








Cite this: DOI: 10.1039/c7dt02827j

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

Anaïs Pitto-Barry, <sup>a</sup> Alexandru Lupan,<sup>b</sup> Markus Zegke, <sup>a</sup> Thomas Swift, <sup>a</sup> Amr A. A. Attia,<sup>b</sup> Rianne M. Lord <sup>a</sup> and Nicolas P. E. Barry <sup>\*,a</sup>

Half-sandwich metal complexes are of considerable interest in medicinal, 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  $\sigma$ -donor 4-dimethylaminopyridine (DMAP) ligand. The Ru, Rh, and Ir complexes accept electrons from the triphenylphosphine ligand ( $\sigma$ -donor,  $\pi$ -acceptor), whilst the Os complexes were found to be the first examples of non-electron-acceptor electron-deficient metal complexes. We rationalised 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 functionalisation 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 broad range of applications.

Received 1st August 2017,  
Accepted 31st August 2017

DOI: 10.1039/c7dt02827j

rsc.li/dalton

## Introduction

Electron-deficient metal complexes play a key role as intermediates in organometallic reactions.<sup>1</sup> They are also known to be extremely unstable as 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,<sup>2–12</sup> but little is known about the reactivity of air and moisture stable 16-e complexes and their properties in solution. Half-sandwich metal complexes are a particular class of organometallics which have attracted enormous attention for the design of catalysts,<sup>13</sup> anticancer drug candidates,<sup>14–24</sup> and as building blocks for supramolecular chemistry.<sup>25–33</sup> The development of novel families of half-sandwich metal complexes is of high interest owing to their synthetic versatility and their broad range of applications. Our

group has recently developed strong interest in two 16-e ruthenium and osmium half-sandwich complexes based on a carborane ligand ([Ru/Os( $\eta^6$ -*p*-cymene)(1,2-dicarba-*closo*-dodecarborane-1,2-dithiolato)]), and investigated their applications in biology<sup>16,34,35</sup> and in the fabrication of nanomaterials.<sup>36–39</sup> The intriguing chemistry in solution of these electron-deficient complexes was also studied in order to understand their biological properties.<sup>40–42</sup> Owing to the steric hindrance of the bulky carborane ligand, which prevents the dimerisation of the compounds and the formation of more electronic favoured 18-e species, these metal carboranes exhibit a remarkable stability as 16-e monomeric species as first demonstrated by Jin and co-workers.<sup>43–48</sup> 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 shift 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( $\eta^6$ -*p*-cymene)(benzene-1,2-dithiolato)] (1), [Os( $\eta^6$ -*p*-cymene)(benzene-1,2-dithiolato)] (2), [Rh( $\eta^5$ -pentamethylcyclopentadiene)(benzene-1,2-dithiolato)] (3) and [Ir( $\eta^5$ -pentamethylcyclopentadiene)(benzene-1,2-dithiolato)] (4), respectively, Fig. 1) based on benzene-1,2-dithiolato, a more readily available, easy to functionalise, and inexpensive ligand than carboranes. The stability and propensity of each monomer in solution to form the more electronically stable

<sup>a</sup>School of Chemistry and Biosciences, University of Bradford, Bradford BD7 1DP, UK.  
E-mail: N.Barry@bradford.ac.uk

<sup>b</sup>Facultatea de Chimie și Inginerie Chimică, Universitatea Babeș-Bolyai, Cluj-Napoca, Romania

† Electronic supplementary information (ESI) available: Materials and methods, synthesis and characterization details, titrations, calculation data, and crystal structure determination details. Processed DOSY spectra, sliced <sup>1</sup>H proton spectra and diffusion data analysis of complex 1. CCDC 1554766–1554769 for complexes 1, 3, 6 and 8. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt02827j

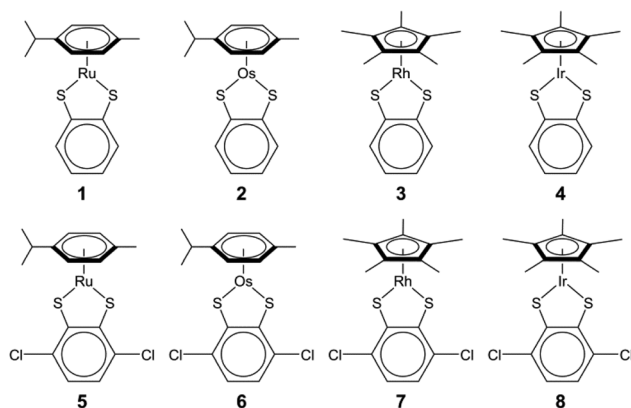


Fig. 1 Molecular structures of the 16-electron complexes studied in this work.

dimeric species have been studied by  $^1\text{H}$  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  $[\text{Ru}(\eta^6\text{-p-cymene})(3,6\text{-dichlorobenzene-1,2-dithiolato})]$  (5),  $[\text{Os}(\eta^6\text{-p-cymene})(3,6\text{-dichlorobenzene-1,2-dithiolato})]$  (6),  $[\text{Rh}(\eta^5\text{-pentamethylcyclopentadiene})(3,6\text{-dichlorobenzene-1,2-dithiolato})]$  (7) and  $[\text{Ir}(\eta^5\text{-pentamethylcyclopentadiene})(3,6\text{-dichlorobenzene-1,2-dithiolato})]$  (8) (Fig. 1). The monomeric *versus* dimeric existence of 5–8, and their reactivity with the same three ligands (pyridine, DMAP, and  $\text{PPh}_3$ ) has been investigated. Using DFT and TDFT calculations, the unexpected and unique properties of this family of electron-deficient complexes have been rationalised, offering insight into the unusual reactivity of pseudo 16-electron half-sandwich complexes.

## 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, rhodium, and iridium dimer. The synthetic pathways for complexes 1, 3, and 4 have been previously reported;<sup>49,50</sup> however,  $[\text{Os}(\eta^6\text{-p-cymene})(1,2\text{-benzenedithiolate})]$ , 2, is an unreported metal complex. All four complexes were characterized by  $^1\text{H}$  NMR spectroscopy (Fig. 2),  $^{13}\text{C}$  NMR spectroscopy (Fig. S1†), infrared spectroscopy (Fig. S2†), mass spectrometry (Fig. S3†) and UV-vis spectroscopy (Fig. 4).

The  $^1\text{H}$  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 com-

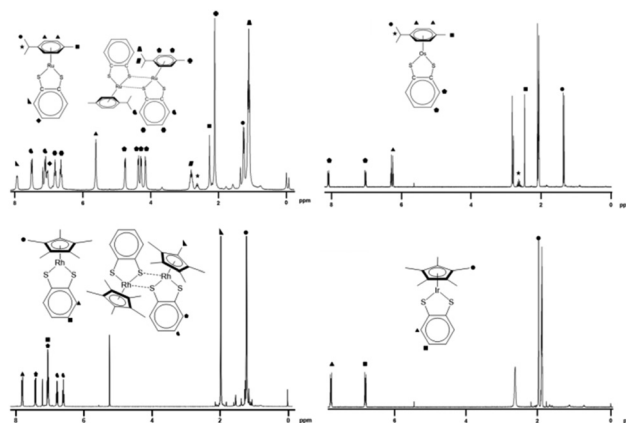


Fig. 2 Assigned  $^1\text{H}$  NMR spectra of complexes 1–4 in  $\text{CDCl}_3$  (1 mM; 298 K; 400 MHz).

plexes (1 and 3, respectively) exist as both dimers and monomers in solution. All complexes were recrystallised 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†).<sup>51,52</sup> The chemical structures of both the monomeric and dimeric structures of 1 and 3 are shown in Fig. 2. The electrospray ionisation 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 corresponding to both monomeric and dimeric species.

To investigate the effect of the concentration on the formation of the dimers,  $^1\text{H}$  NMR spectra were obtained for complex 1 in deuterated chloroform, with concentrations ranging from 0.1 to 20 mM (Fig. 3). At low millimolar concen-

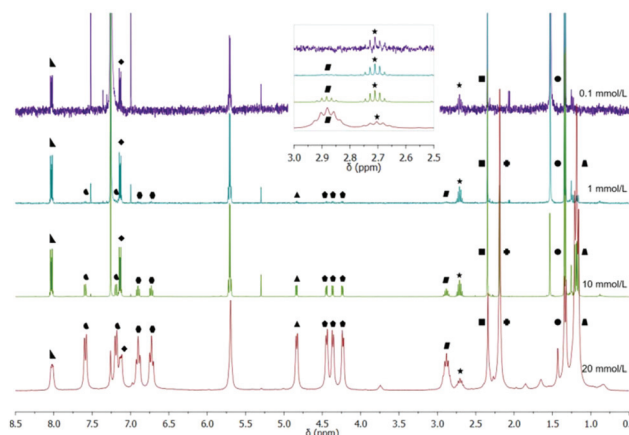


Fig. 3  $^1\text{H}$  NMR spectra of 0.1, 1, 10, and 20 mM solutions of complex 1 in  $\text{CDCl}_3$  (298 K, 400 MHz; see Fig. 2 for the symbols used for the assignment of the resonances). At 0.1 mM, only the monomeric structure of complex 1 is observed in solution. The inset shows the resonances of the isopropyl protons of the *p*-cym ligand at each of the four concentrations.

trations, 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 from monitoring the *p*-cym isopropyl protons by  $^1\text{H}$  spectroscopy (see the inset of Fig. 3).

Investigation of complex **1** in  $\text{CDCl}_3$  (10 mM) *via* diffusion-ordered spectroscopy (DOSY) was carried out to establish the difference in 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 ( $\text{CDCl}_3$  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 S12†). Interestingly, both the diffusion and the ratio between the monomer and dimer changed with the temperature (Fig. S11(B) and (C)†), demonstrating that the equilibrium between the monomeric and dimeric structures is temperature-dependent. These data indicate that the concentration of the dimer is significantly reduced by an increase of temperature; and the concentration of dimer at 328 K was insufficient to determine an accurate diffusion value (Table S11†). Full DOSY results are shown in the ESI.†

#### Investigation of the reactivity of complexes **1–4** with either $\sigma$ -donor, or $\sigma$ -donor and $\pi$ -acceptor ligands

The reactivity of complexes **1–4** was investigated with pyridine as a model  $\sigma$ -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.<sup>40,42</sup> 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** reported here reacts with pyridine, as demonstrated by UV-vis absorption spectroscopy (Fig. S5†). The formation of the 18-e adducts could not be favoured by cooling the complex solutions in dichloromethane to 195 K, and no thermochromism was observed. A linear relationship between the stability of 18-e amine carborane-containing adducts and the basicity ( $\text{pK}_a$  values) of the aromatic amine electron donor ligands was previously observed,<sup>42</sup> 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;  $\text{pK}_a = 9.20$ ), a ligand with a strong  $\sigma$ -donation characteristic from the electron pair on the nitrogen atom, was attempted. To our surprise, no reaction was observed between complexes **1–4** and DMAP (Fig. 4, left column), which suggests that strong  $\sigma$ -donation and high basicity of the ligands do not lead to the functionalisation of the 16-e complexes.

Triphenylphosphine ( $\text{PPh}_3$ ) is known to be a strong electron donor ligand (phosphorus radius: 195 pm; phosphine:  $\sigma$ -donor,  $\pi$ -acceptor) and we previously showed that carborane-

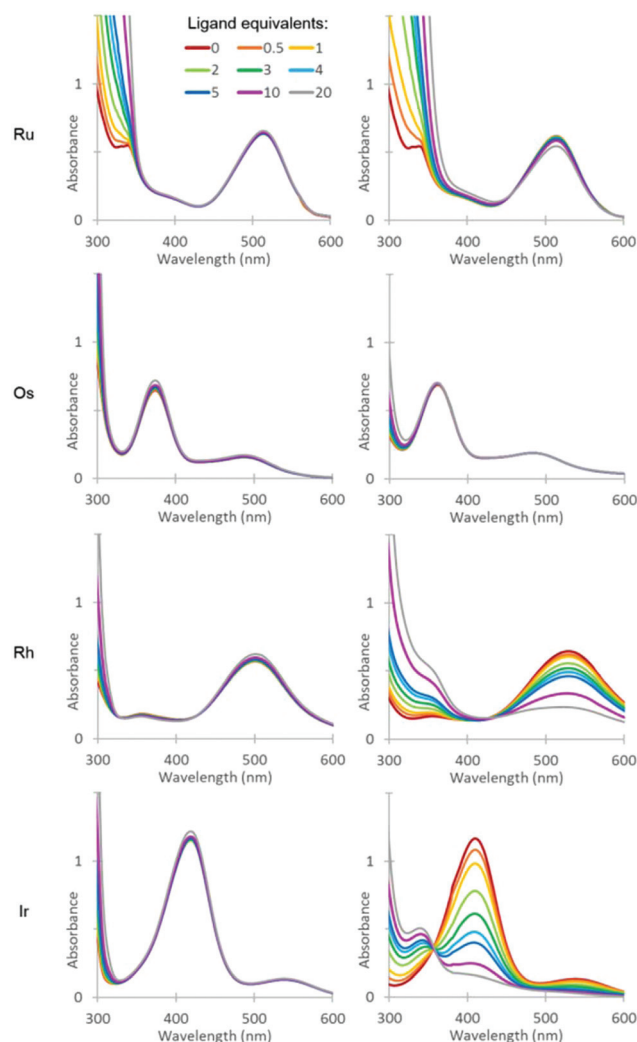


Fig. 4 UV-vis spectra of the titration of complexes **1–4** in  $\text{CH}_2\text{Cl}_2$  ( $10^{-4} \text{ M}$ , 298 K) using DMAP (left) and  $\text{PPh}_3$  (right).

containing 16-electron half-sandwich complexes have a much larger binding constant with triphenylphosphine than with any aromatic amine electron-donor ligand. The carborane-containing half-sandwich complexes have a high affinity for  $\text{PPh}_3$  and a 1 : 1 mol equiv. mixture leads to the formation of the 18-e adducts, with no 16-e complex being observed (no equilibrium). The Rh and Ir complexes (**3** and **4**, respectively) studied in this work do react with  $\text{PPh}_3$ , although 20 mol equiv. of  $\text{PPh}_3$  are needed to form the 18-e complexes [**3-PPh<sub>3</sub>**] and [**4-PPh<sub>3</sub>**] (Fig. 4). Furthermore, even with 20 mol equiv. of  $\text{PPh}_3$ , 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  $\sigma$ -donor and  $\pi$ -acceptor ligand.

From the UV-visible titrations, the binding constants  $K$  between complexes **1–4** and the ligand triphenylphosphine

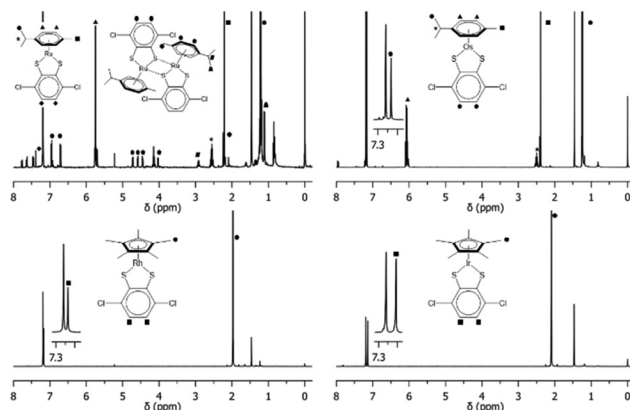
**Table 1** Binding constants  $K$  ( $10^3 \text{ M}^{-1}$ ) and standard deviations, and Gibbs free energies  $\Delta G^\circ$  ( $\text{kcal mol}^{-1}$ , dichloromethane,  $10^{-4} \text{ M}$ , 298 K) for interactions of complexes 1–8 with triphenylphosphine

Complex	Metal	Ligand	$K (\text{M}^{-1})$	$\Delta G^\circ (\text{kcal mol}^{-1})$
1	Ru	Benzenedithiolate	<10	nd
2	Os		<10	nd
3	Rh		$796 \pm 3$	$-3.9 \pm 0.02$
4	Ir		$3305 \pm 15$	$-4.8 \pm 0.01$
5	Ru	Dichloro-1,2-benzenedithiolate	$1883 \pm 9$	$-4.5 \pm 0.02$
6	Os		$4689 \pm 17$	$-5.0 \pm 0.01$
7	Rh		$7800 \pm 22$	$-5.3 \pm 0.01$
8	Ir		$13\,002 \pm 27$	$-5.6 \pm 0.01$

were calculated using the non-linear Thordarson Fitting Program.<sup>53</sup> All the titrations were repeated three times and the standard deviations for the calculated values of  $K$  are given in Table 1. The experimental Gibbs free energy ( $\Delta G^\circ$ ) was obtained from the Gibbs equation using the calculated value of  $K$ .

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

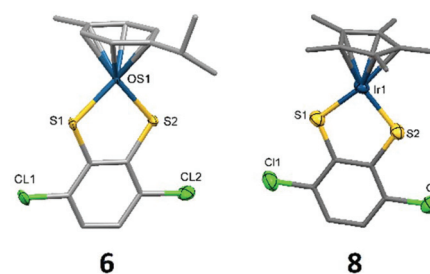
In addition to being more readily available than carboranes, the benzenedithiolate ligands are also easy to functionalise, therefore offering a potential whole new family of ligands allowing for the synthesis of novel electron-deficient half-sandwich metal complexes. In order to illustrate such synthetic versatility, the 3,6-dichloro-1,2-benzenedithiol analogues of complexes 1–4 were prepared, namely  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(3,6\text{-dichlorobenzene-1,2-dithiolato})]$  (5),  $[\text{Os}(\eta^6\text{-}p\text{-cymene})(3,6\text{-dichlorobenzene-1,2-dithiolato})]$  (6),  $[\text{Rh}(\eta^5\text{-pentamethylcyclopentadiene})(3,6\text{-dichlorobenzene-1,2-dithiolato})]$  (7) and  $[\text{Ir}(\eta^5\text{-pentamethylcyclopentadiene})(3,6\text{-dichlorobenzene-1,2-dithiolato})]$  (8). These novel four complexes were synthesised *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  $^1\text{H}$  NMR spectra in  $\text{CDCl}_3$  solution (5 mM, 298 K; 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 and at 298 K. All four complexes were characterised by  $^1\text{H}$  NMR spectroscopy (Fig. 5),  $^{13}\text{C}$  NMR spectroscopy (Fig. S6†), infrared spectroscopy (Fig. S7†), mass spectrometry (Fig. S8†) and UV-vis spectroscopy (Fig. S9†).



**Fig. 5** Assigned  $^1\text{H}$  NMR spectra of complexes 5–8 in  $\text{CDCl}_3$  (1 mM; 400 MHz; 298 K).

All complexes were recrystallised 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 structures of complexes 6 and 8 are shown in Fig. 6.

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  $\text{MS}_2\text{C}_2$  metallacycles are not planar, and in complexes 6 and 8, the out-of- $(\text{S}_2\text{C}_2)$ -plane angles of the metal atom are found to be  $4.01^\circ$  and  $3.49^\circ$ , respectively, which suggests a slight bending of the  $\text{MS}_2\text{C}_2$  cycles. Such a binding of the  $\text{MS}_2\text{C}_2$  metallacycles was also observed in the carborane-containing half-sandwich metal complexes.<sup>42,54</sup> The Os1–S bond lengths in 6 (2.2582(14) and 2.2568(14) Å) are shorter than the expected Os–S bonds in an organometallic complex,<sup>55</sup> which suggests a possible aromaticity of the metallacycle. The short contacts between molecules in the crystals of 6 and 8 are shown in Fig. S10.†



**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 reactivity of complexes **5–8** was also investigated with the electron donor ligands pyridine, DMAP and triphenylphosphine, and showed similar trends as complexes **1–4** (UV-visible titrations are shown in Fig. S9,† and energetics in Table 1). This indicates that the key structural feature in this family of electron-deficient metal complexes is the  $\text{MS}_2\text{C}_2$  metallacycle, 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, which suggests that the metal ion itself plays an important role in the reactivity of the complexes. The functionalisation of the benzene moiety will be investigated in future work, in order to gain an understanding of trends in reactivity 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 utilisation for applications in medicine and materials chemistry 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  $\sigma$ -donor ligands, and triphenylphosphine for  $\sigma$ -donor and  $\pi$ -acceptor ligands) has been studied. The results are summarised in Table 2.

The magnitude of the binding constants between complexes **1–8** and triphenylphosphine (Table 1;  $10^2$ – $10^4 \text{ M}^{-1}$ ) is low compared to the usually observed complexation constants in coordination chemistry ( $\gg 10^6 \text{ M}^{-1}$ ),<sup>56</sup> and is in the range of binding constants observed in host–guest inorganic chemistry (e.g. *via* non-covalent interactions between a metallacycle and an aromatic planar guest molecule,<sup>57–59</sup> 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 in the

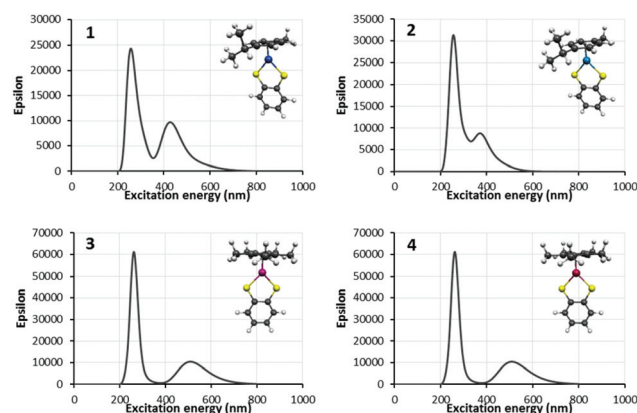
overall reactivity of the metal complex. Dichloro-1,2-benzene-dithiolate-containing complexes (**5–8**) are much more reactive towards  $\text{PPh}_3$  than their benzenedithiolate analogues (**1–4**). Halogens are very electronegative and electron withdrawing, which therefore pulls the electron density 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.<sup>40</sup> 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),<sup>60,61</sup> so the difference in the reactivity between the Ru/Os and Rh/Ir analogues does not seem to arise from steric constraints. Although less significant for metal–phosphorus 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 analogous Os–P complex over a Ru–P complex.

Electronic spectroscopic data for DFT-optimised complexes **1–4** in dichloromethane (cpcm solvation model) were calculated by computing the lowest 50 singlet states using the M11L DFT functional<sup>62</sup> coupled with the SDD basis set<sup>63</sup> for the metal ions and the def2-TZVP basis set<sup>64</sup> for the lighter elements (Fig. 7). The distance matrices of the optimised structures are given in Tables S4–S7† in order to highlight the distance between the atoms of interest.

UV-vis spectra were computed using the time dependent density functional theory (TD-DFT) method on the optimised structures using the same DFT functionals and basis sets (Fig. 8). Excellent agreement between the 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

**Table 2** Structure and reactivity of complexes **1–8** in  $\text{CDCl}_3$  (1 mM) at 298 K

Metal	Structure in solution	Reaction with ligands		
		Pyridine	DMAP	$\text{PPh}_3$
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



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

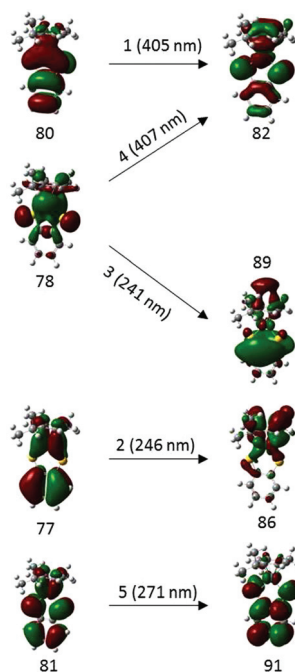


Fig. 8 Molecular orbitals involved in the five main calculated singlet electronic transitions with the ranking order and energy (in a.u.).

$\sigma$  and  $\pi$  orbitals to the metal ion, d-d transitions, and metal-to-ligand charge-transfer (MLCT) from M-S  $\pi$  orbitals to Ru/Os-*p*-cymene or Rh/Ir-Cp\*  $\delta^*$  molecular orbitals. For complex 1, analysis of the main transitions 1–5 shows that the band centered at 252 nm arises mainly from d-d transitions with some sulfur  $\pi$  characteristics, while the band at 404 nm arises from a mixture of ligand-to-metal charge-transfer (LMCT) from sulfur  $\sigma$  and  $\pi$  orbitals to ruthenium, plus d-d transitions, plus metal-to-ligand charge-transfer (MLCT) from Ru-S  $\pi$  orbitals to Ru-*p*-cymene  $\delta^*$  molecular orbitals. These transitions as well as their relative weights are summarised in Table S8.† The molecular orbitals involved in these five transitions 1–5 with the ranking order and energy (in a.u.) used to construct the diagram are shown in Fig. 8, numbered accordingly to their energy levels. MO 80 clearly shows a strong  $\pi$ -interaction between the metal and the  $\pi$ -orbitals of the MS<sub>2</sub>C<sub>2</sub> ring.

To gain an understanding of the absence of reactivity between complexes 1–4 and  $\sigma$ -donor ligands, and the weak reactivity with  $\sigma$ -donor and  $\pi$ -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).

All the processes are slightly endothermic but the  $\Delta G$  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 MS<sub>2</sub>C<sub>2</sub> ring in complexes 1–4. The nucleus-independent chemical shift (NICS) computed values (in the centre of the MS<sub>2</sub>C<sub>2</sub> ring) were found

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 <sup>−1</sup> )
1 + DMAP	10.1
1 + PPh <sub>3</sub>	6.6
1 + Pyridine	12.0
2 + DMAP	11.7
2 + PPh <sub>3</sub>	10.6
2 + Pyridine	13.3
3 + DMAP	11.7
3 + PPh <sub>3</sub>	4.6
3 + Pyridine	12.9
4 + DMAP	13.8
4 + PPh <sub>3</sub>	6.1
4 + Pyridine	15.7

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 hypothesise that the lack of reactivity towards pyridine derivatives may relate to the aromaticity of the five-membered MS<sub>2</sub>C<sub>2</sub> chelate ring by involving sulfur lone pairs in the bonding in the MS<sub>2</sub>C<sub>2</sub> 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 favoured 18-electron configuration and make it unreactive towards bases such as pyridine derivatives, but slightly reactive towards  $\sigma$ -donor and  $\pi$ -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( $\eta^6$ -*p*-cymene)(benzene-1,2-dithiolato)] (1), [Os( $\eta^6$ -*p*-cymene)(benzene-1,2-dithiolato)] (2), [Rh( $\eta^5$ -pentamethylcyclopentadiene)(benzene-1,2-dithiolato)] (3) and [Ir( $\eta^5$ -pentamethylcyclopentadiene)(benzene-1,2-dithiolato)] (4) by reactions between the non-innocent ligand<sup>65</sup> 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 in the 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 (PPh<sub>3</sub>)), whilst complexes 1, 3 and 4 do not react with  $\sigma$ -donor ligands, but react with  $\sigma$ -donor,  $\pi$ -acceptor ligands such as PPh<sub>3</sub>. We then showed that it is possible to synthesise a library of such electron-deficient half-sandwich complexes based on the benzene-dithiol scaffold by synthesis-

ing four novel complexes [Ru( $\eta^6$ -*p*-cymene)(1,2-3,6-dichlorobenzene-1,2-dithiolato)] (5), [Os( $\eta^6$ -*p*-cymene)(1,2-3,6-dichlorobenzene-1,2-dithiolato)] (6), [Rh( $\eta^5$ -pentamethylcyclopentadiene)(1,2-3,6-dichlorobenzene-1,2-dithiolato)] (7) and [Ir( $\eta^5$ -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 as 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 MS<sub>2</sub>C<sub>2</sub> 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 considerable interest in medicine, catalysis, and materials and nanomaterials chemistry. Therefore, the identification of the MS<sub>2</sub>C<sub>2</sub> aromatic metallacycle 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 a low electronic reactivity between electron-donor ligands and electron-deficient metal complexes, we anticipate that the facile derivatisation of the benzene 3,4 positions (exemplified here by the substitution of hydrogens by chlorine atoms) will allow the synthesis of the 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 the synthesis of future non-innocent ligands depending on the type of reactivity which is desired. A higher reactivity at the metal centre will require strong electron-withdrawing groups, whilst a lower reactivity towards  $\sigma$ -donor,  $\pi$ -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.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

We thank the Royal Society (University Research Fellowship No. UF150295 to NPEB) and the University of Bradford for

financial support. Additional computational resources were provided by the high-performance computational facility MADECIP, POSCCE, COD SMIS 48801/1862 co-financed by the European Regional Development Fund of the European Union. Funding from the Romanian Ministry of Research, (Grant No. PN-III-P4-ID-PCE-2016-0089) is gratefully acknowledged.

## Notes and references

- 1 J. E. McGrady and P. J. Dyson, *J. Organomet. Chem.*, 2000, **607**, 203–207.
- 2 R. Noyori and S. Hashiguchi, *Acc. Chem. Res.*, 1997, **30**, 97–102.
- 3 M. Lamberti, G. C. Fortman, A. Poater, J. Broggi, A. M. Z. Slawin, L. Cavallo and S. P. Nolan, *Organometallics*, 2012, **31**, 756–767.
- 4 V. V. Krishna Mohan Kandepi, J. M. S. Cardoso, E. Peris and B. Royo, *Organometallics*, 2010, **29**, 2777–2782.
- 5 U. Koelle, *Chem. Rev.*, 1998, **98**, 1313–1334.
- 6 U. Koelle, C. Rietmann and G. Raabe, *Organometallics*, 1997, **16**, 3273–3281.
- 7 R. E. Blake Jr., R. H. Heyn and T. D. Tilley, *Polyhedron*, 1992, **11**, 709–710.
- 8 R. Shimogawa, T. Takao and H. Suzuki, *Organometallics*, 2014, **33**, 289–301.
- 9 J. M. S. Cardoso, A. Fernandes, B. d. P. Cardoso, M. D. Carvalho, L. P. Ferreira, M. J. Calhorda and B. Royo, *Organometallics*, 2014, **33**, 5670–5677.
- 10 M. D. Walter and P. S. White, *Inorg. Chem.*, 2012, **51**, 11860–11872.
- 11 P. Mondal, M. Chatterjee, A. Paretzki, K. Beyer, W. Kaim and G. K. Lahiri, *Inorg. Chem.*, 2016, **55**, 3105–3116.
- 12 S. Tsukada, T. Sagawa and T. Gunji, *Chem. – Asian J.*, 2015, **10**, 1881–1883.
- 13 P. Kumar, R. K. Gupta and D. S. Pandey, *Chem. Soc. Rev.*, 2014, **43**, 707–733.
- 14 Z. Liu, I. Romero-Canelón, B. Qamar, J. M. Hearn, A. Habtemariam, N. P. E. Barry, A. M. Pizarro, G. J. Clarkson and P. J. Sadler, *Angew. Chem., Int. Ed.*, 2014, **53**, 3941–3946.
- 15 N. P. E. Barry and P. J. Sadler, *Pure Appl. Chem.*, 2014, **86**, 1897–1910.
- 16 N. P. E. Barry, A. Pitto-Barry, I. Romero-Canelon, J. Tran, J. J. Soldevila-Barreda, I. Hands-Portman, C. J. Smith, N. Kirby, A. P. Dove, R. K. O'Reilly and P. J. Sadler, *Faraday Discuss.*, 2014, **175**, 229–240.
- 17 A. A. Nazarov, C. G. Hartinger and P. J. Dyson, *J. Organomet. Chem.*, 2014, **751**, 251–260.
- 18 P. Nowak-Sliwinska, J. R. van Beijnum, A. Casini, A. A. Nazarov, G. Wagnieres, H. van den Bergh, P. J. Dyson and A. W. Griffioen, *J. Med. Chem.*, 2011, **54**, 3895–3902.
- 19 A. M. Basri, R. M. Lord, S. J. Allison, A. Rodríguez-Bárcano, S. J. Lucas, F. D. Janeway, H. J. Shepherd, C. M. Pask, R. M. Phillips and P. C. McGowan, *Chem. – Eur. J.*, 2017, **23**, 6341–6356.

- 20 G. Süß-Fink, *Dalton Trans.*, 2010, **39**, 1673–1688.
- 21 A. M. Pizarro, N. P. E. Barry and P. J. Sadler, in *Comprehensive Inorganic Chemistry II*, ed. J. Reedijk, Elsevier, 2013, vol. 3, pp. 752–784.
- 22 C. S. Allardyce, P. J. Dyson, D. J. Ellis and S. L. Heath, *Chem. Commun.*, 2001, 1396–1397.
- 23 R. E. Morris, R. E. Aird, P. d. S. Murdoch, H. Chen, J. Cummings, N. D. Hughes, S. Parsons, A. Parkin, G. Boyd, D. I. Jodrell and P. J. Sadler, *J. Med. Chem.*, 2001, **44**, 3616–3621.
- 24 Z. Adhireksan, G. Palermo, T. Riedel, Z. Ma, R. Muhammad, U. Rothlisberger, P. J. Dyson and C. A. Davey, *Nat. Commun.*, 2017, **8**, 14860.
- 25 J. Palmucci, F. Marchetti, R. Pettinari, C. Pettinari, R. Scopelliti, T. Riedel, B. Therrien, A. Galindo and P. J. Dyson, *Inorg. Chem.*, 2016, **55**, 11770–11781.
- 26 A. Garci, J. P. Mbakidi, V. Chaleix, V. Sol, E. Orhan and B. Therrien, *Organometallics*, 2015, **34**, 4138–4146.
- 27 V. Vajpayee, S. Lee, S.-H. Kim, S. C. Kang, T. R. Cook, H. Kim, D. W. Kim, S. Verma, M. S. Lah, I. S. Kim, M. Wang, P. J. Stang and K.-W. Chi, *Dalton Trans.*, 2013, **42**, 466–475.
- 28 V. Vajpayee, Y. H. Song, Y. J. Jung, S. C. Kang, H. Kim, I. S. Kim, M. Wang, T. R. Cook, P. J. Stang and K.-W. Chi, *Dalton Trans.*, 2012, **41**, 3046–3052.
- 29 S. Shanmugaraju, V. Vajpayee, S. Lee, K.-W. Chi, P. J. Stang and P. S. Mukherjee, *Inorg. Chem.*, 2012, **51**, 4817–4823.
- 30 A. Mishra, V. Vajpayee, H. Kim, M. H. Lee, H. Jung, M. Wang, P. J. Stang and K.-W. Chi, *Dalton Trans.*, 2012, **41**, 1195–1201.
- 31 A. Mishra, S. Lee, H. Kim, T. R. Cook, P. J. Stang and K.-W. Chi, *Chem. – Asian J.*, 2012, **7**, 2592–2599.
- 32 M. Wang, V. Vajpayee, S. Shanmugaraju, Y.-R. Zheng, Z. Zhao, H. Kim, P. S. Mukherjee, K.-W. Chi and P. J. Stang, *Inorg. Chem.*, 2011, **50**, 1506–1512.
- 33 V. Vajpayee, Y. J. Yang, S. C. Kang, H. Kim, I. S. Kim, M. Wang, P. J. Stang and K.-W. Chi, *Chem. Commun.*, 2011, **47**, 5184–5186.
- 34 I. Romero-Canelón, B. Phoenix, A. Pitto-Barry, J. Tran, J. J. Soldevila-Barreda, N. Kirby, S. Green, P. J. Sadler and N. P. E. Barry, *J. Organomet. Chem.*, 2015, **796**, 17–25.
- 35 M. Pernot, N. P. E. Barry, T. Bastogne, C. Frochot, M. Barberi-Heyob and B. Therrien, *Inorg. Chim. Acta*, 2014, **414**, 134–140.
- 36 A. Pitto-Barry, P. J. Sadler and N. P. E. Barry, *Chem. Commun.*, 2016, **52**, 3895–3898.
- 37 A. Pitto-Barry, L. M. A. Perdigao, M. Walker, J. Lawrence, G. Costantini, P. J. Sadler and N. P. E. Barry, *Dalton Trans.*, 2015, **44**, 20308–20311.
- 38 N. P. E. Barry, A. Pitto-Barry, J. Tran, S. E. F. Spencer, A. M. Johansen, A. M. Sanchez, A. P. Dove, R. K. O'Reilly, R. J. Deeth, R. Beanland and P. J. Sadler, *Chem. Mater.*, 2015, **27**, 5100–5105.
- 39 N. P. E. Barry, A. Pitto-Barry, A. M. Sanchez, A. P. Dove, R. J. Procter, J. J. Soldevila-Barreda, N. Kirby, I. Hands-Portman, C. J. Smith, R. K. O'Reilly, R. Beanland and P. J. Sadler, *Nat. Commun.*, 2014, **5**, 3851.
- 40 A. Pitto-Barry, A. South, A. Rodger and N. P. E. Barry, *Dalton Trans.*, 2016, **45**, 1763–1768.
- 41 N. P. E. Barry, T. F. Kemp, P. J. Sadler and J. V. Hanna, *Dalton Trans.*, 2014, **43**, 4945–4949.
- 42 N. P. E. Barry, R. J. Deeth, G. J. Clarkson, I. Prokes and P. J. Sadler, *Dalton Trans.*, 2013, **42**, 2580–2587.
- 43 Y.-F. Han and G.-X. Jin, *Acc. Chem. Res.*, 2014, **47**, 3571–3579.
- 44 Z.-J. Yao, G. Su and G.-X. Jin, *Chem. – Eur. J.*, 2011, **17**, 13298–13307.
- 45 X.-K. Huo, G. Su and G.-X. Jin, *Dalton Trans.*, 2010, **39**, 1954–1961.
- 46 X. Wang, S. Liu, L.-H. Weng and G.-X. Jin, *Chem. – Eur. J.*, 2007, **13**, 188–195.
- 47 S. Liu and G.-X. Jin, *Dalton Trans.*, 2007, 949–954.
- 48 S. Liu, Y.-F. Han and G.-X. Jin, *Chem. Soc. Rev.*, 2007, **36**, 1543–1560.
- 49 R. Xi, M. Abe, T. Suzuki, T. Nishioka and K. Isobe, *J. Organomet. Chem.*, 1997, **549**, 117–125.
- 50 K. Mashima, H. Kaneyoshi, S.-i. Kaneko, A. Mikami, K. Tani and A. Nakamura, *Organometallics*, 1997, **16**, 1016–1025.
- 51 J. A. Cabeza, S. Garcia-Granda, M. Perez-Priede and J. F. Van der Maelen, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2002, **58**, m189–m190.
- 52 R. Xi, M. Abe, T. Suzuki, T. Nishioka and K. Isobe, *J. Organomet. Chem.*, 1997, **549**, 117–125.
- 53 P. Thordarson, *Chem. Soc. Rev.*, 2011, **40**, 1305–1323.
- 54 M. Herberhold, H. Yan, W. Milius and B. Wrackmeyer, *Chem. – Eur. J.*, 2002, **8**, 388–395.
- 55 N. Zhang, S. R. Wilson and P. A. Shapley, *Organometallics*, 1988, **7**, 1126–1131.
- 56 O. Gutten and L. Rulišek, *Inorg. Chem.*, 2013, **52**, 10347–10355.
- 57 N. P. E. Barry, J. Furrer and B. Therrien, *Helv. Chim. Acta*, 2010, **93**, 1313–1328.
- 58 N. P. E. Barry, J. Furrer, J. Freudenreich, G. Süß-Fink and B. Therrien, *Eur. J. Inorg. Chem.*, 2010, 725–728.
- 59 N. P. E. Barry and B. Therrien, *Eur. J. Inorg. Chem.*, 2009, 4695–4700.
- 60 S. Kotrly and L. Šůcha, in *Handbook of Chemical Equilibria in Analytical Chemistry*, ed. R. A. Chalmers and M. Masson, John Wiley & Sons, Chichester, 1985, pp. 87–108.
- 61 A. F. A. Peacock, M. Melchart, R. J. Deeth, A. Habtemariam, S. Parsons and P. J. Sadler, *Chem. – Eur. J.*, 2007, **13**, 2601–2613.
- 62 R. Peverati and D. G. Truhlar, *J. Phys. Chem. Lett.*, 2012, **3**, 117–124.
- 63 A. Nicklass, M. Dolg, H. Stoll and H. Preuss, *J. Chem. Phys.*, 1995, **102**, 8942–8952.
- 64 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.
- 65 W. Kaim and B. Schwederski, *Coord. Chem. Rev.*, 2010, **254**, 1580–1588.