Different Reactivity Patterns in Dinuclear Pyrazolate-Bridged Complexes: Stereoselective Formation of Ketonic Carbonyls

Daniel Carmona,*[a] Joaquina Ferrer,[a] José Miguel Arilla,[a] Josefa Reyes,[b] Fernando J. Lahoz,[a] Sergio Elipe,[a] Javier Modrego,[a] and Luis A. Oro*[a]

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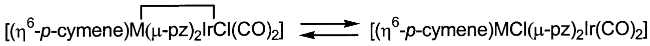
The metal–metal bonded dicarbonyl compounds [(η^6-*p*-cymene)M(μ-pz)$_2$IrCl(CO)$_2$](*M–Ir*) react stereospecifically with PPh$_3$ to yield an enantiomeric pair of ketonic carbonyl compounds [(η^6-*p*-cymene)M(μ-CO)(μ-pz)$_2$IrCl(CO)(PPh$_3$)] [M = Ru (**1**), Os (**2**)] in which the chloride ligand is *trans* to the bridging ketone group. However, the non metal–metal bonded isomers [(η^6-*p*-cymene)MCl(μ-pz)$_2$M′(CO)$_2$], under similar conditions, eliminate CO forming the monosubstitution products [(η^6-*p*-cymene)MCl(μ-pz)$_2$M′(CO)(PPh$_3$)] [M = Ru; M′ = Ir (**3**), Rh (**4**). M = Os; M′ = Rh (**5**)]. Removal of the chloride ligand in **1** affords [RuIr(η^6-*p*-cymene)(CO)$_2$(PPh$_3$)(pz)$_2$]BPh$_4$ as two isomers, **6a**,**b**. The related OsIr compound [(η^6-*p*-cymene)Os(μ-CO)(μ-pz)$_2$Ir(CO)(PPh$_3$)]BPh$_4$ (**9**) has been prepared from [(η^6-*p*-cymene)Os(CO)(μ-pz)$_2$Ir(CO)$_2$]BPh$_4$ (**7**) and PPh$_3$. Again, the OsRh tricarbonyl related to **7** [(η^6-*p*-cymene)Os(CO)(μ-pz)$_2$Rh(CO)$_2$]BPh$_4$ (**8**) reacts differently with PPh$_3$ affording [(η^6-*p*-cymene)Os(CO)(μ-pz)$_2$Rh(CO)(PPh$_3$)]BPh$_4$ (**10**).

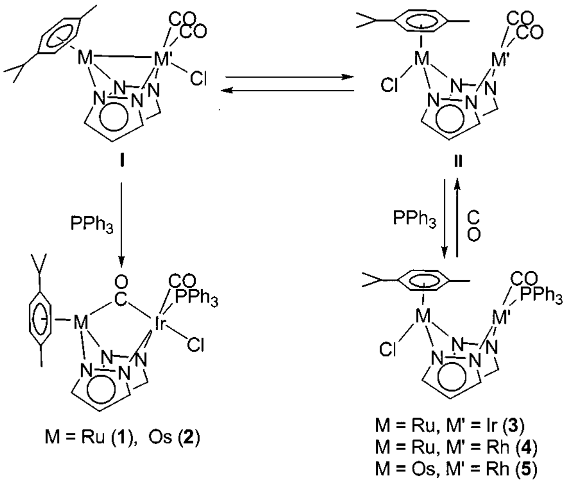
Introduction

Heterodinuclear complexes are promising candidates for new stoichiometric and catalytic reactions.[1] Synergism between the metal centres is believed to be responsible for the improved activity of these heterodimetallic catalysts.[2][3] We have previously described an unusual isomerization equilibrium between heteronuclear pyrazolato complexes implying a chlorotropic shift and the reversible cleavage and formation of M−Ir bonds (M = Ru, Os)[4] according to Equation 1.



$$[(\eta^6\text{-}p\text{-cymene})\overline{\text{M}(\mu\text{-pz})_2\text{Ir}}\text{Cl(CO)}_2] \rightleftharpoons [(\eta^6\text{-}p\text{-cymene})\text{MCl}(\mu\text{-pz})_2\text{Ir(CO)}_2] \quad [1]$$

We now report on the reaction of the above-mentioned complexes towards triphenylphosphane. This reaction is remarkable because it allows the synthesis of new heterodimetallic complexes that contain bridging ketonic carbonyls supported by unusual *cis* frameworks.[5] Furthermore, according to the structural parameters (see below), the reaction implies the oxidation of the iridium from +1 to +3; from theoretical calculations,[6] the ketonic carbonyl group could be envisaged as a CO^{2-} ligand.



Scheme 1. Reaction of isomers **I** and **II** with PPh$_3$

Results and Discussion

Complexes **1** and **2** were prepared in good yield by treating the metal−metal bonded compounds **I** with triphenylphosphane in dichloromethane (Scheme 1). The IR spectra of **1** and **2** showed two strong absorptions in the 2000 and 1650 cm^{-1} regions attributable to ν(CO) stretching modes. The first one is assignable to a terminal metal carbonyl whereas the lower frequency band, in the range expected for organic carbonyls, is typical for ketonic carbonyl ligands.[5] The addition of phosphane caused the molecule to become chiral and, consequently, the ^{1}H NMR spectra of the complexes showed six resonances, each integrating for one proton, attributable to six inequivalent C−H pyrazolate protons, and two AB systems and two doublets assignable to the aromatic and isopropyl methyl

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[a] Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón,
Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain
E-mail: dcarmona@posta.unizar.es
[b] Departamento de Química Inorgánica, Centro Politécnico Superior,
Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC,
E-50015 Zaragoza, Spain

protons of the p-cymene ligand, respectively.[7] The molecular structure of complex **1** was determined by an X-ray crystallographic study (Figure 1). Complex **1** has the ruthenium and iridium atoms triply bridged by two *exo*-bidentate nitrogen-bonded pyrazolates and one CO ligand. The ruthenium atom completes its coordination sphere with an η^6-bonded p-cymene ring. The iridium displays a distorted octahedral geometry typical for Ir^{III} complexes and is also linked to a chloride, *trans* to the carbon atom of the bridging carbonyl [Cl−Ir−C(17) = 167.95(18)°], to a terminal carbonyl and to the triphenylphosphane ligand. The six-membered ring formed by the metals and the pyrazolate nitrogen atoms adopts the usual boat conformation.[8] The Ru···Ir distance observed, 3.4089(5) Å, excludes any significant metal−metal interaction. The structural parameters of the bridging CO ligand [C(17)−O(1) = 1.177(8) Å, Ru−C(17)−Ir = 109.8(3), Ru−C(17)−O(1) = 128.1(6), and Ir−C(17)−O(1) = 121.3(5)°] compare well with those found for ketonic carbonyls[5] suggesting an sp^2 hybridization for the carbon atom. The Ir−N distances, 2.095(6) and 2.069(6) Å, are in the range described for other Ir^{III} complexes with bridging pyrazolate ligands.[8] It is interesting to point out the high stereoselectivity of this reaction; only the enantiomeric pair in which the ketonic carbonyl is *trans* to the chlorine atom has been detected among the three possible geometrical isomers (in the other two the ketonic group would be *trans* to the terminal CO or to the PPh$_3$ ligand).

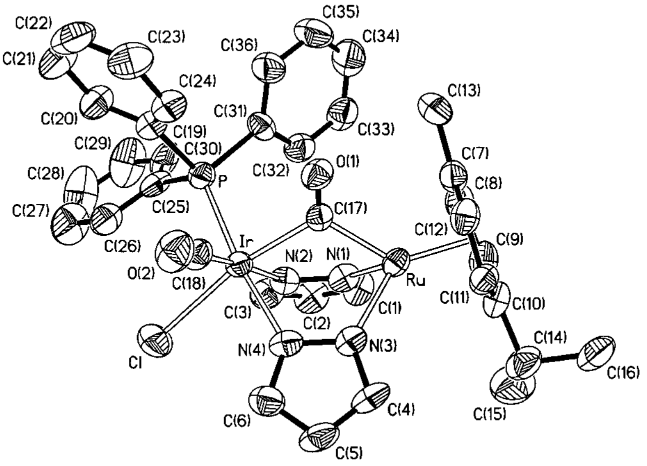


Figure 1. Molecular structure of **1** together with the atom numbering scheme used

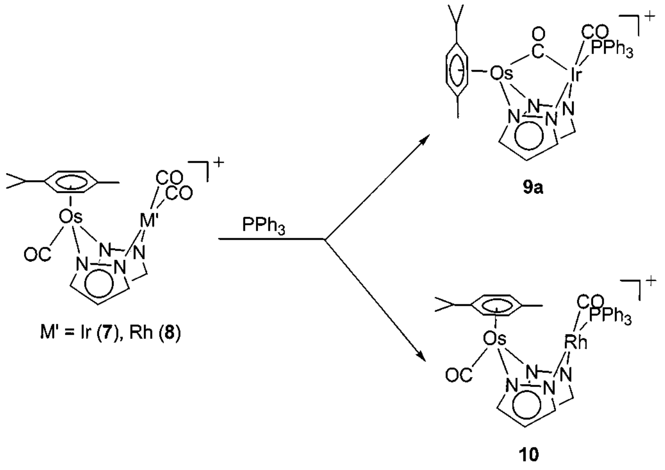
On the other hand, the non metal−metal bonded isomers **II** (Scheme 1) reacted with PPh$_3$ with apparent elimination of CO affording the monocarbonyls **3−5**. Their IR spectra showed a unique strong band at ca. 2000 cm^{-1} corresponding to the ν(CO) stretching mode. The substitution of one of the CO groups by the phosphane also caused the molecules to become chiral as revealed by their ^{1}H NMR spectra (see Experimental Section). As expected, the ^{31}P NMR spectra of the M−Rh complexes **4** and **5** consist of a doublet due to the coupling to ^{103}Rh, whereas a singlet at 1.8 ppm was observed for the Ru−Ir species **3**. The proposed structure for complexes **3−5** is that depicted in Scheme 1 (only one enantiomer has been drawn). The above reaction is reversible: treatment of compounds **3** and **5** with CO afforded the corresponding dicarbonyl species **II**. However, for the RuIr complex, the final isolated product was **1**, because of the chlorotropic equilibrium which operates between **I** and **II**. In fact, complex **3** has only been detected by IR and ^{31}P NMR spectroscopy in the reaction of the appropriate compound **II** with PPh$_3$.

The chloride ligand in **1** can easily be removed by treatment with NaBPh$_4$ in methanol, giving a 45:55 mixture of

Table 1. Selected bond distances (Å) and angles (deg) for the complexes [(η^6-p-cymene)Ru(μ-CO)(μ-pz)$_2$IrCl(CO)(PPh$_3$)] (**1**) and [(η^6-p-cymene)Os(μ-CO)(μ-pz)$_2$Ir(CO)(PPh$_3$)]BPh$_4$ (**9**)

	1 (M = Ru)	**9** (M = Os)		**1** (M = Ru)	**9** (M = Os)
M−N(1)	2.095(6)	2.112(13)	Ir−N(2)	2.069(6)	2.087(11)
M−N(3)	2.097(6)	2.106(12)	Ir−N(4)	2.095(6)	2.113(12)
M−G[a]	1.749(8)	1.741(16)	Ir−Cl	2.586(2)	−
M−C(7)	2.240(8)	2.294(17)	Ir−P	2.339(2)	2.324(4)
M−C(8)	2.197(8)	2.213(15)	Ir−C(17)	2.105(7)	2.184(14)
M−C(9)	2.302(8)	2.232(16)	Ir−C(18)	1.874(8)	1.893(16)
M−C(10)	2.334(7)	2.253(13)	C(17)−O(1)	1.177(8)	1.144(17)
M−C(11)	2.193(7)	2.231(16)	C(18)−O(2)	1.127(8)	1.094(18)
M−C(12)	2.195(7)	2.275(15)	N(1)−N(2)	1.357(8)	1.381(16)
M−C(17)	2.060(7)	2.084(15)	N(3)−N(4)	1.374(8)	1.346(16)
N(1)−M−N(3)	86.2(2)	83.5(5)	N(2)−Ir−N(4)	85.1(2)	85.0(5)
N(1)−M−C(17)	86.8(3)	88.1(5)	N(2)−Ir−C(17)	88.3(3)	90.4(5)
N(1)−M−G[a]	128.9(3)	130.8(7)	N(2)−Ir−C(18)	174.3(3)	176.6(6)
N(3)−M−C(17)	81.6(2)	86.3(5)	N(4)−Ir−P	172.45(18)	173.6(4)
N(3)−M-G[a]	130.2(3)	128.6(6)	N(4)−Ir−C(17)	82.9(2)	85.3(5)
C(17)−M-G[a]	127.2(3)	124.8(7)	N(4)−Ir−C(18)	89.3(3)	91.7(6)
M−C(17)−O(1)	128.1(5)	138.5(12)	P−Ir−C(17)	90.95(18)	99.6(4)
Ir−C(17)−O(1)	121.3(5)	116.2(11)	P−Ir−C(18)	95.1(2)	92.4(5)
M−C(17)−Ir	109.8(3)	105.3(6)	Cl−Ir−C(17)	167.95(18)	−
Ir−C(18)−O(2)	173.5(7)	175.2(15)	Cl−Ir−C(18)	89.8(2)	−

[a] G represents the centroid of the p-cymene ring.



Scheme 2. Reaction of compounds **7** and **8** with PPh$_3$

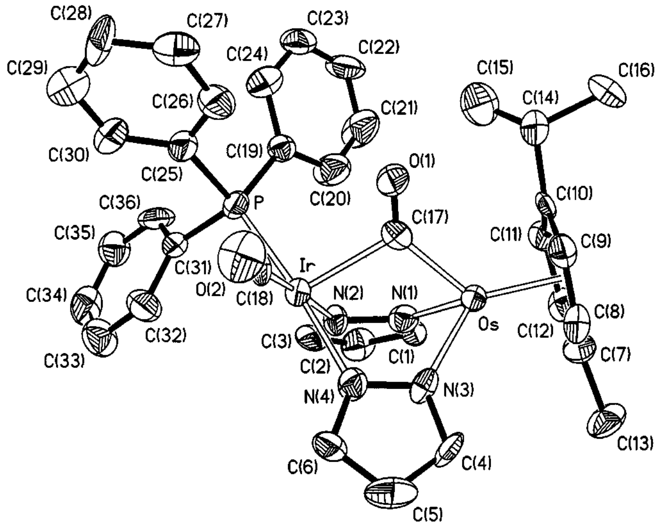


Figure 2. Molecular representation of the dinuclear cation of compound **9** with the atom labelling scheme

two isomers of stoichiometry [RuIr(η^6-*p*-cymene)(CO)$_2$(PPh$_3$)(pz)$_2$]BPh$_4$ (**6a,b**). According to ^{1}H NMR spectroscopic data the minor isomer is chiral while the major is achiral. The IR spectrum of the mixture revealed the presence of both terminal (2035 cm^{-1}) and ketonic (1780 cm^{-1}) CO groups. In this context, it is interesting to mention that the related tricarbonyl compound [(η^6-*p*-cymene)Os(CO)(μ-pz)$_2$Ir(CO)$_2$]BPh$_4$ (**7**)[9] reacts with PPh$_3$ to yield, by CO elimination, the ketonic OsIr complex [(η^6-*p*-cymene)Os(μ-CO)(μ-pz)$_2$Ir(CO)(PPh$_3$)]BPh$_4$ (**9**) whilst the homologous OsRh compound [(η^6-*p*-cymene)Os(CO)(μ-pz)$_2$Rh(CO)$_2$]BPh$_4$ (**8**)[9] yields, under similar conditions, the non-ketonic dicarbonyl compound [(η^6-*p*-cymene)Os(CO)(μ-pz)$_2$Rh(CO)(PPh$_3$)]BPh$_4$ (**10**) (Scheme 2).

The structures of complexes **9** and **10** have been determined by X-ray diffraction methods. For compound **9**, the molecular structure of the dinuclear cation closely resembles that of **1**, after the loss of the terminal chloride ligand (Figure 2). Thus, complex **9** contains the two metal atoms, osmium and iridium, triply bridged by one CO and two pyrazolate ligands. As in **1**, the osmium atom completes its coordination sphere with an η^6-bonded *p*-cymene ring. In this case, however, the iridium centre displays a distorted square-based pyramidal geometry with the carbon atom of the bridging carbonyl ligand occupying the apical position, and with the terminal carbonyl, the triphenylphosphane ligand and the pyrazolate nitrogen atoms forming the polyhedron base. The osmium−iridium separation is very similar to that reported in **1**, 3.3941(12) Å, and excludes any intermetallic interaction. The structural parameters of the bridging carbonyl group serve again to confirm the ketonic nature of this ligand (see Table 1). Unfortunately, in the case of **10**, only very small and weakly diffracting crystals were obtained. Although the data collected for these crystals were of reduced quality, they allowed us to verify the dinuclear framework and, in particular, the absence of any bridging CO group between the two metals.

In conclusion, it is worthwhile to point out the remarkable stereoselectivity encountered in the preparation of **1** and **2** from **I** and in the isolation of **9** from **7**. Furthermore, the different reactivity towards PPh$_3$ that has been found for species **I** and **II**, and for **7** and **8**, is also noteworthy. Most probably, the greater tendency of iridium(I) compared to that of rhodium(I) to pentacoordination and to be oxidised to M^{3+} would explain the obtained results.

Experimental Section

General: All solvents were dried and distilled before use. All reactions were performed under nitrogen. − IR: Perkin−Elmer 783. CH$_2$Cl$_2$ as solvent. − NMR: Varian XL (300.0 MHz and 121.4 MHz, for ^{1}H and ^{31}P, respectively). For ^{1}H NMR, TMS as internal standard; for ^{31}P NMR, CDCl$_3$/CHCl$_3$, (1:1, v/v) as solvent.

[(η^6-*p*-cymene)Ru(μ-CO)(μ-pz)$_2$IrCl(CO)(PPh$_3$)] (1): Triphenylphosphane (60 mg, 0.23 mmol) was added to a solution of [(η^6-*p*-cymene)Ru(μ-pz)$_2$IrCl(CO)$_2$] (150 mg, 0.23 mmol) in dichloromethane (25 mL). After stirring for 12 h the solution was reduced in volume to 0.5 mL under vacuum. Slow addition of diethyl ether led to the precipitation of orange **1** (149 mg, 71%), which was filtered off, washed with diethyl ether and dried under vacuum. Complex **2** was similarly prepared from the corresponding OsIr dicarbonyl. Complexes **4−5** were similarly prepared starting from the corresponding species **II**. The reaction time was 2 h.

1: C$_{36}$H$_{35}$ClIrN$_4$O$_2$PRu (915.43): calcd. C 47.23, H 3.85, N 6.12; found C 46.72, H 3.91, N 6.02. − IR: $\tilde{\nu}$ = 2050, 1650 cm^{-1} (CO). − ^{1}H NMR (CDCl$_3$): δ = 8.03 (d, 1 H, H$_5$ pz), 7.76 (d, 1 H, H$_5$ pz), 7.65 (t, 1 H, H$_3$ pz), 7.11 (d, 1 H, H$_3$ pz), 6.09 (q, $^3J_{H3H4}$ = $^3J_{H5H4}$ = $^4J_{PH}$ = 2.1 Hz, 1 H, H$_4$ pz), 5.92 (t, $^3J_{H3H4}$ = $^3J_{H5H4}$ = 2.1 Hz, 1 H, H$_4$ pz), 5.51, 4.88 (AB system, J_{AB} = 6.4 Hz, C$_6$H$_4$ *p*-cymene), 5.03, 4.66 (AB system, J_{AB} = 5.9 Hz, C$_6$H$_4$ *p*-cymene), 2.72 (sp, 1 H, C*H*Me$_2$ *p*-cymene), 1.81 (s, 3 H, Me *p*-cymene), 1.19 (d, $^3J_{HH}$ = 6.9 Hz, 3 H, CH*Me* *p*-cymene), 1.10 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH*Me* *p*-cymene). − ^{31}P NMR: δ = −14.7 (s).

2: C$_{36}$H$_{35}$ClN$_4$O$_2$PRuOs (1004.59): calcd. C 43.05, H 3.48, N 5.58; found C 42.65, H 2.80, N 5.34. − IR: $\tilde{\nu}$ = 2050, 1640 cm^{-1} (CO). − ^{1}H NMR (CDCl$_3$): δ = 7.98 (br. s, 1 H, H$_5$ pz), 7.75 (br. s, 1 H,

H_5 pz), 7.64 (br. s, 1 H, H_3 pz), 7.03 (d, 1 H, H_3 pz), 5.98 (br. s, 1 H, H_4 pz), 5.81 (br. s, 1 H, H_4 pz), 5.51, 4.92 (AB system, J_{AB} = 5.1 Hz, C_6H_4 *p*-cymene), 5.07, 4.68 (AB system, J_{AB} = 5.7 Hz, C_6H_4 *p*-cymene), 2.62 (sp, 1 H, C*H*Me_2 *p*-cymene), 1.91 (s, 3 H, Me *p*-cymene); 1.10 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, CH*Me* *p*-cymene), 1.05 (d, $^3J_{HH}$ = 6.9 Hz, 3 H, CH*Me* *p*-cymene). − ^{31}P NMR: δ = −13.8 (s).

3: IR: ṽ = 1970 cm^{-1} (CO). − ^{31}P NMR (δ): 1.8 (s).

4: $C_{35}H_{35}ClN_4OPRhRu$ (798.11): calcd. C 52.68, H 4.43, N 7.04; found C 52.43, H 4.91, N 6.92. − IR: ṽ = 1980 cm^{-1} (CO). − ^{1}H NMR ($CDCl_3$) δ = 7.71 (br. s, 1 H, $H_{3/5}$ pz), 7.62 (br. s, 1 H, $H_{3/5}$ pz), 6.67 (d, 1 H, $H_{5/3}$ pz), 6.18 (br. s, 1 H, H_4 pz), 5.80 (t, $^3J_{H3H4}$ = $^3J_{H5H4}$ = 1.8 Hz, 1 H, H_4 pz), 6.13, 5.14 (AB system, J_{AB} = 5.5 Hz, C_6H_4 *p*-cymene), 5.86, 5.00 (AB system, J_{AB} = 5.8 Hz, C_6H_4 *p*-cymene), 2.55 (sp, 1 H, C*H*Me_2 *p*-cymene), 1.77 (s, 3 H, Me *p*-cymene), 1.22 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CH*Me* *p*-cymene), 1.05 (d, $^3J_{HH}$ = 7.0 Hz, 3 H, CH*Me* *p*-cymene). − ^{31}P NMR: δ = 41.9 (d, $^1J_{RhP}$ = 153 Hz).

5: $C_{35}H_{35}ClN_4OOsPRh$ (887.27): calcd. C 47.39, H 3.94, N 6.31; found C 46.63, H 3.64, N 6.06. − IR: ṽ = 1980 cm^{-1} (CO). − ^{1}H NMR ($CDCl_3$): δ = 7.65 (br. s, 1 H, $H_{3/5}$ pz), 7.57 (br. s, 1 H, $H_{3/5}$ pz), 6.54 (br. s, 1 H, $H_{5/3}$ pz), 6.09 (br. s, 1 H, H_4 pz), 5.74 (br. s, 1 H, H_4 pz), 6.57, 5.45 (AB system, J_{AB} = 5.1 Hz, C_6H_4 *p*-cymene), 6.10, 5.22 (AB system, J_{AB} = 5.1 Hz, C_6H_4 *p*-cymene), 2.45 (sp, 1 H, C*H*Me_2 *p*-cymene), 1.77 (s, 3 H, Me *p*-cymene); 1.20 (d, $^3J_{HH}$ = 6.9 Hz, 3 H, CH*Me* *p*-cymene), 1.02 (d, $^3J_{HH}$ = 6.9 Hz, 3 H, CH*Me* *p*-cymene). − ^{31}P NMR: δ = 42.3 (d, $^1J_{RhP}$ = 154 Hz).

[RuIr(η^6-*p*-cymene)(CO)$_2$(PPh$_3$)(pz)$_2$]BPh$_4$ (6a,b): To a solution of [(η^6-*p*-cymene)Ru(μ-CO)(μ-pz)$_2$IrCl(CO)(PPh$_3$)] (**1**) (100 mg, 0.11 mmol) in methanol (40 mL) was added $NaBPh_4$ (79 mg, 0.23 mmol). An orange solid precipitated which, after stirring for 15 h, was filtered off and washed with cold methanol (79 mg, 60%). − $C_{60}H_{55}BIrN_4O_2PRu$ (1199.21): calcd. C 60.11, H 4.62, N 4.69; found C 60.19, H 4.92, N 4.76. − ^{1}H NMR ($CDCl_3$): δ = 6.48 (br. s, pz), 6.20 (br. s, pz), 6.01 (pt, pz), 5.98 (pt, pz), 5.94 (pt, pz), 5.29 (s, C_6H_4 *p*-cymene), 5.13 (br. s, C_6H_4 *p*-cymene), 4.89 (br. s, C_6H_4 *p*-cymene), 2.40 (m, C*H*Me_2 *p*-cymene), 1.81 (s, Me *p*-cymene), 1.79 (s, Me *p*-cymene), 1.13 (d, ^3JHH = 6.7 Hz, CH*Me* *p*-cymene), 0.94 (d, $^3J_{HH}$ = 6.3 Hz, CH*Me* *p*-cymene), 0.94 (d, $^3J_{HH}$ = 6.3 Hz, CH*Me* *p*-cymene). − ^{31}P{^{1}H} NMR: δ = −12.3 (s), 1.2 (s).

[(η^6-*p*-cymene)Os(μ-CO)(μ-pz)$_2$Ir(CO)(PPh$_3$)]BPh$_4$ (9): To a solution of [(η^6-*p*-cymene)Os(CO)(μ-pz)$_2$Ir(CO)$_2$]BPh$_4$ (100 mg, 0.09 mmol) in dichloromethane (20 mL) was added PPh_3 (25 mg, 0.09 mmol). After stirring for 1 h the solution was evaporated to *ca.* 0.5 mL under vacuum. Slow addition of diethyl ether led to a yellow precipitate (107 mg, 88%), which was filtered off, washed with diethyl ether and dried under vacuum. Complex **10** was similarly prepared from the corresponding OsRh tricarbonyl parent compound.

9: $C_{60}H_{55}BIrN_4O_2OsP$ (1288.37) calcd. C 55.95, H 4.27, N 4.35; found C 55.40, H 4.01, N 4.13. − IR: ṽ = 2045, 1745 cm^{-1} (CO). − ^{1}H NMR [$(CD_3)_2CO$]: δ = 8.07 (m, 1 H, $H_{3/5}$ pz), 6.17 (br. s, 1 H, $H_{3/5}$ pz), 6.05 (br. s, 1 H, H_4 pz), 5.96 (br. s, 1 H, H_4 pz), 6.64, 6.29 (AB system, J_{AB} = 6.3 Hz, C_6H_4 *p*-cymene), 5.95, 5.76 (AB system, J_{AB} = 5.7 Hz, C_6H_4 *p*-cymene), 2.89 (sp, 1 H, C*H*Me_2 *p*-cymene), 2.40 (s, 3 H, Me *p*-cymene), 1.30 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, CH*Me* *p*-cymene), 1.06 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, CH*Me* *p*-cymene). − ^{31}P NMR (δ): 1.5 (s).

10: $C_{60}H_{55}BN_4O_2OsPRh$ (1199.05): calcd. C 60.12, H 4.59, N 4.67; found C 59.98, H 4.62, N 4.58. − IR: ṽ = 2019, 1998 cm^{-1} (CO). − ^{1}H NMR [$(CD_3)_2CO$]: δ = 6.60 (br. s, 1 H, $H_{3/5}$ pz), 6.25 (br. s, 1 H, H_4 pz), 5.91 (br. s, 1 H, H_4 pz), 6.12 (AB system, J_{AB} = 6.0 Hz, C_6H_4 *p*-cymene), 5.99 (AB system, J_{AB} = 6.6 Hz, C_6H_4 *p*-cymene), 2.60 (sp, 1 H, C*H*Me_2 *p*-cymene), 1.93 (s, 3 H, Me *p*-cymene), 1.17 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, CH*Me* *p*-cymene), 1.10 (d, $^3J_{HH}$ = 6.9 Hz, 3 H, CH*Me* *p*-cymene). − ^{31}P NMR: δ = 41.3 (d, $^1J_{RhP}$ = 154 Hz).

X-ray Crystal Structure Analysis: Crystal data for **1**: $C_{36}H_{35}ClIrN_4O_2PRu \cdot CHCl_3$, M = 1034.79, orange irregular block (0.35 × 0.29 × 0.19 mm), monoclinic, space group $P2_1/n$, Z = 4, a = 10.8933(7), b = 17.8179(15), c = 20.0620(14) Å, β = 94.908(7)°, V = 3879.7(7) Å^3, D_c = 1.772 g cm^{-3}, μ = 4.171 mm^{-1}, *F(000)* = 2024. Intensity data were collected at 293 K on a Siemens-Stoe AED2 diffractometer with graphite-monochromated Mo-*Kα* radiation (λ = 0.71073 Å) using a $\omega/2\theta$ scan. The structure was solved by Patterson method (SHELXS-97)[11] and refined on F^2 by full-matrix least-squares (532 parameters, 106 restraints; SHELXL-97[11]). Static disorder was observed for the isopropyl group of the *p*-cymene and for a phenyl ring of the phosphane ligand; a chloroform solvent molecule was also found disordered. Anisotropic adps were used for nondisordered non-hydrogen atoms. A total of 6871 unique reflections were obtained from 7257 measured reflections [R_{int} = 0.0236; 4534 with $I > 2\sigma(I)$]. Final agreement factors $R1$ = 0.0420, $wR2$ = 0.0965 and S = 0.904. The final Fourier difference map showed residual peaks in the range 1.57 to −1.86 e/Å^3; the most intense were close to the iridium atom. Crystal data for **9**: $C_{60}H_{55}BIrN_4O_2OsP \cdot (CH_3)_2CO$, M = 1346.34, yellow irregular block (0.32 × 0.17 × 0.08 mm), triclinic, space group $P\bar{1}$, Z = 2, a = 9.623(2), b = 16.991(3), c = 18.605(4) Å, α = 71.390(10), β = 85.13(2), γ = 76.01(2)°, V = 2797.3(10) Å^3, D_c = 1.598 g cm^{-3}, μ = 4.723 mm^{-1}, *F(000)* = 1328. Intensity data were collected at 200 K on a Siemens P4 diffractometer with graphite-monochromated Mo-*Kα* radiation (λ = 0.71073 Å) using a $\theta/2\theta$ scan. The structure was solved by direct methods (SIR92)[12] and refined as described for **1** (SHELXL-97)[11] from 696 parameters and 65 restraints. Disorder was observed for the isopropyl group and for the acetone solvent molecule. 9619 unique reflections from a total of 12234 collected reflections [R_{int} = 0.0825; 6184 with $I > 2\sigma(I)$]. Final refinement with $R1$ = *0*.0690, $wR2$ = *0*.1821 and S = 1.037. The final Fourier difference map showed residual extrema in the range 1.84 to −0.98 e/Å^3; those positive over 1 e/Å^3 where localised close to the metal atoms. Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-131460 (**1**) and CCDC-131461 (**9**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (E-mail: deposit@ccdc.cam.ac.uk).

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