

Oxidative addition of methyl iodide and iodine to new binuclear rhodium(I) and iridium(I) compounds containing diaminoanthraquinonate-bridging ligands.
Crystal structure of $[\text{Rh}_2(\mu\text{-1,4-DA})(\text{CO})_2(\text{PPh}_3)_2]$
(1,4-H₂DA = 1,4-diaminoanthraquinone)

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Abstract

The binuclear rhodium and iridium complexes containing the 1,4-diaminoanthraquinonate ligand (1,4-DA) $[\text{M}_2(\mu\text{-1,4-DA})\text{L}_2]$ (L = COD, M = Rh (1), Ir (2); L = (CO)₂, M = Rh (3), Ir (4); L = (CO)(PPh₃), M = Rh (5), Ir (6)) have been prepared and oxidative addition of the electrophiles MeI and I₂ has been investigated. The molecular structure of an isomer of compound 5 has been determined by X-ray diffraction methods. Complex 5a crystallised in the triclinic space group *P*-1, with *a* = 9.711(5), *b* = 13.701(7), *c* = 17.990(9) Å, α = 68.53(2), β = 76.98(3), γ = 79.72(3)°, and *Z* = 2. The molecule is binuclear with the metals bridged by an approximately planar tetradentate dianionic 1,4-DA ligand. Both rhodium centres exhibit slightly distorted square-planar coordinations with both phosphine groups *trans* disposed to the aminic nitrogen atoms. Addition of MeI to the rhodium complex 5 leads to the diacyl-dirhodium(III) derivative $[\text{Rh}_2(\mu\text{-1,4-DA})(\text{COMe})_2\text{I}_2(\text{PPh}_3)_2]$ (7). However, addition of MeI to the isoelectronic iridium compound 6 yields the dimethyl-diridium(III) compound $[\text{Ir}_2(\mu\text{-1,4-DA})\text{I}_2(\text{Me})_2(\text{CO})_2(\text{PPh}_3)_2]$ (8). Reaction of iodine with compounds 5 or 6, in a molar ratio M/I₂ = 1/1, yields the symmetrical complexes $[\text{M}_2(\mu\text{-1,4-DA})\text{I}_2(\text{CO})_2(\text{PPh}_3)_2]$ (M = Rh (9), Ir (10)). © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Oxidative addition; Rhodium complexes; Iridium complexes; Binuclear complexes

1. Introduction

The synthesis, structure and reactivity of binuclear metal complexes have attracted considerable interest in recent years [1–3]. Part of this interest has been stimulated by their potential use as models for the study of cooperative effects between adjacent centres in heterogeneous catalytic reactions and their applicability in homogeneous catalytic processes requiring two or more steps mediated by different metal centres [4,5]. Most bimetallic systems described by our group are capable of metal–metal bond formation, and some of the more interesting reactions of these systems are related with the making

and breaking of these metal–metal bonds [6–10]. It seemed attractive to us to design rigid bimetallic systems where the metal centres are maintained separated enough to minimise or exclude their direct interaction (or that through the bridging ligand) and, in such a way, being forced to behave independently. Among those the synthesis and reactivity of rhodium(I) complexes containing quinone type ligands have been recently reported [11,12]. In particular, the binuclear compounds $[\text{Rh}_2(\mu\text{-CA})\text{L}_2]$, (CA = chloranilate dianion, L = COD, (CO), PPh₃), have shown an interesting electrochemistry and tendency to undergo oxidative addition reactions.

In this context, we have studied the synthesis and properties of rhodium and iridium complexes containing anthraquinonate-type ligands. Previous investigations related to this

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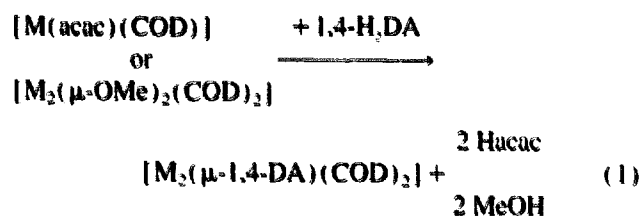
type of ligands cover practically every topic of synthetic and experimental chemistry [13–15], including isolation from natural products [16], total synthesis [17], testing of antimicrobial activity [18], preparation and identification of metal quelates and polymers [19]. In this area, the 1,4-diaminoanthraquinone ligand (1,4-H₂DA) could exhibit a number of different coordination possibilities, being bonded through its nitrogen and/or oxygen donor atoms which make this molecule an interesting potentially polydentate ligand.

Although several mononuclear rhodium and iridium complexes bearing a bidentate nitrogen–oxygen anthraquinone ligand have been described [20–23], we report here the first structurally characterised binuclear complex containing the dianionic form of a diaminoanthraquinone group bridging the metal centres through its four donor atoms.

This paper also describes some results concerning oxidative addition reactions of $[M_2(\mu\text{-}1,4\text{-DA})(\text{CO})_2(\text{PPh}_3)_2]$ ($M = \text{Rh}, \text{Ir}$; 1,4-DA = 1,4-diaminoanthraquinonate dianion) with iodine and methyl iodide. Oxidative additions of substrates, being fundamentally important in many catalytic reactions, have been widely studied on mononuclear metal centres [5]. Similar studies on dinuclear metal centres still continue to be of interest [6–10,24]. A critical consideration in studies involving dinuclear complexes is the potential rigidity that any bridging group could present. The observed rigidity of the bridging anthraquinonate group together with the geometrical localisation of the four donor atoms of the molecule, which should lead to long intermetallic distances, prompted us to examine its oxidative addition reactions. However, identical metal coordination environments have been observed in the isolated binuclear systems probably due to the existence of some intermetallic dependence. Additionally, a different behaviour for the MeI additions has also been recognised, depending on the nature of the metal.

2. Results and discussion

Two general and well-known pathways to prepare binuclear complexes of rhodium(I) or iridium(I) are the treatment of $[M(\text{acac})(\text{diolefin})]$ monomers or $[M_2(\mu\text{-Ome})_2(\text{diolefin})_2]$ dimers with ligands containing acidic protons [6,11,25–27]. Using these synthetic approaches with 1,4-diaminoanthraquinone (1,4-H₂DA) as deprotonable ligand the binuclear rhodium(I) or iridium(I) complexes of general formula $[M_2(\mu\text{-}1,4\text{-DA})(\text{COD})_2]$ ($M = \text{Rh}$ (1), Ir (2)) have been obtained as indicated in Eq. (1).



Compounds 1 and 2 have been isolated as dark green microcrystalline solids and fully characterised by analytical

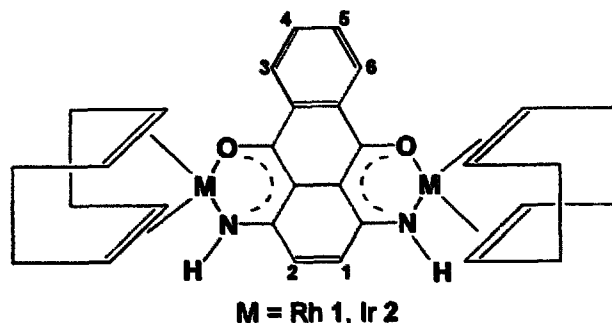


Fig. 1. Proposed molecular structure for complexes 1 and 2 with hydrogen labelling used for NMR studies.

and spectroscopic data. In particular, the ¹H NMR spectra of compounds 1 and 2 show at δ 8.46 and 7.59 ppm (1) or at δ 8.62 and 7.65 ppm (2) the A and X parts of a typical AA'XX' spin system pattern corresponding to the protons 3–6 of the bridging ligands (see Fig. 1). Protons H₁ and H₂ appear as a singlet (6.80 (1) and 7.25 ppm (2)). The amine protons exhibit a singlet at 7.00 (1) and 8.38 ppm (2). The C₂ symmetry of these compounds is confirmed by the signals observed for the cyclooctadiene ligands. The olefinic protons exhibit two broad signals (4.79 and 3.81 ppm (1) or 4.55 and 3.55 ppm (2)) and the aliphatic protons appear as two multiplets at 2.50 and 2.10 ppm (1) or 2.25 and 2.00 ppm (2). The mass spectra of both compounds are consistent with the formation of binuclear species (fast atom bombardment (FAB) $m/z = 658$ (1), 837 (2)). A proposed molecular structure for these compounds is shown in Fig. 1.

Bubbling carbon monoxide through dichloromethane solutions of complexes 1 or 2 leads to the displacement of the cycloocta-1,5-diene ligands and to the formation of the carbonyl derivatives $[M_2(\mu\text{-}1,4\text{-DA})(\text{CO})_4]$ ($M = \text{Rh}$ (3), Ir (4)) [$\nu(\text{CO})(\text{CH}_2\text{Cl}_2)$: 2075, 2010 and 1970 cm^{-1} (3), 2056 and 1985(b) cm^{-1} (4)]. Interestingly, in the solid state, these complexes exhibit very complicated IR spectra in the $\nu(\text{CO})$ region. These spectra and the dark violet colour of the complexes could be indicative of the presence of intermolecular metal–metal interactions [12,27]. In fact, the planarity of the bridging ligand together with the feeble steric demand of the carbonyl groups and the square-planar coordination of the metal centres confer on these molecules a reasonable planarity suitable for the formation of stacked arrangements with potential intermetallic interactions.

The ¹H NMR spectrum of compound 3 shows a typical AA'XX' pattern for the protons of the 1,4-diaminoanthraquinonate ligand centred at 8.57 (A) and 7.78 ppm (X) (see Section 3). Unfortunately, the ¹H NMR spectrum of compound 4 could not be obtained owing to its low solubility in the common solvents.

Further addition of 2 mol of triphenylphosphine to dichloromethane suspensions of compounds 3 or 4 caused the evolution of carbon monoxide and formation of $[M_2(\mu\text{-}1,4\text{-DA})(\text{CO})_2(\text{PPh}_3)_2]$ ($M = \text{Rh}$ (5), Ir (6)). The IR spectra of these compounds show only one broad band (1965 (5), 1950 cm^{-1} (6)) in accordance with a C₂ symmetry. The

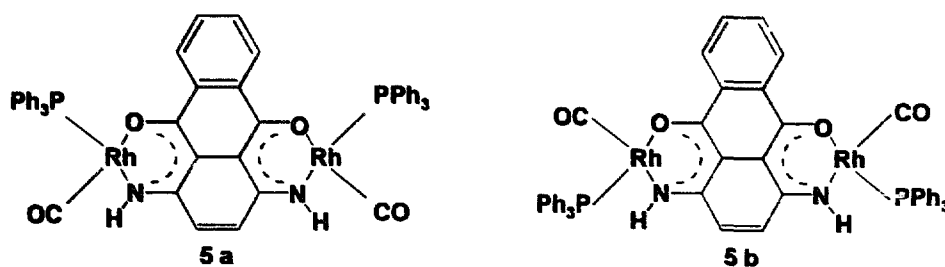


Fig. 2. Proposed molecular structures for the two isomers of 5.

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of compound 5 shows the presence of two doublets of different intensities corresponding to two different isomers whose equivalent phosphorus atoms are *trans* to the same type of donor atom (Fig. 2). The doublet splitting of 149 Hz (δ 41.3 ppm), due to rhodium–phosphorus coupling, could correspond to the isomer having both phosphine ligands *trans* to the nitrogen atoms of the 1,4-diaminoanthraquinonate group (isomer 5a, configuration index *SP-4-3*) [28], the doublet at δ 30.0 ppm ($J_{\text{RhP}} = 129$ Hz) would correspond to the isomer 5b (configuration *SP-4-2*) in which the phosphine groups should be *trans* to the oxygen atoms of the bridging ligand. This tentative assignment has been further confirmed by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum recorded of a CDCl_3 solution of crystals of complex 5a. Analogously, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of compound 6 also indicates the formation of two different isomers (δ 21.9(s) and 4.1 ppm(s)) with *SP-4-2* and *SP-4-3* configuration indexes [28].

By slow diffusion of hexane into a CH_2Cl_2 solution of the reaction mixture of 5, suitable green crystals for only one isomer (5a) were obtained. The crystal structure of 5a consists of neutral binuclear complexes glued by normal dispersion forces. Fig. 3 shows a view of the metallic complex together with the atom labelling scheme, and the selected bond distances and angles are listed in Table 1.

The binuclear complex displays the 1,4-diaminoanthraquinone ligand acting as a dianionic tetradentate bridging group. It coordinates in a chelate fashion to each metal centre through the contiguous ketonic oxygen and aminic nitrogen atoms, forming two additional six-membered metallacycles. Both rhodium atoms complete slightly distorted square-

planar coordinations, being also bonded to a carbonyl ligand and a triphenylphosphine group; the Rh(1) and Rh(2) atoms deviate 0.014(3) and 0.044(3) Å respectively from the mean plane calculated through the coordinated atoms. The relative configurations of ligands around both metal centres, Rh(1) and Rh(2), are identical with the PPh_3 groups *trans* disposed to the aminic nitrogens. Excepting the conformation of the phenyl groups of the phosphines, the whole molecule exhibits a pseudo- C_2 symmetry, showing internal bond distances and angles in the bridging ligand — as well as those of the metal coordination spheres — statistically equivalent at both pseudo-equivalent half-molecules (see Table 1). This feature is in accordance with the NMR and IR spectroscopic data observed in solution (see above).

The central framework of the bridging ligand consisting of three fused six-membered rings is rather planar (no deviation greater than 0.080(7) Å, C(5)). The external unsubstituted carbocycle (C(9)–C(14)) is strictly planar, whereas those substituted exhibit slightly puckered rings: the central one could be considered planar within 0.038(6), and 0.022(7) Å that containing the aminic groups. The metal coordination planes are almost coplanar with the mean plane through the anthraquinone ligand, making dihedral angles of 6.5(1) and 10.6(1)°, for Rh(1) and Rh(2) respectively.

It is quite interesting to note the modifications that the 1,4-diaminoanthraquinone ligand experiences upon coordination. If we compare the internal bond distances in the bridging ligand with those reported for the free 1,4-diaminoanthraquinone molecule [29], a clear modification of the localisation of the π -electron density is evident (Scheme 1). As it is usual for metal-coordinated ketones the metal–oxygen bond

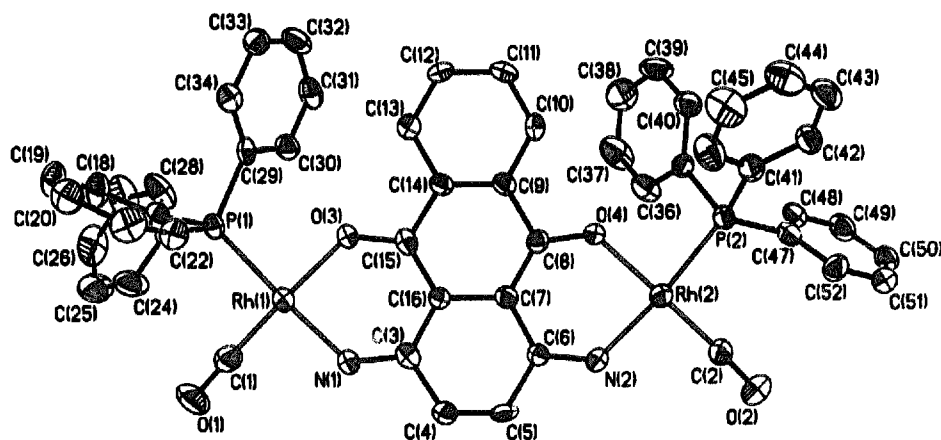


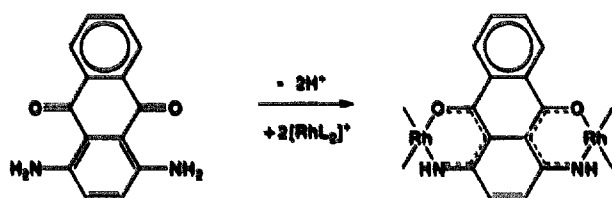
Fig. 3. Molecular representation of complex 5a with the same numbering scheme.

Table 1
Selected bond lengths (Å) and angles (°) for the complex $[\text{Rh}_2(\mu\text{-}1,4\text{-DA})(\text{CO})_2(\text{PPh}_3)_2]$ (**5a**)^a

Rh(1)–P(1)	2.276(2)	Rh(2)–P(2)	2.271(2)
Rh(1)–O(3)	2.014(4)	Rh(2)–O(4)	2.014(4)
Rh(1)–N(1)	2.003(5)	Rh(2)–N(2)	2.004(5)
Rh(1)–C(1)	1.790(7)	Rh(2)–C(2)	1.806(7)
C(1)–O(1)	1.165(7)	C(2)–O(2)	1.142(7)
O(3)–C(15)	1.297(6)	O(4)–C(8)	1.286(6)
N(1)–C(3)	1.301(7)	N(2)–C(6)	1.330(7)
C(3)–C(4)	1.459(8)	C(5)–C(6)	1.455(7)
C(3)–C(16)	1.434(7)	C(6)–C(7)	1.437(7)
C(4)–C(5)	1.309(8)	C(7)–C(16)	1.477(7)
C(7)–C(8)	1.404(7)	C(15)–C(16)	1.410(8)
C(8)–C(9)	1.462(8)	C(14)–C(15)	1.473(7)
C(9)–C(10)	1.419(8)	C(13)–C(14)	1.426(8)
C(10)–C(11)	1.374(8)	C(12)–C(13)	1.363(8)
C(9)–C(14)	1.383(7)	C(11)–C(12)	1.391(8)
P(1)–C(Ph) ^b	1.829(4)	P(2)–C(Ph) ^b	1.824(4)
P(1)–Rh(1)–O(3)	91.63(12)	P(2)–Rh(2)–O(4)	88.10(12)
P(1)–Rh(1)–N(1)	177.2(2)	P(2)–Rh(2)–N(2)	172.7(2)
P(1)–Rh(1)–C(1)	90.8(2)	P(2)–Rh(2)–C(2)	93.0(2)
O(3)–Rh(1)–N(1)	85.8(2)	O(4)–Rh(2)–N(2)	85.8(2)
O(3)–Rh(1)–C(1)	174.9(2)	O(4)–Rh(2)–C(2)	178.5(2)
N(1)–Rh(1)–C(1)	91.9(3)	N(2)–Rh(2)–C(2)	93.1(2)
Rh(1)–C(1)–O(1)	176.5(6)	Rh(2)–C(2)–O(2)	177.3(6)
Rh(1)–O(3)–C(15)	131.1(4)	Rh(2)–O(4)–C(8)	130.7(4)
Rh(1)–N(1)–C(3)	131.5(4)	Rh(2)–N(2)–C(6)	130.9(4)
N(1)–C(3)–C(16)	124.8(5)	N(2)–C(6)–C(7)	124.4(5)
N(1)–C(3)–C(4)	117.3(5)	N(2)–C(6)–C(5)	116.7(5)
O(3)–C(15)–C(16)	125.7(5)	O(4)–C(8)–C(7)	127.2(5)
O(3)–C(15)–C(14)	115.8(5)	O(4)–C(8)–C(9)	114.3(5)
Rh(1)–P(1)–C(Ph) ^b	115.4(1)	Rh(2)–P(2)–C(Ph) ^b	114.9(1)
C(Ph)–P(1)–C(Ph) ^b	103.0(2)	C(Ph)–P(2)–C(Ph) ^b	103.3(2)

^a Molecular parameters have been organised to include in each column related parameter values according to the C_2 pseudo-symmetry of the molecule (see text).

^b Mean values for bond distances and angles including the *ipso*-carbons of the phenyl groups have been incorporated.



Scheme 1.

formation leads to elongation of the ketonic C=O distance, (from 1.254(2) Å in the free ligand to 1.297 and 1.286(6) Å in **5a**) and, additionally, the C(6)–C(7) and C(3)–C(16) bonds are also lengthened (from 1.413(2) to 1.434 and 1.437(7) Å in **5a**). On the other hand, a significant shortening of the C–N separation (from 1.348(2) to 1.301 and 1.330(7) Å in **5a**) and of the C(7)–C(8) and C(15)–C(16) bond distances (from 1.440(2) to 1.404(7) and 1.410 Å in **5a**) is also apparent. All these structural changes reflect a certain redistribution of the π -electron density from the diaminic carbon ring towards the formed metallacycle (Scheme 1). Surprisingly these modifications are also asso-

ciated to a significant shortening of the C(4)–C(5) bond (1.337(3) Å in the free 1,4-DA molecule) which shows a distance, 1.309(8) Å, clearly in the range of C–C double bonds.

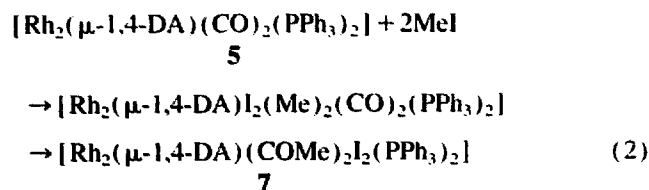
The Rh–N and Rh–O bond distances (mean values 2.003(4) and 2.014(3) Å) are both significantly shorter than those reported in related neutral rhodium(I) complexes in which a monoanionic *N,O*-chelate ligand is bonded to the 'Rh^I(CO)(PPh₃)' moiety (Rh–N 2.039–2.162(6), and Rh–O 2.027–2.070(7) Å) [30]. These are, for instance, the cases of the closely related complexes of general formulae $[\text{Rh}^{\text{I}}(\text{N},\text{O}\text{-L})(\text{CO})(\text{PPh}_3)]$ with *N,O*-L being 8-hydroxyquinolinate (Rh–N 2.098(9), Rh–O 2.042(5) Å) [31], *o*-tolylsalicylaldiminate (Rh–N 2.092(7), Rh–O 2.027(6) Å) [22], 2-quinolinecarboxylate (Rh–N 2.162(6), Rh–O 2.035(5) Å) [32], and 2-imino-4-pentanone (Rh–N 2.045, Rh–O 2.044 Å) [33]. Probably, the electron density delocalised in the N–C–C–O group would be also extended to the whole metallacycle reinforcing partially the Rh–N and Rh–O bonds.

A survey in the CSD Database showed that the values observed for the Rh–P and Rh–CO bond lengths in **5a** (means 2.274(2) and 1.803(5) Å) compare well with the average values observed in related square-planar rhodium(I) complexes which contain a carbonyl and a triphenylphosphine coordinated in a *cis* configuration (mean values 2.30(4) and 1.81(3) Å, respectively) [30].

2.1. Oxidative addition of MeI to $[\text{M}_2(\mu\text{-}1,4\text{-DA})(\text{CO})_2(\text{PPh}_3)_2]$ (*M* = Rh (**5**), Ir (**6**))

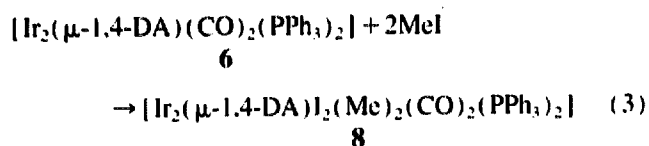
The addition of methyl iodide to a dichloromethane solution of compound $[\text{Rh}_2(\mu\text{-}1,4\text{-DA})(\text{CO})_2(\text{PPh}_3)_2]$ (**5**) in a CH₂Cl₂/Rh = 5/1 molar ratio progressively causes the colour of the solution to become darker. After stirring for 5 min the solution's IR spectrum shows a very small band at 2060 cm⁻¹, corresponding to terminal carbonyl ligands, a broad band at 1715 cm⁻¹, indicating the formation of acyl derivatives [34], and a band at 1965 cm⁻¹ from the starting material **5** still remaining in solution. After 10 min of reaction the signal at 2060 cm⁻¹ disappeared. The IR spectra were periodically recorded every 30 min. After 8 h of stirring only the band at 1715 cm⁻¹ remains while the signal at 1965 cm⁻¹ has completely disappeared. The ³¹P{¹H} NMR spectrum of the isolated green compound shows the presence of two doublets of different intensities (43.3 ppm (*J*_{RhP} = 155 Hz) major, 43.0 ppm (*J*_{RhP} = 155 Hz) minor). All these data indicate the formation of two different acyl derivatives, both formulated as $[\text{Rh}_2(\mu\text{-}1,4\text{-DA})(\text{COMe})_2\text{I}_2(\text{PPh}_3)_2]$ (**7**), whose phosphorus ligands are equivalent and imply the addition of one molecule of methyl iodide to each rhodium centre and further migration of the methyl groups to the nearest carbonyl ligand. The ease of formation for the acyl group in these rhodium complexes made it difficult to study the process in solution and it was not possible to isolate the

proposed rhodium(III) intermediates presumably formulated as $[\text{Rh}_2(\mu\text{-}1,4\text{-DA})\text{I}_2(\text{Me})_2(\text{CO})_2(\text{PPh}_3)_2]$ (see Eq. (2)).



It is well known that iridium complexes present a higher tendency to undergo oxidative addition reactions and also a lower tendency towards carbonyl migration processes than rhodium analogues [35,36]. In such a way, we proposed to study the addition of methyl iodide to the isoelectronic iridium complex $[\text{Ir}_2(\mu\text{-}1,4\text{-DA})(\text{CO})_2(\text{PPh}_3)_2]$ (**6**) in the hope that some intermediates could be isolated to help explain the dynamic development of this type of process.

The addition of methyl iodide to a dichloromethane solution of compound **6** in a $\text{CH}_3\text{I}/\text{Ir} = 5/1$ molar ratio caused the immediate formation of a dark green solution. The IR spectrum was monitored every 20 min. After 5 h of stirring the IR spectrum shows only one band at 2030 cm^{-1} , assignable to the presence of terminal carbonyl ligands, while the band at 1950 cm^{-1} of the starting compound **6** had completely disappeared. These data together with the presence of only one singlet at -7.8 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this solution indicate the formation of a compound with identical environments for the two metal centres. Also the ^1H NMR spectrum of the isolated compound agrees with this proposal. It exhibits one singlet at 1.64 ppm , integrating for six protons, indicative of the equivalence of the terminal methyl groups. Consequently, the reaction occurs by coordination of a methyl group and an iodide ligand to each iridium centre and the formation of the iridium(III) complex $[\text{Ir}_2(\mu\text{-}1,4\text{-DA})\text{I}_2(\text{Me})_2(\text{CO})_2(\text{PPh}_3)_2]$ (**8**) (see Eq. (3)). By contrast with the behaviour observed for rhodium compound **7**, migration of the methyl groups in compound **8**, does not occur even on raising the temperature and in the presence of carbon monoxide.



This observation agrees with that previously described for some oxidative addition reactions of alkyl halides to mononuclear rhodium and iridium complexes [36]. It has been suggested that since the M–C bonds ($\text{M} = \text{Rh}, \text{Ir}$) are thus in the same environments in the two complexes, the easier migration which occurs for rhodium may be a consequence of the relative strengths of the M–C bonds. Bonds to 5d elements are generally stronger than those to the corresponding 4d metal [37]. This proposal also implies significant weakening of the M–C bond in the transition state for migration.

In conclusion, the reaction of methyl iodide with the iridium complex **6** provides an interesting counterpoint in relation with the isoelectronic rhodium complex **5**. There is a significant difference between the two. For rhodium, oxidative addition of methyl iodide is followed by rapid migratory insertion to give the acyl derivative **7** while the iridium compound **6** yields a stable methyliridium complex **8**, for which migratory insertion does not occur.

The planar rigid structure imposed by the bridging ligand should maintain the metal atoms widely separate, $d(\text{Rh}\cdots\text{Rh}) = 8.397(1)\text{ \AA}$, (**5a**), excluding a direct intermetallic interaction and then each metal centre could behave relatively independently with regard to reactions which take place at the second metal site. However, attempts to prepare mixed valence compounds by reacting $[\text{M}_2(\mu\text{-}1,4\text{-DA})(\text{CO})_2(\text{PPh}_3)_2]$ ($\text{M} = \text{Rh}$ (**5**), Ir (**6**)) with methyl iodide in a molar ratio $\text{M}/\text{MeI} = 2/1$ gave equimolecular mixtures of compounds **5** and **7** when $\text{M} = \text{Rh}$, or **6** and **8** when $\text{M} = \text{Ir}$.

2.2. Reaction of molecular iodine with $[\text{M}_2(\mu\text{-}1,4\text{-DA})(\text{CO})_2(\text{PPh}_3)_2]$ ($\text{M} = \text{Rh}$ (**5**), Ir (**6**))

A similar result, formation of binuclear rhodium(III) or iridium(III) derivatives, is obtained by reaction of molecular iodine with dichloromethane solutions of $[\text{M}_2(\mu\text{-}1,4\text{-DA})(\text{CO})_2(\text{PPh}_3)_2]$ ($\text{M} = \text{Rh}$ (**5**), Ir (**6**)). The addition of 2 mol of molecular iodine gave compounds $[\text{M}_2(\mu\text{-}1,4\text{-DA})\text{I}_4(\text{CO})_2(\text{PPh}_3)_2]$ ($\text{M} = \text{Rh}$ (**9**), Ir (**10**)). The increase of the formal oxidation number from I to III parallels the increase in the carbonyl stretching wave numbers from 1965 to 2080 cm^{-1} when $\text{M} = \text{Rh}$, and from 1950 to 2060 cm^{-1} when $\text{M} = \text{Ir}$. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of complexes **9** and **10** show two doublets of different intensities (-2.2 ppm , $J_{\text{RhP}} = 79\text{ Hz}$; -2.6 ppm , $J_{\text{IrP}} = 80\text{ Hz}$) for **9** or two singlets (-11.5 and -25.1 ppm) for **10**, arising from two different isomers whose phosphorus donor ligands are equivalent. The decrease of the rhodium–phosphorus coupling constant values for compound **9** is also consistent with the formation of rhodium(III) derivatives. Thus the reaction should imply the coordination of two iodide groups to each metal centre.

As described in the case of the MeI reactions, the addition of only 1 mol of iodine to dichloromethane solutions of compounds **5** and **6** leads to equimolecular mixtures of the metal(I)–metal(I) (**5** or **6**) and metal(III)–metal(III) (**9** or **10**) derivatives. A similar behaviour has recently been observed in the oxidative addition reactions on binuclear rhodium systems containing a chloranilate or a squarate ligand bridging both metal centres [12,38].

3. Experimental

All reactions were carried out under nitrogen using standard Schlenk techniques and were monitored by solution IR spectroscopy (carbonyl stretching region). $[\text{M}(\text{acac})(\text{COD})]$ [39,40] and $[\text{M}_2(\mu\text{-}1,4\text{-DA})(\text{COD})_2]$ [41,42]

were prepared according to literature methods. Solvents were purified according to standard procedures and distilled under nitrogen prior to use. All other reagents were purchased from Aldrich and used as received. Solution IR spectra were recorded on a Nicolet Magna 550 spectrometer. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were carried out in CDCl_3 solutions at room temperature on a Varian XL 300 spectrometer. ^{31}P chemical shifts are positive downfield from external 85% H_3PO_4 in D_2O . Elemental analyses were carried out with a Perkin-Elmer 240B microanalyser. FAB mass spectra were recorded on a AUTOSPEC V6 spectrometer.

3.1. Preparation of $[\text{Rh}_2(\mu\text{-}1,4\text{-DA})(\text{COD})_2] (\mathbf{1})$

3.1.1. Method 1

A suspension of 1,4- H_2DA (98.4 mg, 0.413 mmol) in acetone (5 ml) was added to a solution of $[\text{Rh}_2(\mu\text{-OMe})_2(\text{COD})_2]$ (200 mg, 0.413 mmol) also in acetone (10 ml). The resulting dark green solution was stirred for 40 min. Then, the solvent was evaporated to dryness. Addition of hexane (8 ml) gave a dark green solid which was isolated by filtration, washed with hexane and vacuum dried (yield 85%). *Anal.* Found: C, 54.51; H, 5.17; N, 4.38. Calc. for $\text{C}_{30}\text{H}_{32}\text{N}_2\text{O}_2\text{Rh}_2$: C, 54.73; H, 4.90; N, 4.25%. FAB m/z : 658 (calc. for $\text{C}_{30}\text{H}_{32}\text{N}_2\text{O}_2\text{Rh}_2$: 658.4). NMR (CDCl_3): ^1H , δ 8.46 (A, AA'XX'; $J_{\text{H}^{\text{H}^{\text{A}}}} = 6.3$, $J_{\text{H}^{\text{H}^{\text{A}}}} = 3.2$ Hz, H^{A} and $\text{H}^{\text{A}'}$, 1,4-DA), 7.59 (X, AA'XX'; $J_{\text{H}^{\text{H}^{\text{X}}}} = 6.3$, $J_{\text{H}^{\text{H}^{\text{X}}}} = 3.2$ Hz, H^{X} and $\text{H}^{\text{X}'}$, 1,4-DA), 7.00 (s, NH), 6.80 (s, H^1 and H^2 , 1,4-DA), 4.79 (b, CH, COD), 3.81 (b, CH, COD), 2.50 (m, CH_2 , COD), 2.10 (m, CH_2 , COD).

3.1.2. Method 2

A suspension of 1,4- H_2DA (47.0 mg, 0.197 mmol) in acetone (5 ml) was added to a solution of $[\text{Rh}(\text{acac})(\text{COD})]$ (122.0 mg, 0.393 mmol) also in acetone (10 ml). The resulting dark green solution was stirred for 60 min. Evaporation of the solvent to dryness and addition of hexane (15 ml) gave a dark green solid which was filtered, washed with hexane and vacuum dried (yield 60%).

3.2. Preparation of $[\text{Ir}_2(\mu\text{-}1,4\text{-DA})(\text{COD})_2] (\mathbf{2})$

3.2.1. Method 1

A suspension of 1,4- H_2DA (180 mg, 0.754 mmol) in acetone (5 ml) was added to a solution of $[\text{Ir}_2(\mu\text{-OMe})_2(\text{COD})_2]$ (500 mg, 0.754 mmol) in acetone (15 ml). The starting yellow solution immediately became dark blue. After stirring for 40 min, the solvent was evaporated to dryness. Addition of hexane (8 ml) gave a dark blue-green solid which was isolated by filtration, washed with hexane and vacuum dried (yield 92%). *Anal.* Found: C, 42.89; H, 3.80; N, 3.17. Calc. for $\text{C}_{30}\text{H}_{32}\text{N}_2\text{Ir}_2\text{O}_2$: C, 43.05; H, 3.85; N, 3.35%. FAB m/z : 837 (calc. for $\text{C}_{30}\text{H}_{32}\text{N}_2\text{Ir}_2\text{O}_2$: 837.04). NMR (CDCl_3): ^1H , δ 8.62 (A, AA'XX'; $J_{\text{H}^{\text{H}^{\text{A}}}} = 10.5$, $J_{\text{H}^{\text{H}^{\text{A}}}} = 2.8$ Hz, H^{A} and $\text{H}^{\text{A}'}$, 1,4-DA), 8.38 (s, NH), 7.65 (X, AA'XX'; $J_{\text{H}^{\text{H}^{\text{X}}}} = 6.3$, $J_{\text{H}^{\text{H}^{\text{X}}}} = 3.2$ Hz, H^{X} and $\text{H}^{\text{X}'}$, 1,4-

DA), 7.25 (s, H^1 and H^2 , 1,4-DA), 4.55 (b, CH, COD), 3.55 (b, CH, COD), 2.25 (m, CH_2 , COD), 2.00 (m, CH_2 , COD).

3.2.2. Method 2

A suspension of 1,4- H_2DA (47.0 mg, 0.197 mmol) in acetone (5 ml) was added to a solution of $[\text{Ir}(\text{acac})(\text{COD})]$ (157.0 mg, 0.393 mmol) also in acetone (10 ml). The resulting dark blue solution was stirred for 60 min. Evaporation of the solvent to dryness and addition of hexane (15 ml) gave a dark green solid which was filtered, washed with hexane and vacuum dried (yield 70%).

3.3. Preparation of $[\text{Rh}_2(\mu\text{-}1,4\text{-DA})(\text{CO})_2] (\mathbf{3})$

Carbon monoxide was bubbled through a solution of $[\text{Rh}_2(\mu\text{-}1,4\text{-DA})(\text{COD})_2]$ (300 mg, 0.456 mmol) in dichloromethane (15 ml) for 20 min to give a dark violet suspension. Evaporation of the solvent to dryness and addition of hexane (15 ml) gave a dark violet solid which was filtered, washed with hexane and vacuum dried (yield 78%). *Anal.* Found: C, 39.40; H, 1.57; N, 5.07. Calc. for $\text{C}_{18}\text{H}_8\text{N}_2\text{O}_6\text{Rh}_2$: C, 39.02; H, 1.46; N, 5.06%. FAB m/z : 554 (calc. for $\text{C}_{18}\text{H}_8\text{N}_2\text{O}_6\text{Rh}_2$: 554.08). IR (CH_2Cl_2): 2075, 2010 and 1970 cm^{-1} [$\nu(\text{CO})$]. NMR ($(\text{CD}_3)_2\text{CO}$): ^1H , δ 10.00 (s, NH), 8.57 (A, AA'XX'; $J_{\text{H}^{\text{H}^{\text{A}}}} = 9.5$, $J_{\text{H}^{\text{H}^{\text{A}}}} = 2.8$ Hz, H^{A} and $\text{H}^{\text{A}'}$, 1,4-DA), 7.78 (X, AA'XX'; $J_{\text{H}^{\text{H}^{\text{X}}}} = 9.5$, $J_{\text{H}^{\text{H}^{\text{X}}}} = 3.2$ Hz, H^{X} and $\text{H}^{\text{X}'}$, 1,4-DA), 7.27 (s, H^1 and H^2 , 1,4-DA).

3.4. Preparation of $[\text{Ir}_2(\mu\text{-}1,4\text{-DA})(\text{CO})_2] (\mathbf{4})$

Carbon monoxide was bubbled through a solution of $[\text{Ir}_2(\mu\text{-}1,4\text{-DA})(\text{COD})_2]$ (163 mg, 0.195 mmol) in dichloromethane (20 ml) for 20 min. The starting violet solution became darker. Evaporation of the solvent to dryness and addition of hexane (15 ml) gave a dark violet solid which was separated by filtration, washed with hexane and vacuum dried (yield 70%). *Anal.* Found: C, 29.16; H, 1.56; N, 3.96. Calc. for $\text{C}_{18}\text{H}_8\text{N}_2\text{Ir}_2\text{O}_6$: C, 29.05; H, 1.10; N, 3.82%. IR (CH_2Cl_2): 2056, and 1985 cm^{-1} [$\nu(\text{CO})$].

3.5. Preparation of $[\text{Rh}_2(\mu\text{-}1,4\text{-DA})(\text{CO})_2(\text{PPh}_3)_2] (\mathbf{5})$

A stoichiometric amount of solid triphenylphosphine (142 mg, 0.541 mmol) was added to a solution of $[\text{Rh}_2(\mu\text{-}1,4\text{-DA})(\text{CO})_2]$ (3) (150 mg, 0.270 mmol) in dichloromethane (15 ml) and the resulting dark green solution was stirred for 40 min. Evaporation of the solvent to dryness and addition of hexane (10 ml) gave a dark green solid which was filtered, washed with hexane and dried under vacuum (yield 90%). *Anal.* Found: C, 61.34; H, 3.40; N, 2.58. Calc. for $\text{C}_{32}\text{H}_{38}\text{N}_2\text{O}_4\text{P}_2\text{Rh}_2$: C, 61.07; H, 3.74; N, 2.74%. IR (CH_2Cl_2): 1965 cm^{-1} [$\nu(\text{CO})$]. NMR: $^{31}\text{P}\{^1\text{H}\}$ (C_6D_6), δ 41.3 (d, $J_{\text{RHP}} = 149$ Hz) **5a**, 30.0 (d, $J_{\text{RHP}} = 129$ Hz) **5b**. ^1H (CDCl_3), δ 8.53 (s, NH), 7.71 (m, PPh_3 and 1,4-DA), 7.33 (m, PPh_3 and 1,4-DA), 6.99 (s, H^1 and H^2 , 1,4-DA) **5a**, 8.53

(s, NH), 7.71 (m, PPh₃ and 1,4-DA), 7.33 (m, PPh₃ and 1,4-DA), 6.81 (m, H¹ and H², 1,4-DA) **5b**.

3.6. Preparation of [Ir₂(μ-1,4-DA)(CO)₂(PPh₃)₂] (**6**)

Addition of triphenylphosphine (251 mg, 0.957 mmol) to a suspension of [Ir₂(μ-1,4-DA)(CO)₂] **4** (350 mg, 0.478 mmol) in dichloromethane (15 ml) led to evolution of carbon monoxide. The resulting dark green solution was evaporated to ca. 1 ml and diethylether (1 ml) followed by hexane (10 ml) added after 30 min of stirring. The dark green solid obtained was filtered, washed with hexane and vacuum dried (yield 68%). *Anal.* Found: C, 52.25; H, 3.30; N, 2.25. Calc. for C₅₂H₃₈N₂I₂O₄P₂: C, 51.94; H, 3.18; N, 2.33%. FAB *m/z*: 1201 (calc. for C₅₂H₃₈N₂I₂O₄P₂: 1201.28). IR (CH₂Cl₂): 1950 cm⁻¹ [ν(CO)]. NMR: ³¹P{¹H} ((CD₃)₂CO), δ 21.9 (s) **6a**, 4.1 (s) **6b**. ¹H ((CD₃)₂CO), δ 7.25 (m, PPh₃ and 1,4-DA) **6a**.

3.7. Preparation of [Rh₂(μ-1,4-DA)(COMe)₂I₂(PPh₃)₂] (**7**)

MeI (93.4 μl, 1.5 mmol) was added to a solution of complex [Rh₂(μ-1,4-DA)(CO)₂(PPh₃)₂] **5** (300 mg, 0.300 mmol) in dichloromethane (15 ml). The mixture was stirred at room temperature for 8 h while the colour of the solution became darker. The solvent was removed under reduced pressure to 1 ml, and the addition of hexane (8 ml) afforded a green solid which was separated by filtration, washed with hexane and vacuum dried (yield 82%). *Anal.* Found: C, 49.59; H, 3.20; N, 1.91. Calc. for C₅₄H₄₄N₂I₂O₄P₂Rh₂: C, 49.64; H, 3.39; N, 2.14%. FAB *m/z*: 1306 (calc. for C₅₄H₄₄N₂I₂O₄P₂Rh₂: 1306.5). IR (CH₂Cl₂): 1715 cm⁻¹ [ν(COMe)]. NMR: ³¹P{¹H} (C₆D₆), δ 43.3 (d, *J*_{RhP} = 155 Hz) **7a**, 43.0 (d, *J*_{RhP} = 155 Hz) **7b**. ¹H (C₆D₆), δ 9.55 (m, NH), 8.00 (m, PPh₃ and 1,4-DA), 7.39 (m, H¹ and H⁵, 1,4-DA), 7.07 (m, PPh₃ and 1,4-DA), 3.12 (s, Me) **7a**, 9.55 (m, NH), 8.00 (m, PPh₃ and 1,4-DA), 7.39 (m, H¹ and H⁵, 1,4-DA), 7.07 (m, PPh₃ and 1,4-DA), 3.07 (s, Me) **7b**.

3.8. Preparation of [Ir₂(μ-1,4-DA)I₂(Me)₂(CO)₂(PPh₃)₂] (**8**)

Addition of methyl iodide (39 μl, 0.62 mmol) to a solution of [Ir₂(μ-1,4-DA)(CO)₂(PPh₃)₂] **6** (150 mg, 0.125 mmol) in dichloromethane (15 ml) led to a dark green solution which was stirred for 9 h. The solvent was evaporated to dryness and addition of hexane (15 ml) gave a dark green solid which was separated by filtration, washed with hexane and vacuum dried (yield 61%). (Found: C, 43.49; H, 2.99; N, 1.81. Calc. for C₅₄H₄₄N₂I₂O₄P₂: C, 43.67; H, 2.97; N, 1.89%). IR (CH₂Cl₂): 2030 cm⁻¹ [ν(CO)]. NMR: ³¹P{¹H} (C₆D₆), δ -7.8 (s). ¹H (CDCl₃), δ 7.36 (m, PPh₃ and 1,4-DA), 1.64 (s, Me).

3.9. Preparation of [Rh₂(μ-1,4-DA)I₂(CO)₂(PPh₃)₂] (**9**)

Iodine (49.6 mg, 0.200 mmol) was added to a solution of [Rh₂(μ-1,4-DA)(CO)₂(PPh₃)₂] (100 mg, 0.100 mmol) in dichloromethane (15 ml). The resulting dark green solution was stirred at room temperature. After 90 min, the IR spectrum revealed the absence of starting material. Concentration of the solvent (1 ml) and addition of hexane (8 ml) gave a green solid which was filtered and washed with hexane (yield 78%). *Anal.* Found: C, 41.07; H, 2.54; N, 1.79. Calc. for C₅₂H₃₈N₂I₂O₄P₂Rh₂: C, 40.81; H, 2.50; N, 1.83%. FAB *m/z*: 1530 (calc. for C₅₂H₃₈N₂I₂O₄P₂Rh₂: 1530.3). IR (CH₂Cl₂): 2080 cm⁻¹ [ν(CO)]. NMR: ³¹P{¹H} (C₆D₆), δ -2.2 (d, *J*_{RhP} = 79 Hz) **9a**, -2.6 (d, *J*_{RhP} = 80 Hz) **9b**. ¹H (C₆D₆), δ 7.60 (m, PPh₃ and 1,4-DA) **9a** and **9b**.

3.10. Preparation of [Ir₂(μ-1,4-DA)I₂(CO)₂(PPh₃)₂] (**10**)

The stoichiometric amount of molecular iodine (34 mg, 0.133 mmol) was added to a solution of [Ir₂(μ-1,4-DA)(CO)₂(PPh₃)₂] **6** (80 mg, 0.066 mmol) in dichloromethane (15 ml). After stirring for 40 min, at room temperature, the solution became darker. The solvent was evaporated to 1 ml and hexane (8 ml) was added to give a green solid, which was filtered, washed with hexane and dried under vacuum (yield 77%). *Anal.* Found: C, 36.58; H, 2.45; N, 1.54. Calc. for C₅₂H₃₈N₂I₂O₄P₂: C, 36.55; H, 2.24; N, 1.64%. IR (CH₂Cl₂): 2060 cm⁻¹ [ν(CO)]. NMR: ³¹P{¹H} (C₆D₆), δ -11.5 (s) **10a**, -25.1 (s) **10b**. ¹H ((CD₃)₂CO), δ 7.60 (m, PPh₃ and 1,4-DA) **10a** and **10b**.

3.11. Crystal structure determination of complex [SP-4-3]-[Rh₂(μ-1,4-DA)(CO)₂(PPh₃)₂] (**5a**)

Dark green single crystals of **5a** were obtained by slow diffusion of hexane into a dichloromethane solution of the reaction mixture of **5**; a plate of approx. dimensions 0.42 × 0.40 × 0.08 mm was selected. Diffraction data were collected with a Stoe-Siemens AED-2 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Cell constants were obtained from the least-squares fit on the setting angles of 50 reflections in the range 15 ≤ 2θ ≤ 25°. Reflections with 2θ in the range 3–50° (-11 ≤ h ≤ 11; -16 ≤ k ≤ 15; -21 ≤ l ≤ 1) were measured using the ω/2θ scan technique. Data were corrected for Lorentz and polarisation effects. Reflections were also corrected for absorption by an empirical method (11 reflections) [43]. Three standard reflections were measured every hour as a check on crystal and instrument stability; no significant variation was observed. Other details of the data collection are given in Table 2.

The structure was solved by direct methods (SIR92) [44] and difference Fourier techniques and refined by full-matrix least-squares on F² (SHELXL93) [45], first with isotropic and then with anisotropic displacement parameters for the non-hydrogen atoms. The starting positions for the hydrogen

Table 2
Crystallographic data and data refinement for $[\text{Rh}_2(\mu\text{-}1,4\text{-DA})(\text{CO})_2\text{-}(\text{PPh}_3)_2] (\mathbf{5a})$

Formula	$\text{C}_{52}\text{H}_{38}\text{N}_2\text{O}_4\text{P}_2\text{Rh}_2$
Formula weight	1022.60
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	9.711(5)
<i>b</i> (Å)	13.701(7)
<i>c</i> (Å)	17.990(9)
α (°)	68.53(2)
β (°)	76.98(3)
γ (°)	79.72(3)
<i>V</i> (Å ³)	2158(2)
<i>Z</i>	2
ρ_{calc} (g cm ⁻³)	1.574
μ (mm ⁻¹)	0.889
Absorption correction method	ψ -scan
Min., max. transmission factors	0.810, 0.860
Temperature (K)	200.0(2)
$R(F)$ [$F^2 > 2\sigma(F^2)$] ^a	0.0469
$wR(F^2)$ [all data] ^b	0.0997
<i>S</i> ^c	0.991

^a $R(F) = \sum |F_o| - |F_c| / \sum |F_o|$, for 4186 observed reflections.

^b $wR(F^2) = (\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2])^{1/2}$.

^c $S = [\sum [w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$; *n* = number of reflections, *p* = number of parameters.

atoms for the 1,4-anthraquinonate ligand were located on a difference Fourier map, but those of the phenyl rings were calculated geometrically. All hydrogen atoms were refined riding on carbon or nitrogen atoms with two common isotropic displacement parameters, one for the phenyl groups and one for the hydrogens of the bridging ligand. The refinement converged at $wR(F^2) = 0.0997$ for 561 parameters and 7581 unique reflections, from a total of 7883 collected ($R_{\text{int}} = 0.0590$). The calculated weighting scheme applied is $1 / [\sigma^2(F_o^2) + (0.0373P)^2]$, with $P = (F_o^2 + 2F_c^2) / 3$. Scattering factors were used as implemented in the refinement program [45].

4. Conclusions

Binuclear complexes containing the rigid 'M₂(μ-1,4-DA)' system (M = Rh^I, Ir^I) react with I₂ and MeI to yield binuclear Rh^{III} and Ir^{III} derivatives. A different chemical behaviour in the methyl iodide addition has been observed depending on the nature of the metal. Since acetyl derivatives are the final product of the addition on the rhodium systems, no methyl migration has been detected in the isoelectronic iridium complex.

5. Supplementary material

A table of X-ray crystallographic data, including complete positional parameters, anisotropic thermal parameters, bond

distances, bond angles (CIF file, 9 pages) and observed and calculated structure factors (17 pages) are available from the authors upon request.

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