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Pseudo electron-deficient organometallics: limited reactivity towards electron-donating ligands

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Anaïs Pitto-Barry,¹ Alexandru Lupan,² Markus Zegke,¹ Thomas Swift,¹ Amr A. A. Attia,² Rianne M. Lord,¹ and Nicolas P. E. Barry^{1*}

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Abstract: Half-sandwich metal complexes are of considerable interest in medicine, material, and nanomaterial chemistry. The design of libraries of such complexes with particular reactivity and properties is therefore a major quest. Here, we report the unique and peculiar reactivity of eight apparently 16-electron half-sandwich metal (ruthenium, osmium, rhodium, and iridium) complexes based on benzene-1,2-dithiolato and 3,6-dichlorobenzene-1,2-dithiolato chelating ligands. These electron-deficient complexes do not react with electron-donor pyridine derivatives, even with the strong σ -donor 4-dimethylaminopyridine (DMAP) ligand. The Ru, Rh, and Ir complexes accept electrons from the triphenylphosphine ligand (σ -donor, π -acceptor), whilst the Os complexes were found to be the first examples of non-electron-acceptor electron-deficient metal complexes. We rationalized these unique properties by a combination of experimental techniques and DFT/TDFT calculations. The synthetic versatility offered by this family of complexes, the low reactivity at the metal center, and the facile functionalization of the non-innocent benzene ligands is expected to allow the synthesis of libraries of pseudo electron-deficient half-sandwich complexes with unusual properties for a large range of applications.

Introduction

Electron-deficient metal complexes play a key role as intermediates in organometallic reactions.¹ They are also known to be extremely unstable and most organometallics follow the 18-electron rule. Some stable coordinatively unsaturated 16-electron (16-e) complexes have been isolated in particular by the groups of Koelle, Tilley, Suzuki, among others,²⁻¹² but little is known about the reactivity of air and moisture stable 16-e complexes and about their properties in solution. Half-sandwich metal complexes are a particular class of organometallics which has attracted an enormous attention for the design of catalysts,¹³ anticancer drug candidates,^{14-22,23, 24} and as building blocks for supramolecular chemistry.²⁵⁻³³ The synthetic versatility of half-sandwich metal complexes, and the number of areas in which they are utilized make the development of novel families of such complexes of potential high interest and broad impact for a number of researchers. Our group has recently developed a strong interest in two 16-e ruthenium and osmium half-sandwich complexes based on a carborane ligand ([Ru/Os(η^6 -*p*-cymene)(1,2-dicarba-*closo*-

dodecarborane-1,2-dithiolato))), and investigated their applications in biology^{16, 34, 35} and in the fabrication of nanomaterials.³⁶⁻³⁹ The intriguing chemistry in solution of these electron-deficient complexes was also studied in order to understand their biological properties.⁴⁰⁻⁴² Owing to the steric hindrance of the bulky carborane ligand, which prevents the dimerization of the compounds and the formation of more electronic favored 18-e species, these metal-carboranes exhibit remarkable stability as 16-e monomeric species as first demonstrated by Jin and co-workers.⁴³⁻⁴⁸ However, when reacted with aromatic amines, the 16-e blue (Ru) and red (Os) complexes are in equilibrium with their yellow 18-electron adducts, and the thermal displacement of the equilibrium results in marked thermochromic properties. Fascinated by the chemistry of such electron-deficient complexes, we report here the unexpected, and highly peculiar reactivity of a family of 16-e complexes of Ru, Os, Rh, and Ir, ([Ru(η^6 -*p*-cymene)(benzene-1,2-dithiolato)] (1), [Os(η^6 -*p*-cymene)(benzene-1,2-dithiolato)] (2), [Rh(η^5 -pentamethylcyclopentadiene)(benzene-1,2-dithiolato)] (3)) and [Ir(η^5 -pentamethylcyclopentadiene)(benzene-1,2-dithiolato)] (4), Fig. 1) based on benzene-1,2-dithiolato, a more readily available, easier to functionalize, and cheaper ligand than carboranes. The stability and propensity of each monomer in solution to form the more electronic stable dimeric species has been studied by ¹H NMR spectroscopy. Their reactivity towards aromatic amines and triphenylphosphine has also been investigated.

To illustrate the versatility of the benzene-1,2-dithiolato scaffold to form a library of electron-deficient half-sandwich metal complexes, the 3,6-dichloro-1,2-benzenedithiol analogues of complexes 1 – 4 were prepared, namely [(Ru(η^6 -*p*-cymene)(3,6-dichlorobenzene-1,2-dithiolato)] (5), [Os(η^6 -*p*-cymene)(3,6-dichlorobenzene-1,2-dithiolato)] (6), [Rh(η^5 -pentamethylcyclopentadiene)(3,6-dichlorobenzene-1,2-dithiolato)] (7) and [Ir(η^5 -pentamethylcyclopentadiene)(3,6-dichlorobenzene-1,2-dithiolato)] (8); Fig. 1). The monomeric *versus* dimeric existence of 5 – 8, and their reactivity with the same three ligands (pyridine, DMAP, PPh₃) has been investigated. Using DFT and TDFT calculations, the unexpected and unique properties of this family of electron-deficient complexes has been rationalized, offering an insight into the unusual reactivity of pseudo 16-electron half-sandwich complexes.

¹ School of Chemistry and Biosciences, University of Bradford, Bradford BD7 1DP, United Kingdom. Email: N.Barry@bradford.ac.uk

² Facultatea de Chimie și Inginerie Chimică, Universitatea Babeș-Bolyai, Cluj-Napoca, Romania.

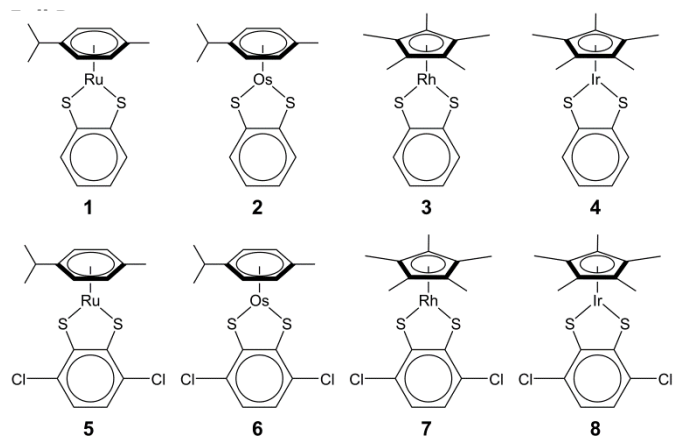


Fig. 1 Molecular structures of the 16-electron complexes studied in this work.

Results

Synthesis of metal complexes 1 – 4 and investigation of their monomeric versus dimeric structures in solution

Complexes **1** – **4** were synthesized *via* the same general procedure of deprotonating benzene-1,2-dithiolato using sodium methoxide, followed by the addition of the respective ruthenium, osmium, ruthenium, and iridium dimer. The synthetic pathways for complexes **1**, **3**, and **4** have been previously reported;^{49, 50} however [Os(η^6 -*p*-cymene)(1,2-benzenedithiolate)], **2**, is an unreported metal complex. All four complexes were characterized by ¹H NMR spectroscopy (Fig. 2), ¹³C NMR spectroscopy (Fig. S1), infra-red spectroscopy (Fig. S2), mass spectrometry (Fig. S3) and UV-Vis spectroscopy (Fig. 4).

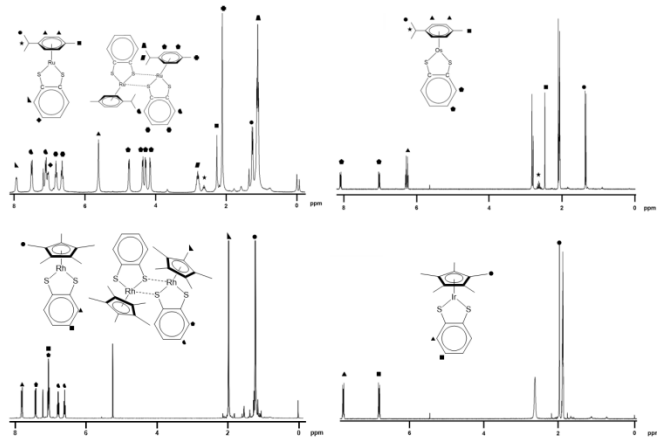


Fig. 2 Assigned ¹H NMR spectra of complexes **1** – **4** in CDCl₃ (1 mM; 298 K; 400 MHz).

The ¹H NMR spectra show stark differences in the structures of complexes **1** – **4**. The osmium and iridium complexes exist in solution in the monomeric state only, similar to their carborane analogues. However, ruthenium and rhodium complexes (**1** and **3**, respectively) exist as both dimers and monomers in solution. All complexes were recrystallized from dichloromethane/hexane layered diffusion and red crystals suitable for X-ray diffraction were obtained for complexes **1** and **3** (Fig. S4). The molecular structures confirm the dimeric structures observed in the NMR spectra for both compounds (Fig. 2), and are in accordance with previously reported dimeric structures (note below Fig. S4).^{51, 52} The chemical structure of both the monomeric and dimeric structures of **1** and **3**

are shown in Fig. 2. The electrospray ionization mass spectra of complexes **1** and **3** in methanol (Fig. S3) also show the existence of the monomeric and dimeric species with *m/z* peaks observed for both monomers and dimers.

To investigate the effect of the concentration on the formation of the dimers, ¹H NMR spectra were obtained of complex **1** in deuterated chloroform, with concentrations ranging from 0.1 to 20 mM (Fig. 3). At low millimolar concentration, only the 16-electron monomer is present in solution, whilst the formation of the more electronically stable 18-e species is observed at concentrations above 1 mM. The disappearance of the resonances of the dimeric structure of **1** is evidenced when the concentration is decreased from 20 mM to 0.1 mM, and is clearly evident by monitoring the *p*-cym isopropyl protons by ¹H spectroscopy (see inset of Fig. 3).

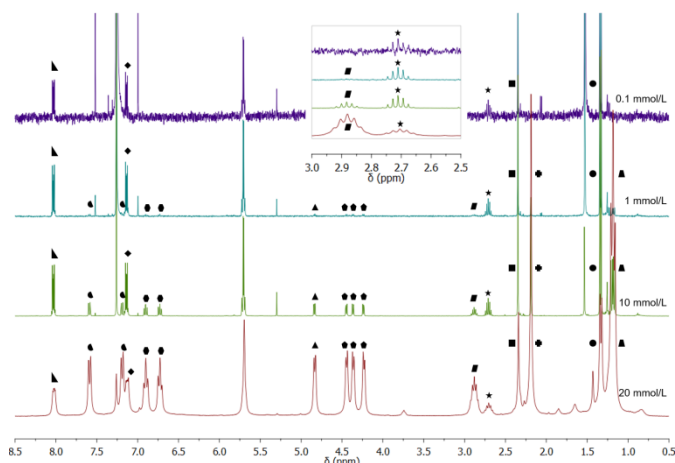


Fig. 3 ¹H NMR spectra of 0.1, 1, 10, and 20 mM solutions of complex **1** in CDCl₃ (298 K, 400 MHz; see Fig. 2 for the symbols used for the assignment of the resonances). At 0.1 mM only the monomeric structure of complex **1** is observed in solution. The inset shows the resonances of the isopropyl protons of the *p*-cym ligand at each of the four concentrations.

Investigation of complex **1** in CDCl₃ (10 mM) *via* diffusion-ordered spectroscopy (DOSY) was carried out to establish the difference of diffusion between the monomeric and dimeric metal species in the same sample. Peaks were identified arising from either the monomeric or dimeric forms and gave distinct diffusion values (CDCl₃ 298 K, $D_{\text{Monomer}} = 1.52 \text{ m}^2 \text{ s}^{-1}$, $D_{\text{Dimer}} = 1.75 \text{ m}^2 \text{ s}^{-1}$, respectively; Fig. S11(A) and Fig. S12). Interestingly, both the diffusion and the ratio between the monomer and dimer changed with temperature (Figs. S11(B) and (C)), demonstrating that the equilibrium between monomeric and dimeric structures is temperature-dependent. This data indicates that as the temperature was increased the concentration of dimer was reduced significantly, so that at 328 K there was insufficient concentration of dimer to determine an accurate diffusion value (Table S11). Full DOSY results are shown in the supporting information.

Investigation of the reactivity of complexes 1 – 4 with σ -donor, and σ -donor and π -acceptor ligands

The reactivity of complexes **1** – **4** was investigated with pyridine as model σ -electron donor ligand. Studies on the carborane analogues

of complexes **1** – **4** showed that electron-deficient half-sandwich complexes of ruthenium and osmium readily form 18-e adducts with the pyridine ligand.^{40, 42} At ambient temperature, the 18-e pyridine adducts were found to be in equilibrium with the 16-e precursors, leading to thermochromic properties. Surprisingly, none of the four benzene-1,2-dithiolato complexes **1** – **4** studied reported here reacts with pyridine, as demonstrated by UV-vis absorption spectroscopy (Fig. S5). The formation of the 18-e adducts could not be favored by cooling the complex solutions in dichloromethane to 195 K, and no thermochromism was observed. A linear relationship between the stability of 18-electron amine carborane-containing adducts and basicity (pK_a values) of the aromatic amine electron donor ligands was previously observed,⁴² which demonstrated that the electron donor strength of the amine nitrogen plays a major role in determining the stability of the 18-electron adduct. Therefore, the functionalization of complexes **1** – **4** with 4-dimethylaminopyridine (DMAP; $pK_a = 9.20$), a ligand with a strong σ -donation character from the electron pair on the nitrogen atom, was attempted. To our surprise no reaction could be observed between complexes **1** – **4** and DMAP (Fig. 4, left column), which suggests that strong σ -donation and high basicity of the ligands do not lead to the functionalization of the 16-e complexes.

Triphenylphosphine (PPh_3) is known to be a strong electron donor ligand (phosphorous radius: 195 pm; phosphine: σ -donor, π -acceptor) and we previously showed that carborane-containing 16-electron half-sandwich complexes have a much larger binding constant with triphenylphosphine than with any aromatic amine electron-donor ligands. The carborane-containing half-sandwich complexes have a high affinity for PPh_3 and a 1:1 mol equiv. mixture leads to the formation of the 18-e adducts, and no 16-e complex being observed (no equilibrium). The Rh and Ir complexes (**3**, **4**, respectively) studied in this work do react with PPh_3 , although 20 mol equiv. of PPh_3 are needed to form the 18-electron complexes [**3**- PPh_3] and [**4**- PPh_3] (Fig. 4). Furthermore, even with 20 mol equiv. of PPh_3 , the binding of the ligand with Ru complex **1** is almost negligible. Even more surprisingly, the osmium complex **2** does not react with triphenylphosphine. To the best of our knowledge, complex **2** is the first example of an electron-deficient half-sandwich metal complex that does not accept electrons, even in the presence of a strong σ -donor and π -acceptor ligand.

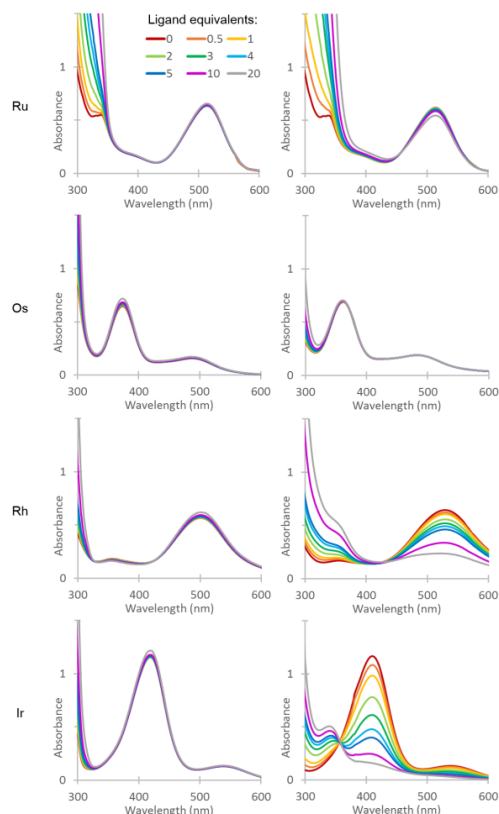


Fig. 4 UV-Vis spectra of the titration of complexes **1** – **4** in CH_2Cl_2 (10^{-4} M, 298 K) by DMAP (left) and PPh_3 (right).

From the UV-visible titrations, the binding constants K between complexes **1** – **4** and the ligand triphenylphosphine were calculated using the non-linear ThordarsonFittingProgram.⁵³ All the titrations were repeated three times and the standard deviation for the calculated values of K are given in Table 1. The experimental Gibbs free energy (ΔG°) was obtained from the Gibbs equation using the calculated value of K .

Table 1. Binding constants K ($10^3 M^{-1}$) and standard deviations, and Gibbs free energies ΔG° (kcal·mol⁻¹, dichloromethane, 10^{-4} M, 298 K) for interactions of complexes **1** – **8** with triphenylphosphine.

Complex	Metal	Ligand	$K M^{-1}$	ΔG° kcal·mol ⁻¹
1	Ru	benzenedithiolate	< 10	nd
2	Os		< 10	nd
3	Rh		796 ± 3	-3.9 ± 0.02
4	Ir		3305 ± 15	-4.8 ± 0.01
5	Ru	dichloro-1,2-benzenedithiolate	1883 ± 9	-4.5 ± 0.02
6	Os		4689 ± 17	-5.0 ± 0.01
7	Rh		7800 ± 22	-5.3 ± 0.01
8	Ir		13002 ± 27	-5.6 ± 0.01

Investigation of the generality of the benzene-dithiol scaffold for the synthesis of electron-deficient half-sandwich complexes

In addition to being more readily available than carboranes, the benzenedithiolate ligands are also easier to functionalize, therefore offering a potential whole new family of ligands allowing for the synthesis of novel electron-deficient half-sandwich metal

complexes. In order to illustrate such synthetic versatility, the 3,6-dichloro-1,2-benzenedithiol analogues of complexes **1** – **4** were prepared, namely $[(\text{Ru}(\eta^6\text{-}p\text{-cymene})(3,6\text{-dichlorobenzene-1,2-dithiolato}))_2]$ (**5**), $[\text{Os}(\eta^6\text{-}p\text{-cymene})(3,6\text{-dichlorobenzene-1,2-dithiolato})_2]$ (**6**), $[\text{Rh}(\eta^5\text{-pentamethylcyclopentadiene})(3,6\text{-dichlorobenzene-1,2-dithiolato})_2]$ (**7**) and $[\text{Ir}(\eta^5\text{-pentamethylcyclopentadiene})(3,6\text{-dichlorobenzene-1,2-dithiolato})_2]$ (**8**). These novel four complexes were synthesized *via* the same general procedure of deprotonating 3,6-dichloro-1,2-benzenedithiol using sodium methoxide, followed by the addition of the respective ruthenium, osmium, rhodium, and iridium dimer. Similarly to their benzenedithiol analogues, the Os and Ir complexes have a monomeric structure in solution, as exemplified by the ^1H NMR spectra in CDCl_3 solution (5 mM, 298K; Fig. 5), whilst the Ru complex **5** is present as its monomer and dimer at millimolar concentrations. Interestingly, the presence of the bulky Cl atoms leads to a distortion of the dimeric structures of complex **5**, exemplified by the presence of two resonances for the protons of the isopropyl groups in the dimeric structures (three resonances in total with the one accounting for the monomeric structure; Fig. 5), and to the sole presence of the monomeric structure for the Rh complex **7** at 1 mM concentration at 298 K. All four complexes were characterized by ^1H NMR spectroscopy (Fig. 5), ^{13}C NMR spectroscopy (Fig. S6), infra-red spectroscopy (Fig. S7), mass spectrometry (Fig. S8) and UV-Vis spectroscopy (Fig. S9).

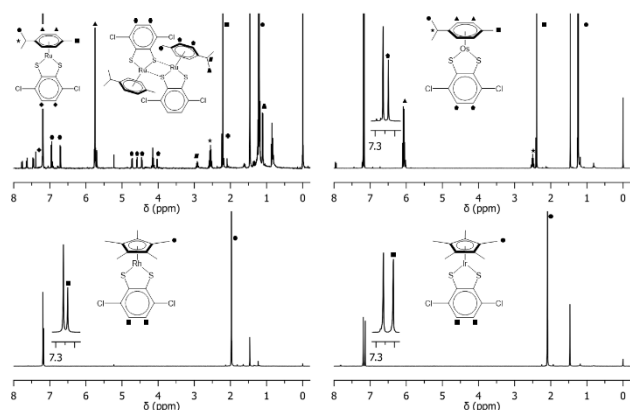


Fig. 5 Assigned ^1H NMR spectra of complexes **5** – **8** in CDCl_3 (1 mM; 400 MHz; 298 K).

All complexes were recrystallized from dichloromethane/hexane layered diffusion and red crystals suitable for X-ray diffraction were obtained for complexes **6** and **8**. Crystallographic data are listed in Table S1 and selected bond lengths and angles in Tables S2 and S3, respectively. The structure of complexes **6** and **8** are depicted in Figure 6.

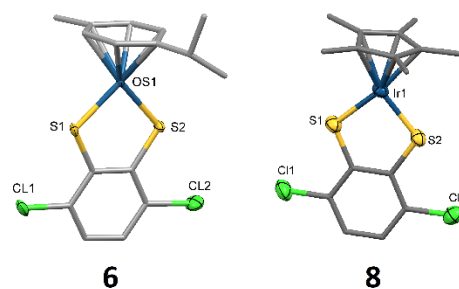


Fig. 6 Solid state structures of **6** and **8** with thermal ellipsoids at 50% probability (**6**) and 50% probability (**8**) levels. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles ($^\circ$): **6**: Os1-Cg 1.690 Os1-S1 2.2582(14) Os1-S2 2.2568(14) S1-Os1-Cg 135.69 S2-Os1-Cg 136.41 S1-Os1-S2 87.68(5) **8**: Ir1-Cg 1.818 Ir1-S1 2.249(3) Ir1-S2 2.246(3) S1-Ir1-Cg 137.34 S2-Ir1-Cg 134.31 S1-Ir1-S2 88.35(11).

The structural determinations of complexes **6** and **8** confirm a typical half-sandwich *pseudo*-octahedral structure with chelated thiolate sulfur atoms from the 3,6-dichlorobenzene-1,2-dithiolato ligand. The MS_2C_2 metalla-cycles are not planar, and in complexes **6** and **8**, the out-of- (S_2C_2) -plane angles of the metal atom are found to be 4.01 and 3.49 $^\circ$, respectively, which suggests a slight bending of the MS_2C_2 cycles. Such a binding of the MS_2C_2 metalla-cycles was also observed in the carborane-containing half-sandwich metal complexes^{42, 54} The Os1-S bond lengths in **6** (2.2582(14) and 2.2568(14) Å) are shorter than expected Os-S bonds in an organometallic complex,⁵⁵ which suggests a possible aromaticity of the metalla-cycle. The short contacts between molecules in the crystals of **6** and **8** are shown in Figure S10.

The reactivity of complexes **5** – **8** with the electron donor ligands pyridine, DMAP, and triphenylphosphine was then investigated. The reactivity between **5** – **8** and these ligands was found similar to the one with complexes **1** – **4** (UV-visible titrations are shown in Fig. S9, energetics in Table 1). This indicates that the key structural feature in this family of electron-deficient metal complexes is the MS_2C_2 metalla-cycle, therefore opening-up a large number of possibilities for the design of libraries of 16-e half-sandwich metal complexes. The reactivity of complex **8** with pyridine is an exception in this series, and suggests that the metal ion itself plays an important role in the reactivity of the complexes. The functionalization of the benzene moiety will be investigated in future work, and the additional ligands will be used to investigate, gain an understanding and provide structure-activity relationships. Such electron-deficient metal complexes with low, but controllable, reactivity at the metal center are expected to possess unexpected properties, and their utilization for applications in medicine and in materials will be investigated.

Discussion

This work reports the synthesis of a library of electron-deficient half-sandwich metal complexes of ruthenium, osmium, rhodium, and iridium. The stability of the monomeric structures has been investigated depending on the concentration and their reactivity

towards model ligands (pyridine and DMAP for σ -donor ligands, and triphenylphosphine for σ -donor and π -acceptor ligands) has been studied. The results are summarized in Table 2.

Table 2. Structure and reactivity of complexes **1** – **8** in CDCl_3 (1 mM) at 298 K.

Metal	Structure in solution	Reaction with ligands		
		pyridine	DMAP	PPh_3
1	Ru Monomer + dimer	No	No	Yes
2	Os Monomer	No	No	No
3	Rh Monomer + dimer	No	No	Yes
4	Ir Monomer	No	No	Yes
5	Ru Monomer + dimer	No	No	Yes
6	Os Monomer	No	No	No
7	Rh Monomer	No	No	Yes
8	Ir Monomer	Yes	No	Yes

The magnitude of the binding constants between complexes **1** – **8** and triphenylphosphine (Table 1; 10^2 – 10^4 M^{-1}) is low as compared to the usually observed complexation constants in coordination chemistry ($>>10^6 \text{ M}^{-1}$)⁵⁶, and is in the range of binding constants observed in host-guest inorganic chemistry (*e.g. via* non-covalent interactions between a metalla-cage and an aromatic planar guest molecule⁵⁷⁻⁵⁹), which is also consistent with a weak binding.

The determination of the binding constants highlights some clear differences between the metal complexes. The first difference is the role that the non-innocent ligand plays into the overall reactivity of the metal complex. Dichloro-1,2-benzenedithiolate-containing complexes (**5** – **8**) are much more reactive towards PPh_3 than their benzenedithiolate analogues (**1** – **4**). Halogens are very electronegative and electron withdrawing, which therefore pulls the electron density away from the metal centre, favouring the formation of the more electronically stable 18-electron species. The second conclusion that can be drawn from the determination of the binding constants is that the nature of the metal ion itself seems to be of particular importance, a fact that we also observed (although in a different context) with $([\text{Ru}/\text{Os}(\eta^6\text{-}p\text{-cymene})(1,2\text{-dicarba-closo-dodecarborane-1,2-dithiolato})])$ complexes.⁴⁰ It is clear that the more kinetically inert metals osmium and iridium lead to a much stronger binding than their ruthenium and rhodium counterparts. Ruthenium and osmium possess similar atomic radii (178, and 185 pm, respectively – the lanthanide contraction),^{60, 61} so the difference of reactivity between the Ru/Os and Rh/Ir analogues does not seem to arise from steric constraints. Although less significant for metal-phosphorous bonds, relativistic effects (stronger with Os/Ir than with Ru/Rh – Os and Ir being heavier) are of importance in metal-metal bonds, and should favour the formation of an Os-P complex analogous over a Ru-P complex.

Electronic spectroscopic data for DFT-optimized complexes **1** – **4** in dichloromethane (cpcm solvation model) were calculated by computing the lowest 50 singlet states using the M11-L DFT functional⁶² coupled with the SDD basis set⁶³ for the metal ions and the def2-TZVP basis set⁶⁴ for the lighter elements (Fig. 7). The distance matrices of the optimized structures are given in Tables S4-

S7 in order to highlight the distance between atoms considered of interest for this work.

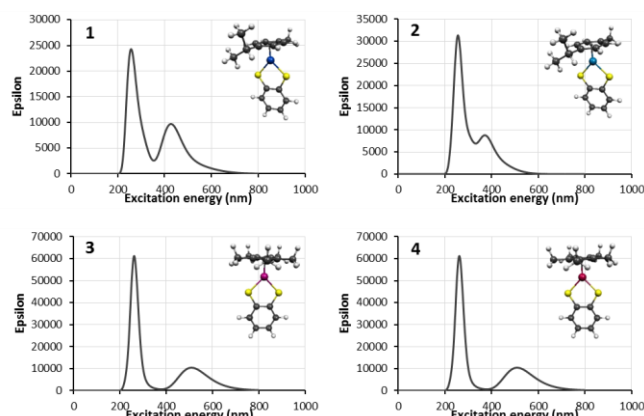


Fig. 7 DFT-optimized structures of complexes **1** – **4** and calculated UV-vis spectra in dichloromethane cpcm solvation model.

UV-vis spectra were computed using the time dependent density functional theory (TD-DFT) method on the optimized structures using the same DFT functionals and basis sets (Fig. 8). An excellent agreement between experimental and calculated spectra was observed, with strong absorption bands for complexes **1** – **4** between 400 and 600 nm. This arises from a mixture of ligand-to-metal charge-transfer (LMCT) from sulfur σ and π orbitals to the metal ion, d-d transitions, and metal-to-ligand charge-transfer (MLCT) from M-S π orbitals to Ru/Os-*p*-cymene or Rh/Ir-Cp* δ^* molecular orbitals. For complex **1**, analysis of the main transitions 1 – 5 shows that the band centered at 252nm arises mainly from d-d transitions with some sulfur π character, while the band at 404 nm arises from a mixture of ligand-to-metal charge-transfer (LMCT) from sulfur σ and π orbitals to ruthenium, plus d-d transitions, plus metal-to-ligand charge-transfer (MLCT) from Ru-S π orbitals to Ru-*p*-cymene δ^* molecular orbitals. These transitions as well as their relative weights are summarized in Table S8. The molecular orbitals involved in these five transitions 1 – 5 with ranking order and energy (in a.u.) used to construct the diagram are depicted in Figure 8, numbered accordingly to their energy levels. MO 80 clearly shows a strong π -interaction between the metal and the π -orbitals of the MS_2C_2 ring.

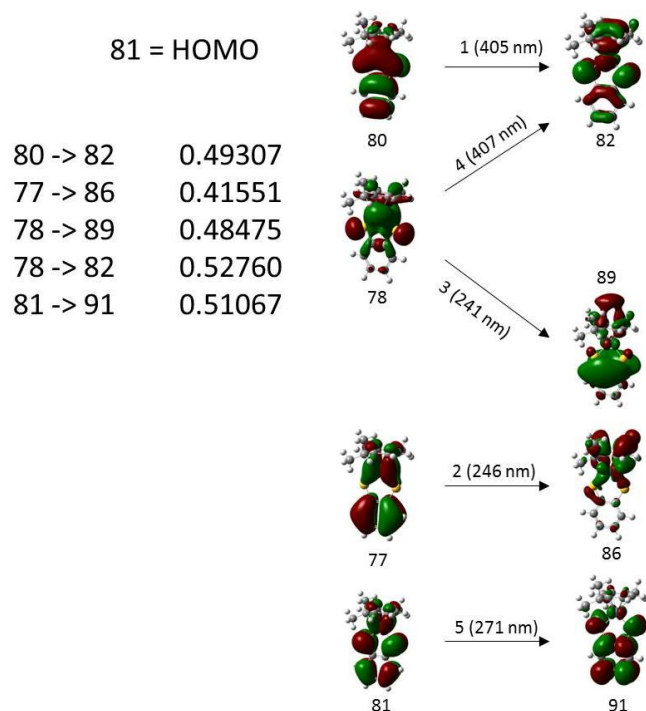


Fig. 8 Molecular orbitals involved in the five main calculated singlet electronic transitions with ranking order and energy (in a.u.).

To gain an understanding on the absence of reactivity between complexes **1** – **4** and σ -donor ligands, and the weak reactivity with σ -donor and π -acceptor ligands, the reactions were computed and the thermochemistry parameters of the different reactions between complexes **1** – **4**, pyridine, DMAP, and triphenylphosphine were calculated (Table 3).

Table 3. Thermochemistry of the reactions between complexes **1** – **4**, pyridine, DMAP, and triphenylphosphine. The computed zero point corrected Gibbs free energies of all the species involved are provided in Table S10).

Structure	Binding energy (kcal/mol)
1 + DMAP	10.1
1 + PPh ₃	6.6
1 + Pyridine	12.0
2 + DMAP	11.7
2 + PPh ₃	10.6
2 + Pyridine	13.3
3 + DMAP	11.7
3 + PPh ₃	4.6
3 + Pyridine	12.9
4 + DMAP	13.8
4 + PPh ₃	6.1
4 + Pyridine	15.7

All the processes are slightly endothermic but the ΔG values are very low, which is in agreement with the experimental data. To determine if the unexpected low reactivity between pyridine derivatives and the metal complexes supersedes a thermochemistry process, we calculated the absolute magnetic shielding at the centroid of the MS₂C₂ ring in complexes **1** – **4**. The nucleus-independent chemical shift (NICS) computed values (in the centre

of the MS₂C₂ ring) were found at -9.9, -9.4, -9.2, and -9.7 for complexes **1** – **4**, respectively, which indicates that all the metallarings are aromatic. This is in agreement with the M-S bond lengths determined by X-ray crystallography. We therefore hypothesize that the lack of reactivity towards pyridine derivatives may relate to the aromaticity of the five-membered MS₂C₂ chelate ring by involving sulfur lone pairs in the bonding in the MS₂C₂ chelate ring. Thus, one of the sulfur atoms might be a three-electron donor to the metal atom and the other only a one-electron donor. This would give the metal the favored 18-electron configuration and make it unreactive towards bases such as pyridine derivatives, but slightly reactive towards σ -donor and π -acceptor ligands, such as triphenylphosphine. The actual structure of such metal complexes would thus be a resonance hybrid of the two canonical structures with the sulfur atoms in the two states, which leads to a pseudo 16-electron configuration.

Conclusions

We studied the reactivity of four 16-electron complexes [Ru(η^6 -*p*-cymene)(benzene-1,2-dithiolato)] (**1**), [Os(η^6 -*p*-cymene)(benzene-1,2-dithiolato)] (**2**), [Rh(η^5 -pentamethylcyclopentadiene)(benzene-1,2-dithiolato)] (**3**) and [Ir(η^5 -pentamethylcyclopentadiene)(benzene-1,2-dithiolato)] (**4**) by reactions between the non-innocent ligand⁶⁵ 1,2-benzenedithiol and the corresponding metal dimers. Complexes **2** and **4** are only present as the monomeric 16-e species in solution, whilst the less kinetically inert complexes **1** and **3** are present as both 16-e monomeric and 18-e dimeric structures in solution. The four complexes exhibit dramatic differences of reactivity towards aromatic amines and triphenylphosphine: complex **2**, although electron-deficient, does not react with electron-donor and electron-acceptor ligands (even with 50 mol equiv. of triphenylphosphine (PPh₃)), whilst complexes **1**, **3** and **4** do not react with σ -donor ligands, but react with σ -donor, π -acceptor ligands such as PPh₃. We then showed that it is possible to synthesize a library of such electron-deficient half-sandwich complexes based on the benzenedithiol scaffold by synthesizing four novel complexes [(Ru(η^6 -*p*-cymene)(1,2-3,6-dichlorobenzene-1,2-dithiolato)] (**5**), [Os(η^6 -*p*-cymene)(1,2-3,6-dichlorobenzene-1,2-dithiolato)] (**6**), [Rh(η^5 -pentamethylcyclopentadiene)(1,2-3,6-dichlorobenzene-1,2-dithiolato)] (**7**) and [Ir(η^5 -pentamethylcyclopentadiene)(1,2-3,6-dichlorobenzene-1,2-dithiolato)] (**8**). Their monomeric structures were confirmed by a combination of NMR spectroscopy and X-ray crystallography experiments, except for the Ru complex which exists as both the monomeric and dimeric species in solution. Interestingly, the reactivity of these four complexes towards pyridine, DMAP, and triphenylphosphine follows the same trend than previously observed with the benzene-dithiolate complexes. DFT and TDFT calculations were used to optimize the structures of complexes **1** – **4**, by computing their UV-vis absorption spectra, calculate the thermochemistry parameters of the different reactions between **1** – **4** and pyridine, DMAP, and triphenylphosphine, and to determine the NICS values of the MS₂C₂ chelate ring. We conclude that the lack of reactivity of these

electron-deficient metal complexes is a consequence of their actual structures being resonance hybrids of the two canonical structures with the sulfur atoms in two states, thus offering metal complexes with a pseudo 16-electronic configuration.

Half-sandwich metal complexes have raised a considerable interest in medicine, catalysis, materials and nanomaterials areas. Therefore the identification of the MS₂C₂ aromatic metalla-cycle as the key structural feature in this family of electron-deficient metal complexes opens up new avenues for the synthesis of a large number of pseudo electron-deficient molecules. In addition to offering an intriguing example of low electronic reactivity between electron-donor ligands and electron-deficient metal complexes, we anticipate that the facile derivatization of the benzene 3,4 positions (exemplified here by the substitution of hydrogens by chlorine atoms) will allow the synthesis of libraries of metal complexes with a very particular type of reactivity. The knowledge gained from this work on the importance of the nature of the metal ion, as well as the crucial importance of the inductive effect of the groups on the benzene 3,4 positions, will inform the structural features and synthesis of future non-innocent ligands depending on the type of reactivity which is desired. Higher reactivity at the metal centre will require strong electron-withdrawing groups, whilst a lower reactivity towards σ -donor, π -acceptor ligands will involve electron-donating functional groups. Such libraries will be of interest in a number of different fields, such as liquid crystal synthesis, medicinal inorganic chemistry, supramolecular chemistry and catalysis.

Associated content

Supporting Information. Materials and methods, synthesis and characterization details, titrations, calculations data, and crystal structure determination details. The cif files for complexes **1**, **3**, **6** and **8** were deposited to the CCDC 1554766-1554769. Processed DOSY spectra, sliced 1H proton spectra and diffusion data analysis of complex **1**.

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