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ARTICLE

Group 9 Bimetallic Carbonyl Permethylpentalene Complexes

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We describe the synthesis, structure and bonding of the first iridium and rhodium permethylpentalene complexes, *syn*-[M(CO)₂]₂(μ:η⁵:η⁵-Pn*) (M = Rh, Ir). In fact, [Ir(CO)₂]₂(μ:η⁵:η⁵-Pn*) is the first iridium pentalene complex. We observe an interesting preference for the isolation of the sterically more demanding *syn*-isomer is observed and substantiated by DFT analysis. Upon photolysis, the rhodium analogue yields an unusual tetrameric species Rh₄(CO)₆(μ:η³:η⁵-Pn*)₂ with bridging carbonyls and Rh-Rh bonds, which has been characterised by single crystal X-ray diffraction and by solution NMR spectroscopy.

Introduction

Pentalene (Pn, C₈H₆) can be thought of as two ring-fused cyclopentadienyl units, with two fewer electrons and has captivated chemists for nearly a hundred years.^{1–3} As a neutral moiety it has 8π electrons and is predicted by Hückel theory to be anti-aromatic.^{4,5} However, as a dianion, with 10π electrons, it is aromatic and may be used as a ligand in coordination chemistry.^{6,7} The ability of pentalene to adopt multiple hapticities (allowing it to satisfy differing electronic demands of various metals) makes it a tantalising carbocyclic ancillary ligand.^{8–13} Furthermore when bound to multiple metal centres it may bind them either on the same face or on opposing faces. When in the former *syn*-binding mode the metal centres are forced close together allowing for metal-metal interactions. When bound as the latter *anti*-binding mode the metal centres may still communicate electronically through the delocalised π-framework of the ligand.¹⁴ An elegant example of the *syn*-binding is observed in the 'super-sandwich', Rh₂Pn^R₂ [R = 1,4-(SiⁱPr₃)₂], synthesised by Cloke and co-workers.^{15,16} This species is noteworthy due to its stability (most rhodacene derivatives are kinetically unstable at room temperature) and due to a metal-metal bonding interaction. The first example of a rhodium hydropentalene compound Rh(PnH)COD, was reported by Katz in 1967.¹⁷ This was extended by Manriquez and co-workers who managed to make an anti-heterobimetallic analogue by metallating the opposing side of the pentalene ring first (with RuCp*) to form [Cp*Ru][μ:η⁵:η³-Pn][Rh(η⁴-COD)] (COD = C₈H₁₂).^{18,19} This

species showed high selectivity and activity for the dehydrogenative silylation of styrene.

In 2006 our group successfully synthesised the permethylated pentalene derivative (Pn* = C₈Me₆).^{11,20} Utilising the organic synthon Pn*' [Pn*' = C₈HMe₅(=CH₂)] a cobalt carbonyl complex was synthesised *via* a C-H activation pathway: *syn*-[Co(CO)₂]₂(μ:η⁵:η⁵-Pn*) (**A**).²¹ Inspired by this and the exciting history of C-H activation by the photolysis of group 9 carbonyl complexes we aimed to synthesise the rhodium and iridium congeners.^{22,23} To date Pn* chemistry of the 4d and 5d series has been limited to the early transition metals, this work extends the investigations into the late transition metals, nominally group 9, and presents the first example where iridium had been used in the coordination chemistry of pentalene.

Results and discussion

Synthesis and characterisation of *syn*-[Rh(CO)₂]₂(μ:η⁵:η⁵-Pn*) (**1**)

Syn-[Rh(CO)₂]₂(μ:η⁵:η⁵-Pn*) (**1**) can be synthesised in moderate yield from the reaction of equimolar amounts of [RhCl(CO)₂]₂ with *syn*-(SnMe₃)₂Pn* (selectively made *in situ*).⁹ This route is in contrast to that of **A** where the organic Pn*' synthon is used. **1** is an air-sensitive, microcrystalline, orange solid. The solution phase ¹H NMR spectrum of **1** displays two resonances in a 2:1 intensity ratio with the latter resonance being a doublet (δ = 1.55 and 2.00 ppm). These represent the non-wingtip (NWT, C1, C3, C5, C7 in Fig. 1) and wingtip (WT, C2, C6 in Fig 1) methyl protons respectively. It is interesting to note that the WT-Me protons couple to the rhodium centre (³J_{Rh-H} = 1.5 Hz) whereas for the NWT-Me protons no coupling is observed. This and ¹³C NMR data are consistent with the C_{2v} structure observed in the solid state (*vide infra*), with the carbonyl resonance being considerably shifted downfield (δ = 196 ppm) and coupled to the rhodium centre (¹J_{Rh-C} = 49 Hz).

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Electronic Supplementary Information (ESI) available: Crystallographic information files for structures **1-3** and calculated Cartesian coordinates available. See DOI: 10.1039/x0xx00000x

Table 1: Selected structural parameters for *syn*-[M(CO)₂]₂(μ:η⁵:η⁵-Pn*) (M = Co, Rh, Ir), experimental and calculated (the latter in italics). Ct is the centroid of the C5 rings on the pentalene ligand. Δ is defined as the difference between the mean distances of the metal to bridgehead carbon atoms and those to the remaining non-bridgehead carbon atoms.^{13,24,25}

<i>Syn</i> -[M(CO) ₂] ₂ (μ:η ⁵ :η ⁵ -Pn*)	r(M-C _{ring}) (Å)	r(M-CO) (Å)	r(M-Ct) (Å)	r(M-M) (Å)	Δ
<i>Syn</i> -[Co(CO) ₂] ₂ (μ:η ⁵ :η ⁵ -Pn*) (A) ²¹	2.150(4) <i>2.153</i>	1.748(2) <i>1.735</i>	1.772(4) <i>1.794</i>	2.675(3) <i>2.800</i>	0.217(4) <i>0.259</i>
<i>Syn</i> -[Rh(CO) ₂] ₂ (μ:η ⁵ :η ⁵ -Pn*) (1)	2.321(5) <i>2.367</i>	1.866(5) <i>1.878</i>	1.976(6) <i>2.027</i>	2.913(6) <i>2.998</i>	0.269(6) <i>0.297</i>
<i>Syn</i> -[Ir(CO) ₂] ₂ (μ:η ⁵ :η ⁵ -Pn*) (2)	2.354(8) <i>2.389</i>	1.867(9) <i>1.870</i>	2.167(8) <i>2.053</i>	2.932(4) <i>3.048</i>	0.304(8) <i>0.341</i>

The coupling constant is somewhat lower compared to that observed for Cp*RhCO fragments and more typical of a bridging carbonyl moiety.^{26,27} This difference may arise from the more electron deficient nature on Pn* compared to Cp*. No coupling is observed between any of the methyl carbon resonances and the rhodium centre. This is consistent with the lack of coupling observed for the methyl resonances in Cp*Rh(CO)₂.²⁸ IR spectroscopy shows four bands in the carbonyl region, one extra from that predicted for C_{2v} symmetry (A₁ + B₁ + B₂). The extra band could be due to minor differences in packing that cause the molecule to be less symmetric.

Synthesis and characterisation of *syn*-[Ir(CO)₂]₂(μ:η⁵:η⁵-Pn*) (2)

An analogous synthesis to **1** may be employed for the heavier iridium congener. [IrCl(CO)₂]₂ was formed *in-situ*,²⁹ and the yellow solution was added dropwise to the pentalene synthon *cis*-(SnMe₃)₂Pn* in acetonitrile at room temperature. Extraction with hexane and slow cooling to -35 °C yielded an orange crystalline solid identified as *syn*-[Ir(CO)₂]₂(μ:η⁵:η⁵-Pn*) (**2**).

The ¹H NMR spectrum of **2** reveals two singlet resonances for the Pn* methyl protons in a 2:1 ratio. The ¹³C NMR displays six resonances, occurring in the expected chemical shift range with the carbonyl resonance occurring at δ = 177 ppm. The NMR data imply a solution phase structure consistent with C_{2v}

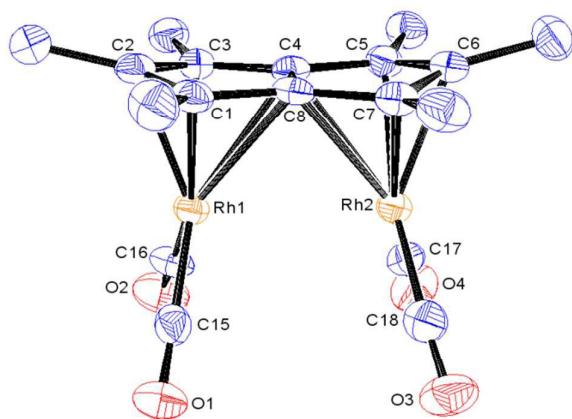


Fig. 1: The single crystal X-ray structure of **1**. Hydrogen atoms are omitted for clarity, and thermal probability ellipsoids are at the 50% level.

symmetry observed in the solid state. Similarly to **1** four stretches occur in the carbonyl region (although three bands are predicted by C_{2v} symmetry).

X-ray crystallographic analysis of **1** and **2**

Single crystals of **1** suitable for X-ray diffraction can be grown by slow-cooling a saturated hexane solution to -35 °C (Fig. 1). **1** crystallises in the P 2₁/n space group with a single molecule in the asymmetric unit. A similar route allows for the crystallisation of **2**, which is isostructural to **1**. Some structural features are listed in Table 1.

The two Rh(CO)₂ fragments are coordinated in a *syn*-disposition about the pentalene ring, with each rhodium having a total of 18 valence electrons (counting the pentalene as η⁵ bound). There is no evidence of bond alternation around the ring with an average C-C bond length of 1.45(2) Å implying the ring system to be fully delocalised. Similarly, the mean C-C bond length in **2** is 1.45(2) Å and is consistent with full delocalisation of the π system.

The Rh-Rh distance in **1** is 2.913(6) Å, which is considerably greater than that of the formally Rh(II) complex Rh₂(μ:η⁵:η⁵-Pn^R)₂ (R = 1,4-SiⁱPr₃, d_{Rh-Rh} = 2.707(1) Å)¹⁶ and implies there is no Rh-Rh interaction. Another factor for this greater distance may be that the five membered rings of the pentalene in **1** are bent away from one another (the angle between their two best planes is 7.0°). This is proposed to be due to the steric repulsion of the two *syn*-metal fragments. This steric repulsion also affects the Rh-C_{ring} distances, where an elongation of the Rh-C_{bridgehead} distance is observed and the metal moves towards more of an η³-binding mode. This ring-slipping phenomenon is well documented in indenyl chemistry and will be discussed later.^{30,31}

The Ir-Ir distance of **2** [2.932(4) Å] exceeds the sum of the covalent radii for two Ir centres (2.52 Å)³² and therefore suggests there is no evidence for an Ir-Ir interaction.

The first row congener of **1** and **2**, *syn*-[Co(CO)₂]₂Pn* (**A**), has previously been synthesised by O'Hare *et al.* and by analysing the three structures potential trends down the group may be identified.²¹ Their key structural parameters are shown in table 1. Attempts to produce a reliable synthesis of any of the *anti*-isomers of **1**, **2** and **A** have to date failed, with DFT calculations showing that the *anti*-isomer of **A** to be 8 kJ mol⁻¹ less stable than the *syn*-isomer, suggesting a stabilising interaction exists between the two metal centres, albeit less than that from a Co-Co bond.

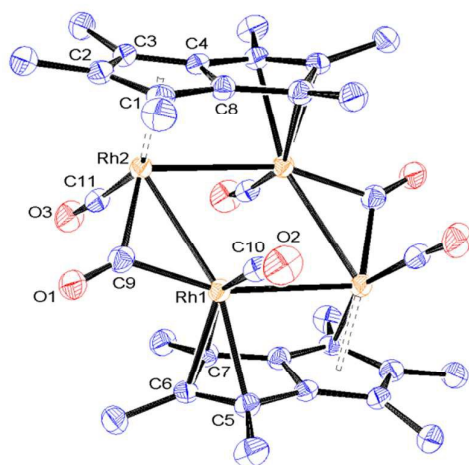


Fig. 2: The single crystal X-ray structure of **3**. Hydrogen atoms are omitted for clarity, and thermal probability ellipsoids are at the 50% level.

In previous examples of rhodium pentalene chemistry the rhodium has favoured binding in an η^3 -manner in order to gain a total 16 electron count. In **1** an 'ene-allyl' shift is observed, if somewhat less marked than in previous examples.^{30,31} The parameter Δ illustrates the ring slippage and hence the deviation from η^5 to η^3 . Δ is defined as the difference between the mean distances of the metal to bridgehead (BH, C4 and C8 in Fig. 1) carbon atoms and those to the remaining non-BH carbon atoms.^{13,24,25} In the previously synthesised double sandwich compounds which involved η^3 binding $M_2Pn^*_2$ ($M = Co, Ni$), values of $\Delta = 0.367$ ($M = Co$) and 0.277 ($M = Ni$) were observed. In the Co analogue, which is also simultaneously bonded η^5 , a value of $\Delta = 0.089$ is measured for that coordination mode.¹³ The values of Δ in Table 1 are considerably less than those measured in the homoleptic sandwich when binding η^3 but a substantial ring slippage is still observed. It is therefore postulated that there is still an interaction with the bridgehead bond (making it formally η^5) however this is significantly less than the interaction with the non-bridgehead carbons. There is also an increase in the value of Δ down the group for the *syn*-bimetallic species, accompanied by an increase in the metal centroid distance. From **A** to **1** we attribute this to an increase in atomic size. This continues from **1** to **2** however and with rhodium and iridium being of a similar size this change is attributed to a weaker interaction between the Pn^* moiety and the metal centre. This is also reflected in the hinge angle, which decreases from **1** to **2**. The hinge angle is a measure of the deviation from planarity of the C5 rings and is defined as the angle between the plane of the WT carbon and NWT carbons and the plane of the NWT carbons and the BH carbons. The hinge angles are 6.8° (for the Co congener **A**), 11.4° (**1**) and 10.9° (**2**). As with Δ , the increase from **A** to **1** is a result of an increase in size of the constituent metals.³² There is also an increase in the M-CO distance on descending from the Co *syn*-bimetallic to the Rh and Ir *syn*-bimetallics (d_M ,

d_{Co} is the same, within error, for **1** and **2**). This is presumably due to the relative size of the central atom, however there is also an increase in the IR stretching frequencies of **1** and **2** compared with **A**, which may also indicate a slightly greater degree of backbonding in the two compounds presented in this work.

Preliminary photolysis experiments of **1**

The photolysis of late transition metal carbonyl complexes has shown to be a promising route to the activation of inert C-H bonds.^{23,33,34,22,35-38} Due to this it was hypothesised that photolysis of these bimetallic carbonyl systems may offer intriguing reactive species.

Photolysis of **1** in C_6D_6 for 24 hours gave rise to three new resonances in the 1H NMR (however resonances assigned to **1** were still present). After this period dark orange crystals began to form and these were found to be suitable for single crystal X-ray diffraction (Fig. 2) and were shown to be an unusual tetrametallic species: $Rh_4(CO)_4(\mu-CO)_2(\mu:\eta^3:\eta^5-Pn^*)_2$ (**3**). Photolysis in a hexane or cyclopentane medium gave rise to the same species, albeit much more rapidly since they do not absorb UV light to the same extent as C_6D_6 .

The 1H NMR spectrum supports the structure data since there are three distinctive Pn^* proton environments, the resonances at $\delta = 1.25$ and 1.83 ppm are broad suggesting a fluxional process (hypothesized to be the Rh atoms switching coordination modes), hence these are assigned to the two NWT environments. Such fluxionality has been previously observed.^{9,39,40} Extraction with CD_2Cl_2 leaves only trace **1** present and reveals the third Me environment ($\delta = 2.29$ ppm), which couples to Rh ($J_{H-Rh} = 1.5$ Hz), giving evidence that this resonance is due to the WT-Me protons. **3** can be synthesised on a large scale but due to difficulty in separation from its parent compound it has not been possible to isolate the bulk material pure.

3 has C_i molecular symmetry. The Rh centres are in very different environments with the two crystallographically inequivalent atoms adopting different binding modes with the pentalene framework [$Rh(2)-\eta^5$ and $Rh(1)-\eta^3$]. For example the Pn^* ligand bound to Rh(2) has a hinge angle of 3.9° (and $\Delta = 0.107$) whereas that bound to Rh(1) has a hinge angle of 14.4° (and $\Delta = 0.434$). Not only is there a slippage towards the WT carbon but there is also a lateral slip towards one of the sides of the Pn^* , illustrated by the Rh(2)-C(1), and Rh(2)-C(3) distances [$2.282(4)$ Å and $2.229(4)$ Å] and the Rh(1)-C(5) and Rh(1)-C(7) distances [$2.243(4)$ Å and $2.275(4)$ Å].

The terminal Rh-CO distances in **3** are nearly the same within the 3σ experimental error [$1.849(4)$ Å for Rh(2) and $1.867(4)$ Å for the Rh(1)]. These are comparable to those observed in **1** [ranging from $1.851(6)$ Å to $1.880(6)$ Å]. The Rh-Rh distances (for the two Rh atoms bound to the same pentalene) are also the same within experimental error [$2.913(6)$ Å for **1** compared to $2.917(4)$ Å for **3**]. The Rh-(μ -CO) distances show a considerable elongation, compared to the terminal Rh-CO, [$2.008(4)$ Å and $2.010(4)$ Å], as is expected for a carbonyl bridging two metal centres. It is interesting that despite the differing Pn^* binding modes to the two Rh centres, the μ -CO

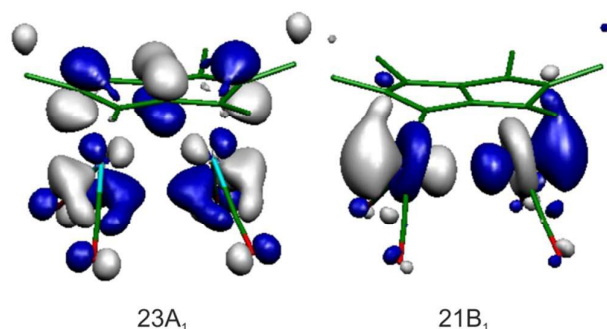


Fig. 3: Iso-surfaces for the HOMO ($23A_1$) and HOMO-1 ($21B_1$) for **1**. (Hydrogen atoms omitted for clarity).

ligands appear to be bound in a symmetrical fashion. The bridging CO also has the effect of bringing the Rh centres into closer proximity, indeed they are closer than those bound to the same Pn^* ring [$2.823(4)$ Å compared to $2.917(4)$ Å]. Though this is the shortest M-M distance reported in this work (excluding **A**), it is still far longer than Cloke's homoleptic sandwich: $Rh_2Pn^R_2$ [$R = 1,4-(Si^iPr_3)_2$, Rh-Rh = $2.707(1)$ Å],¹⁵ and therefore any bond interaction may be negligible. The μ -CO shows a slight lengthening in its bond [$1.172(5)$ Å, the terminal CO distances in **1** and **3** ranges from $1.139(6)$ Å – $1.152(7)$ Å], which is to be expected with two metals being available for π -backbonding.

There are two likely mechanisms for the formation of **3**. One is the collision of two active fragments of $[Rh_2(CO)_3Pn^*]$ following the loss of CO from **1**. Another possible mechanism would be that an active fragment of $[Rh_2(CO)_3Pn^*]$ reacts with a molecule of **1** releasing a CO molecule. DFT experiments favor the former (*vide infra*). There is no evidence of the fragment coordinating any solvent which suggests the activation barrier for coordination is too high compared to the alternative pathway of the formation of **3**. Similar photolysis experiments using $Cp^*Rh(CO)_2$ have also yielded the known bridged dimer $[Cp^*Rh(\mu-CO)]_2$ and the non-carbonyl bridged dimer $[Cp^*Rh(CO)]_2$.^{41,42}

Unfortunately photolysis of **2** and **A** in aromatic solvent led to no discernible reaction. After prolonged photolysis ligand degradation occurred and no products were identified.

DFT analysis of group 9 bimetallic carbonyl permethylpentalene complexes

Geometries of $syn-M_2(CO)_4Pn^*$ ($M = Co, Rh, Ir$) were optimised

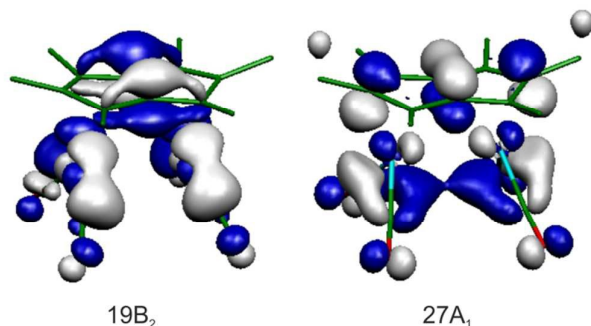


Fig. 4: Iso-surfaces for the LUMO ($19B_2$) and HOMO ($27A_1$) of **2**. (Hydrogen atoms omitted for clarity).

with the symmetry constrained to C_{2v} and in general gave good agreement between experimental and calculated geometries – though the calculated bond lengths were consistently marginally longer than the experimental values (Table 1). Fragment analyses were carried out to determine the M-M bond order and the results were -0.11 for **A**, -0.06 for **1** and 0.16 for **2**. Therefore it is proposed that no metal-metal bonds are present in these molecules. However the bond order does increase down the group and it can be concluded that there is a stable, albeit small, interaction between the $Ir(CO)_2$ moieties. The HOMO and HOMO-1 for **1** are the $23A_1$ and $21B_1$ orbitals respectively (Fig. 3). On second order perturbation grounds, it could be argued that the HOMO and LUMO are the dominant factors in coupling constants. There is significant contribution to these orbitals from the WT-Me carbons which might explain why a $^1H-^{103}Rh$ coupling is observed in the 1H NMR. These two highest occupied orbitals have reversed their order between **1/2** and **A**. It is likely that the M-M antibonding interactions shown in these iso-surfaces cause the ene-ally shift previously described.³¹

For all three congeners the *syn* isomer is considerably more stable than the *anti*-isomer (8 kJ mol⁻¹ for Co, 30.5 kJ mol⁻¹ for Rh, 40.8 kJ mol⁻¹ for Ir). A stable interaction between the $Ir(CO)_2$ moieties can be observed in the HOMO ($27A_1$) (Fig. 4). It also shows that there is a preference for the *syn* complex to form and explains why there is no *anti* product observed in any of the syntheses attempted.

Calculations were performed on **1** to examine the stability of the product after CO loss. It was found that a symmetric *syn*- $Rh_2(CO)_3Pn^*$ complex with a bridging CO between the Rh centres is stable with respect to **1** and is likely to be the intermediate which then dimerises to form the tetrametallic product **3**. DFT optimization of **3** reproduced the structural features found experimentally (see ESI). Again the HOMO of **3** shows a small contribution from the WT-Me protons, perhaps explaining the $^1H-^{103}Rh$ coupling in the 1H NMR (Fig. 5). Also there is a clear bonding interaction between the Rh atoms via the bridging CO and thus it is likely that this interaction holds the tetramer together.

Experimental

General Procedures

General considerations. All reactions were performed under an

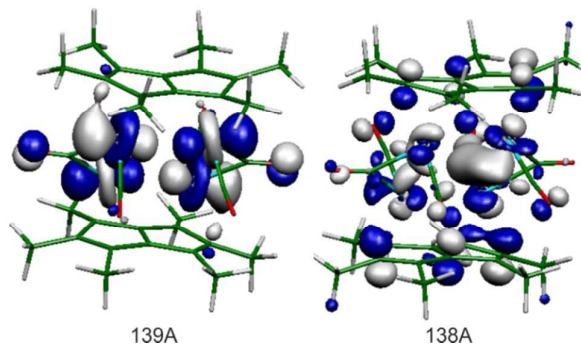


Fig. 5: Iso-surfaces of the LUMO ($139A$) and HOMO ($138A$) of **3**.

inert atmosphere of nitrogen either using standard Schlenk techniques on a dual vacuum/inlet gas manifold or by employment of an MBraun glove box. All glassware was heated in an oven at 180 °C for at least four hours prior to use. Pentane, hexane, benzene, toluene and acetonitrile were dried and degassed using an MBraun SPS-800 solvent purification system and all solvents except acetonitrile were stored in potassium mirrored ampoules. Acetonitrile was stored over 3 Å molecular sieves. Deuterated NMR solvents were purchased from Goss Scientific and were dried over the appropriate drying agent and freeze-thaw-degassed three times: potassium (benzene- d^6), calcium hydride (dichloromethane- d^2).

The following compounds were prepared according to published procedures: $\text{Li}_2\text{Pn}^*(\text{TMEDA})_x$,¹¹ $\text{syn}-(\text{SnMe}_3)_2\text{Pn}^*$,⁹ $\text{syn}-\text{Co}_2(\text{CO})_4(\mu\text{:}\eta^5\text{:}\eta^5\text{-Pn}^*)$,²¹ $[\text{RhCl}(\text{CO})_2]_2$,⁴³ $[\text{IrCl}(\text{COE})_2]_2$,⁴⁴ $[\text{IrCl}(\text{CO})_2]_2$.²⁹

NMR spectroscopy. ^1H and ^{13}C NMR spectra were recorded using a Varian Mercury VX-Works 300 MHz spectrometer. Spectra were referenced via the residual protio-solvent peak.

IR spectroscopy. Fourier transform infra-red spectra were recorded using a Perkin-Elmer PARAGON 1000 FT-IR spectrometer (range 4000 cm^{-1} to 400 cm^{-1}) as KBr discs or in a NaCl solution cell of 1 mm thickness. In the case of air-sensitive solid samples the compound was finely ground with KBr and loaded into a die within a glovebox, before being quickly pressed into a pellet on the open-bench. Air-sensitive solutions were also prepared in a glovebox. Both types had their spectra recorded immediately when ready to load in the spectrometer.

Crystallography. Crystals suitable for X-ray diffraction were mounted on glass fibres using perfluoropolyether oil, transferred to a goniometer head on the diffractometer and cooled rapidly to 150 K in a stream of cold nitrogen using an Oxford Cryosystems CRYOSTREAM unit.⁴⁵ Data collections were performed using an Enraf-Nonius FR590 KappaCCD diffractometer, utilising graphite-monochromated Mo K_α X-ray radiation ($\lambda = 0.71073 \text{ \AA}$). Intensity data were processed using the DENZO-SMN package.⁴⁶ Structures were solved using direct-methods program SIR92⁴⁷ and refined using full matrix least squares refinement on all F^2 data using the CRYSTALS program suite.^{48,49} Detailed parameters for each structure can be found in the supplementary information.

Other techniques. Elemental analyses were conducted by Stephen Boyer at London Metropolitan University, London. Electron ionisation (EI) mass spectra were recorded by Colin Sparrow of the Chemistry Research Laboratory, Oxford.

Computational methods. DFT calculation were performed using the ADF program suite.^{50,51} Vosko, Wilke and Nusair's local functional,⁵² were used together with the Becke 88^{53,54} and the Perdew 86⁵⁵ non local exchange and correlation gradient corrections. The basis sets used were uncontracted triple- ζ Slater-type orbitals (STOs). Hydrogen and carbons were given extra polarisation functions (2p on H and 3d of C). The cores of atoms were frozen, C up to the 1s level, 2p for Co, 3d for Rh, 4d for Ir. Local minima were confirmed by frequency calculations.

Synthetic procedures

Syn- $[\text{Rh}(\text{CO})_2]_2(\mu\text{:}\eta^5\text{:}\eta^5\text{-Pn}^*)$ (1). $\text{Syn}-(\text{SnMe}_3)_2\text{Pn}^*$ was made *in-situ* by a method previously described.⁹ $\text{Li}_2\text{Pn}^*(\text{TMEDA})_x$ ($x = 0.11$, 0.14 g, 0.64 mmol) was reacted with two equivalents of SnMe_3Cl (0.27 g, 1.35 mmol) in benzene. The resultant solution was added dropwise *via* cannula to an equimolar amount of $[\text{RhCl}(\text{CO})_2]_2$ (0.25 g, 0.64 mmol) in toluene at -78°C . The red solution immediately darkens. The reaction was allowed to warm to room temperature and stir for a further four hours, after which the solvent was removed and resultant solid dried *in vacuo* ($< 1 \times 10^{-2}$ mbar) for four hours. Extraction with a minimum volume of hexane followed by cooling of the saturated solution to -35°C yielded 1 as a micro-crystalline orange solid. Yield 0.13 g (0.26 mmol, 40.1%). Elemental analysis found (calculated) for $\text{C}_{18}\text{H}_{18}\text{O}_4\text{Rh}_2$: C 42.88 (42.92), H 3.60 (3.55). MS (EI): $m/z = 504$ (M^+), 476 (M^+-CO), 448 (M^+-2CO), 418 (M^+-3CO), 390 (M^+-4CO), 186 (Pn^+). IR (KBr, ν_{CO} , cm^{-1}): 1946, 1965, 1999, 2034 (all s). ^1H NMR (300 MHz, C_6D_6): 1.55 (12H, s), 2.00 (6H, d, $^3J_{\text{Rh-H}} = 1.5$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, C_6D_6): 11.2 (Me), 11.8 (Me), 71.0 (quat. C), 104.8 (quat. C), 113.8 (quat. C), 196.3 (CO, d, $^1J_{\text{Rh-C}} = 49.1$ Hz). CCDC 1417859

Syn- $[\text{Ir}(\text{CO})_2]_2(\mu\text{:}\eta^5\text{:}\eta^5\text{-Pn}^*)$ (2). $[\text{IrCl}(\text{CO})_2]_2$ was prepared *in situ* by reacting $[\text{IrCl}(\text{COE})_2]_2$ (0.70 g, 0.78 mmol) in acetonitrile (50 ml) with CO (1 atm) at room temperature with stirring. The orange solution turned into a dark blue slurry, which was transferred *via* cannula to a solution of $\text{syn}-(\text{SnMe}_3)_2\text{Pn}^*$ (0.40 g, 0.78 mmol) in acetonitrile. The solution was stirred 18 hours and then the acetonitrile was removed under reduced pressure and the resultant solid dried under vacuum for four hours ($< 1 \times 10^{-2}$ mbar). The product was extracted with hot hexane ($\sim 40^\circ\text{C}$) and cooled to -35°C to yield 2 as an orange micro-crystalline solid. Yield = 0.09 g (0.13 mmol, 16.9%). Elemental analysis found (calculated) for $\text{C}_{18}\text{H}_{18}\text{O}_4\text{Ir}_2$: C 31.30 (31.58), H 2.72 (2.65). MS (EI): $m/z = 684$ (M^+), 656 (M^+-CO), 628 (M^+-2CO), 600 (M^+-3CO), 572 (M^+-4CO). IR (KBr, ν_{CO} , cm^{-1}): 1932, 1953, 1999, 2021 (all s). ^1H NMR (300 MHz, C_6D_6): 1.53 (12H, s), 2.13 (6H, s). $^{13}\text{C}\{^1\text{H}\}$ NMR (300 MHz, C_6D_6): 10.6 (Me), 11.9 (Me), 63.1 (quat. C), 99.5 (quat. C), 115.5 (quat. C), 176.9 (CO). CCDC 1417860.

Photolysis of 1 to partially form $\text{Rh}_4(\text{CO})_6(\mu\text{:}\eta^3\text{:}\eta^5\text{-Pn}^*)_2$ (3). A solution of 1 (0.04 g, 0.08 mmol) in hexane (15 ml) was stirred in a quartz ampoule and subjected to UV light (254 nm). After 2 hours of photolysis dark orange crystals of 3 started to form. Mechanical separation allowed for a crystal structure to be determined. After 12 hours of photolysis the solvent was removed under reduced pressure, extraction with dichloromethane- d^2 gave a mixture of product and starting material. Even with careful workup of the crystalline material starting material was observed in the product, thus precluding complete characterisation. ^1H NMR (300 MHz, CD_2Cl_2): 1.29 (12H, br. s), 2.18 (12H, br. s), 2.47 (12H, d, $^3J_{\text{Rh-H}} = 1.5$ Hz). CCDC 1417861.

Conclusions

Two new group 9 *syn*-bimetallic Pn* complexes, $[M(CO)_2]_2(\mu:\eta^5:\eta^5-Pn^*)$ ($M = Rh, Ir$) have been synthesised and characterised in solution and in the solid state. $[Ir(CO)_2]_2(\mu:\eta^5:\eta^5-Pn^*)$ is the first example of pentalene ligand coordination to an iridium metal centre. Photolysis of $[Rh(CO)_2]_2(\mu:\eta^5:\eta^5-Pn^*)$ leads to loss of two CO moieties and the formation of the unusual tetrametallic species, $Rh_4(CO)_6(\mu:\eta^3:\eta^5-Pn^*)_2$ which is fluxional in solution on the NMR timescale.

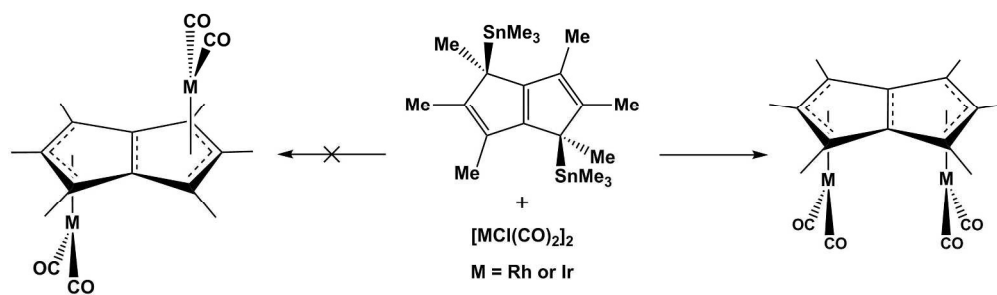
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