0.02	0.28 × 0.22 × 0.18	0.27 × 0.23 × 0.20	0.20 × 0.10 × 0.02	0.28 × 0.26 × 0.22	0.20 × 0.05 × 0.04	0.28 × 0.19 × 0.05	0.28 × 0.20 × 0.16	0.18 × 0.15 × 0.13
$T_{min/max}$	0.79	0.81	0.71	0.65	0.93	0.71	0.67	0.69	0.81
$2\theta_{max}$ (°)	58	70	75	50	65	58	50	52.5	60
N_t	104848	61243	71854	21783	40649	24409	99764	82591	116361
N (R_{int})	7820 (0.15)	14721 (0.039)	18183 (0.036)	7787 (0.10)	20029 (0.016)	13647 (0.039)	26258 (0.076)	8705 (0.068)	12388 (0.095)
N_o	4693	10862	11625	4444	16335	9144	18968	6398	8158
R	0.060	0.041	0.036	0.088	0.045	0.050	0.092	0.054	0.041
R_w (n_w)	0.074 (4)	0.050 (8)	0.044 (6)	0.11 (23)	0.074 (1.5)	0.062 (1.5)	0.13 (70)	0.075 (32)	0.054 (15)

[a] Difference map residues modelled as methanol of solvation, the second molecule disordered over two sites, occupancies set at 0.5 after trial refinement, hydroxyl hydrogen atoms not located. Micaceous specimen.

[b] T ca. 300 K, the specimen disintegrating at low temperature.

[c] The precision of the determination was limited by the available specimen size; the disordered solvent of the 'isomorphous' following two structures is absent here.

[d] Micaceous specimen quality, limited data and consequent imprecision supporting meaningful anisotropic displacement parameter refinement for Rh, P only.

was recrystallised from dichloromethane/petrol and passed through a plug of silica (5% methanol/dichloromethane) to give the product as an orange solid (80 mg, 87%).

^{1}H NMR (500.13 MHz, acetone-d_6): δ 7.75–7.82 (m, 4H, Ar H), 7.36–7.43 (m, 4H, Ar H), 7.33 (s, 4H, Im H), 6.60 (d, $J = 14.1$ Hz, 4H, *endo* CH*H*), 5.18 (d, $J = 14.1$ Hz, 4H, *exo* CH*H*), 4.40–4.46 (m, 4H, cod CH), 2.50–2.60 (m, 4H, cod CH$_2$), 2.12–2.20 (m, 4H, cod CH$_2$).

^{13}C NMR (125.8 MHz, acetone-d_6): δ 178.02 (C2), 136.75 (Ar C), 133.43, 130.48 (Ar CH), 121.78 (C4/C5), 78.02 (cod CH), 52.29 (benzyl CH$_2$), 31.94 (cod CH$_2$).

Anal. Calc. for C$_{30}$H$_{32}$F$_6$IrN$_4$P: C, 45.87; H, 4.10; N, 7.13. Found: C, 45.59; H, 3.89; N, 7.02%.

Crystals suitable for X-ray diffraction studies were grown by diffusion of vapours between diethyl ether and a solution of the complex in acetonitrile.

3.2.3. LRh(nbd) · PF$_6$ (5)

A mixture of di-μ-chlorobis(η^4-norbornadiene)dirhodium (11.5 mg, 25 μmol), LH$_2$ · 2Br (28 mg, 56 μmol) and potassium *tert*-butoxide (20 mg, 180 μmol) in dry DMSO (1 mL) was stirred for 2 h. Water (0.2 mL) was added and the solution was poured into a solution of potassium hexafluorophosphate (80 mg, 0.43 mmol) in water (10 mL). The solid was collected, washed with water (3 × 10 mL) and dried in vacuo. The residue was subjected to flash chromatography on silica (5% methanol/dichloromethane) to give the product as an orange solid (29 mg, 85%).

^{1}H NMR (600.13 MHz, acetone-d_6): δ 7.76–7.81 (m, 4H, Ar H), 7.38–7.43 (m, 4H, Ar H), 7.23 (s, 4H, Im H), 6.83 (d, $J = 14.2$ Hz, 4H, *endo* NCH*H*), 5.24–5.27 (m, 4H, nbd vinyl CH), 5.18 (d, $J = 14.2$ Hz, 4H, *exo* NCH*H*), 4.26–4.30 (m, 2H, nbd allyl CH), 1.64 (t, $J = 1.6$ Hz, nbd CH$_2$).

^{13}C NMR (150.9 MHz, acetone-d_6): δ 184.69 (d, $J_{Rh-C} = 56.3$ Hz, NCN), 136.95 (Ar C), 133.41 (Ar CH), 130.44 (Ar CH), 122.01 (d, $J_{Rh-C} = 0.9$ Hz, Im CH), 78.19 (d, $J_{Rh-C} = 7.1$ Hz, nbd vinyl CH), 68.47 (d, $J_{Rh-C} = 3.6$ Hz, nbd CH$_2$), 54.71 (d, $J_{Rh-C} = 0.6$ Hz, nbd allyl CH), 52.66 (NCH$_2$).

Anal. Calc. for C$_{29}$H$_{28}$F$_6$N$_4$PRh: C, 51.19; H, 4.15; N, 8.23. Found: C, 50.85; H, 4.11; N, 8.10%.

A less pure product may also be prepared by refluxing a solution of the dicarbonyl (7) and excess norbornadiene in acetonitrile for 16 h, and recrystallising the residue from dichloromethane/ether (ca. 90% pure by ^{1}H NMR, yield 97%).

3.2.4. LRh(cod) · Br (6)

A solution of LH$_2$ · 2Br (250 mg, 0.498 mmol), di-μ-chlorobis(η^4-1,5-cyclooctadiene)dirhodium (121 mg, 0.245 mmol) and sodium acetate (82 mg, 1.00 mmol) in DMF (10 mL) and DMSO (4 mL), was heated in a

thick walled flask that was sealed with a Young's tap, at 98 °C for 3 days. The volatiles were removed under reduced pressure at ca. 60 °C, and the yellow residue was recrystallised from wet methanol to yield the product as yellow crystals (187 mg, 60%).

HRMS (FAB): Calc. for C$_{30}$H$_{32}$N$_4$Rh ([LRh(cod)]$^+$): 551.1682. Found: 551.1675.

Anal. Calc. for C$_{30}$H$_{32}$N$_4$BrRh · 1.75(H$_2$O): C, 54.35; H, 5.40; N, 8.45. Found: C, 54.35; H, 5.38; N, 8.07%.

Crystals suitable for X-ray diffraction studies were grown by diffusion of vapours between diethyl ether and a solution of the complex in methanol.

3.2.5. LRh(CO)$_2$ · PF$_6$ (7)

A solution of 3 (34 mg, 48.8 μmol) in dichloromethane (5 mL) was stirred under an atmosphere of carbon monoxide for 16 h. The solvent was removed in vacuo and the residue was recrystallised from dichloromethane/di-isopropyl ether to give the product as a pale yellow solid (31 mg, 99%).

IR (KBr): *ν* max 2085, 2025 cm^{-1} (CO).

^{1}H NMR (500.13 MHz, acetone-d_6): δ 7.82–7.88 (m, 4H, Ar H), 7.45–7.49 (m, 4H, Ar H), 7.41 (s, 4H, Im H), 6.39 (d, $J = 14.4$ Hz, 4H, *endo* CH*H*), 5.25 (d, $J = 14.4$ Hz, 4H, *exo* CH*H*).

^{13}C NMR (125.8 MHz, acetone-d_6): δ 188.67 (d, $J_{Rh-C} = 57.5$ Hz, CO), 172.14 (d, $J_{Rh-C} = 44.1$ Hz, NCN), 136.48 (Ar C), 133.54 (Ar CH), 130.88 (Ar CH), 123.32 (Im CH), 53.22 (CH$_2$).

Anal. Calc. for C$_{24}$H$_{20}$F$_6$N$_4$O$_2$PRh: C, 44.74; H, 3.13; N, 8.70. Found: C, 44.47; H, 2.99; N, 8.61%.

Crystals suitable for X-ray diffraction studies were grown by diffusion of vapours between diethyl ether and a solution of the complex in nitromethane. A cocrystal (1:1) of 3 and 7 was grown by diffusion of vapours between diethyl ether and a solution of the complexes (ca. 1:2, respectively) in nitromethane.

3.2.6. LIr(CO)$_2$ · PF$_6$ (8)

A solution of 4 (70 mg, 89 μmol) in dichloromethane (10 mL) was stirred under an atmosphere of carbon monoxide for 2 h. The solution was evaporated to dryness and the residue was recrystallised from dichloromethane/di-isopropyl ether and dichloromethane/ethanol to give the product as a yellow solid (63.5 mg, 97%).

IR (KBr): *ν* max 2075, 2008 cm^{-1} (CO).

^{1}H NMR (500.13 MHz, CD$_3$CN): δ 7.63–7.78 (m, 4H, Ar H), 7.43–7.47 (m, 4H, Ar H), 7.13 (s, 4H, Im H), 6.21 (d, $J = 14.4$ Hz, 4H, *endo* CH*H*), 4.98 (d, $J = 14.4$ Hz, 4H, *exo* CH*H*).

^{13}C NMR (125.8 MHz, CD$_3$CN): δ 182.73 (CO), 168.40 (NCN), 136.11 (Ar C), 133.56 (Ar CH), 131.14 (Ar CH), 123.06 (Im CH), 53.18 (NCH$_2$).

Anal. Calc. for $C_{24}H_{20}F_6IrN_4O_2P$: C, 39.29; H, 2.75; N, 7.64. Found: C, 39.59; H, 2.48; N, 7.77%.

Crystals suitable for X-ray diffraction studies were grown by diffusion of vapours between diethyl ether and a solution of the complex in nitromethane.

3.2.7. LRh(dppe) · PF₆ (9)

A solution of bis(diphenylphosphino)ethane (8.0 mg, 20 μmol) in dichloromethane (1 mL) was added dropwise to a solution of $LRh(CO)_2 \cdot PF_6$ (9.0 mg, 14 μmol) in dichloromethane (1 mL) and the solution was stirred for 1 h. The solvent was removed by evaporation and the residue was recrystallised from dichloromethane/ benzene and dichloromethane/isopropanol to give the product as a yellow solid (11.0 mg, 80%).

^{1}H NMR (500.13 MHz, acetone-d_6): δ 7.67–7.73 (m, 8H, PAr H), 7.58–7.63 (m, 4H, Ar H), 7.42–7.50 (m, 12H, PAr H), 7.29–7.35 (m, 4H, Ar H), 7.09 (s, 4H, Im H), 6.47 (d, $J = 13.9$ Hz, 4H, *endo* NC*H*H), 4.35 (d, $J = 13.9$ Hz, 4H, *exo* NCH*H*), 2.50–2.65 (m, 4H, CH_2CH_2).

^{13}C NMR (125.8 MHz, acetone-d_6): δ 188.20 (ddd, $J_{P-C} = 104.7$ Hz, $J_{Rh-C} = 46.8$ Hz, $J_{P-C} = 18.9$ Hz, NCN), 138.13 (m, PAr C), 137.23 (Ar C), 133.24 (apparent t, splitting 5.9 Hz, PAr CH), 133.12 (Ar C3/6), 130.55 (PAr CH), 130.15 (Ar CH), 129.52 (apparent t, splitting 4.5 Hz, PAr CH), 121.34 (Im CH), 52.60 (NCH$_2$), 29.49 (apparent t, splitting 24.7 Hz, CH$_2$CH$_2$).

^{31}P NMR (202.5 MHz, acetone-d_6): δ 64.10 (d, $J_{Rh-P} = 127.5$ Hz, PPh$_2$), -143.00 (sextet, $J_{F-P} = 707.3$ Hz, PF$_6$).

Anal. Calc. for $C_{48}H_{44}F_6N_4RhP_3$: C, 58.43; H, 4.49; N, 5.68. Found: C, 58.50; H, 4.65; N, 5.75%.

Crystals suitable for X-ray diffraction studies were grown by diffusion of vapours between diethyl ether and a solution of the complex in acetonitrile.

3.2.8. LIr(dppe) · PF₆ (10)

A solution of **8** (12 mg, 16.4 μmol) and 1,2-bis(diphenylphosphino)ethane (8 mg, 20 μmol) in dichloromethane (1 mL) was stirred for 3 h. Toluene (0.3 mL) was added and the mixture was evaporated to dryness. The residue was washed with toluene (2 × 3 mL) and ether (2 × 3 mL). The solid was recrystallised from dichloromethane/isopropanol and dried in vacuo to give the product as an orange solid (16 mg, 91%).

^{1}H NMR (500.13 MHz, acetone-d_6): δ 7.67–7.75 (m, 8H, PAr H), 7.55–7.62 (m, 4H, Ar H), 7.4–7.5 (m, 12H, PAr H), 7.28–7.34 (m, 4H, Ar H), 7.10 (s, 4H, Im H), 6.60 (d, $J = 13.9$ Hz, 4H, *endo* NC*H*H), 4.26 (d, $J = 13.9$ Hz, 4H, *exo* NCH*H*), 2.45–2.60 (m, 4H, CH_2CH_2).

^{13}C NMR (125.8 MHz, acetone-d_6): δ 181.66 (dd, $J_{P-C} = 98.2$ Hz, $J_{P-C} = 10.3$ Hz, NCN), 137.18 (d, $J_{P-C} = 45.1$ Hz, PAr C), 137.13 (Ar C), 133.11 (m, PAr

CH), 133.10 (Ar CH), 130.60 (PAr CH), 130.11 (Ar CH), 129.39 (m, PAr CH), 120.97 (Im CH), 52.22 (NCH$_2$), 30.61 (m, CH$_2$CH$_2$).

^{31}P NMR (202.5 MHz, acetone-d_6): δ 53.67 (PPh$_2$), -142.98 (sextet, $J_{F-P} = 707.6$ Hz, PF$_6$).

Anal. Calc. for $C_{48}H_{44}F_6IrN_4O_2P_3$: C, 53.58; H, 4.12; N, 5.21. Found: C, 53.34; H, 4.12; N, 5.18%.

Crystals suitable for X-ray diffraction studies were grown by diffusion of vapours between diethyl ether and a solution of the complex in acetonitrile.

3.2.9. LRh(CO)(PPh₃) · PF₆ (11)

A solution of triphenylphosphine (13 mg, 50 μmol) and $LRh(CO)_2 \cdot PF_6$ (8.3 mg, 12.9 μmol) in dichloromethane (1 mL) was stirred for 30 min. The solution was evaporated to dryness and the residue was recrystallised from dichloromethane/toluene and washed with ether to give the product as a yellow solid (10.8 mg, 95%).

IR (KBr): v max 1985 cm^{-1} (CO).

^{1}H NMR (500.13 MHz, acetone-d_6): δ 7.83 (dd, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 2H, Ar H), 7.69–7.76 (m, 6H, PAr H), 7.61 (dd, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 2H, Ar H), 7.48–7.59 (m, 9H, PAr H), 7.43 (td, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 2H, Ar H), 7.38 (td, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz, 2H, Ar H), 7.34 (dd, $J_{P-H} = 0.9$ Hz, $J_{Rh-H} = 0.4$ Hz, 2H, Im H *trans* to P), 7.01 (t, $J_{Rh-H} = J_{P-H} = 0.4$ Hz, Im H *cis* to P), 6.83 (d, $J = 14.2$ Hz, *endo* C*H*H *trans* to P), 6.16 (d, $J = 14.0$ Hz, *endo* C*H*H *cis* to P), 5.23 (d, $J = 14.2$ Hz, *exo* CH*H* *trans* to P), 4.36 (d, $J = 14.0$ Hz, *exo* CH*H* *cis* to P).

^{13}C NMR (125.8 MHz, acetone-d_6): δ 193.98 (dd, $J_{Rh-C} = 60.2$ Hz, $J_{P-C} = 14.7$ Hz, CO), 181.50 (dd, $J_{Rh-C} = 43.4$ Hz, $J_{P-C} = 14.5$ Hz, NCN *cis* to P), 178.91 (dd, $J_{P-C} = 94.8$ Hz, $J_{Rh-C} = 45.8$ Hz, NCN *trans* to P), 136.95 (Ar C), 136.66 (Ar C), 135.14 (dd, $J_{P-C} = 42.6$ Hz, $J_{Rh-C} = 0.8$ Hz, PAr C), 134.63 (dd, $J_{P-C} = 12.6$ Hz, $J_{Rh-C} = 0.9$ Hz, PAr CH), 133.45 (Ar CH), 133.18 (Ar CH), 131.47 (d, $J_{P-C} = 2.1$ Hz, PAr CH), 130.59, 130.54 (Ar C4, Ar CH), 129.69 (d, $J_{P-C} = 9.8$ Hz, PAr CH), 122.48 (dd, $J_{P-C} = 3.0$ Hz, $J_{Rh-C} = 1.1$ Hz, Im CH *trans* to P), 122.06 (d, $J_{Rh-C} = 1.1$ Hz, Im CH *cis* to P), 53.31 (d, $J_{Rh-C} = 1.3$ Hz, NCH$_2$ *trans* to P), 52.69 (d, $J_{Rh-C} = 1.1$ Hz, NCH$_2$ *cis* to P).

^{31}P NMR (202.5 MHz, acetone-d_6): δ 41.65 (d, $J_{Rh-P} = 122.7$ Hz, PPh$_3$), -138.40 (septet, $J_{F-P} = 707.4$ Hz, PF$_6$).

Anal. Calc. for $C_{41}H_{34}F_6N_4OP_2Rh$: C, 56.05; H, 4.02; N, 6.38. Found: C, 55.96; H, 4.03; N, 6.54%.

$LRh(CO)(PPh_3) \cdot BPh_4$ was obtained by metathesis of **11** with NaBPh$_4$ in acetone, precipitation by addition of water, and recrystallisation from CH$_2$Cl$_2$/hexanes. Crystals of $LRh(CO)(PPh_3) \cdot BPh_4$ (**11a**) suitable for X-ray diffraction studies were obtained by diffusion of

vapours between diethyl ether and a solution of $LRh(CO)(PPh_3) \cdot BPh_4$ in acetone.

3.3. Structure determinations

Full spheres of 'low'-temperature CCD area-detector diffractometer data were measured (Bruker AXS instrument, ω-scans; monochromatic Mo Kα radiation, $\lambda = 0.7107_3$ Å; T ca. 153 K) yielding N_{total} reflections, these merging to N unique after 'emipirical'/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma\,(F)$ considered 'observed' and used in the full matrix least squares refinements, refining anisotropic displacement parameter forms for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimates. Conventional residuals R, R_w at convergence are cited (weights: $(\sigma^2(F) + 0.000n_wF^2)^{-1}$). Neutral atom complex scattering factors were employed within the XTAL 3.7 program system [29]. Pertinent results are given below and in the tables and figures, the latter showing 50% probability amplitude displacement envelopes for the non-hydrogen atoms; hydrogen atoms, where shown, have arbitrary radii of 0.1 Å. Individual divergences in procedure are footnoted in Table 4, numerous difference map residues being modelled in terms of (often disorderly) solvent molecules, not infrequently associated/concomitant with anion disorder, refinement of these entities on occasion carried out with constrained geometries.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 243722–243730. Copies of this information may be obtained free of charge from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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