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COMMUNICATION

Synthesis of a new type of alkene metal complex using face-capping thione-alkene ligands†

Cite this: DOI: 10.1039/x0xx00000x

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Accepted 00th March 2015

DOI: 10.1039/x0xx00000x

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A series of complexes of novel chelating thione-alkene $S(\eta^2-C=C)S$ tridentate ligands bound to late transition metals (Ir, Rh, Pd) were isolated and characterised. Counter-anions play an important role in the binding of the alkene moiety to the metals. Different solvents were observed to affect the stability of the rhodium complexes.

Olefin ligands are omnipresent in organometallic chemistry, which is reflected by the myriad of applications involving olefin-bearing metal catalysts in areas ranging from homo- and hetero-geneous catalysis to material science.¹ In fact, one of the first organometallic complexes to ever be isolated, Zeise's salt, is an olefin complex. Its true nature was unambiguously determined about a century after its discovery.² As an archetype of the π -coordination mode, the studies of coordination complexes contain η^2 -ethylene ligands led to fundamental insights into the nature of the chemical bond.³ Considerable attention has been paid to the use of chiral olefins as steering ligands in asymmetric catalysis.^{3i,3j} Transition metal complexes of a class of neutral chelating ligands containing a central alkene and two phosphine groups have been reported.⁴

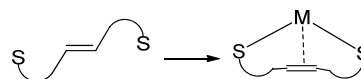
Thiones are an underexplored ligand class in organometallic

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† Electronic supplementary information (ESI) available: Full experimental details, molecular structures of **L1**, **1-(NO₃)₂**, and selected NMR spectra. CCDC 1053190-1053196. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/



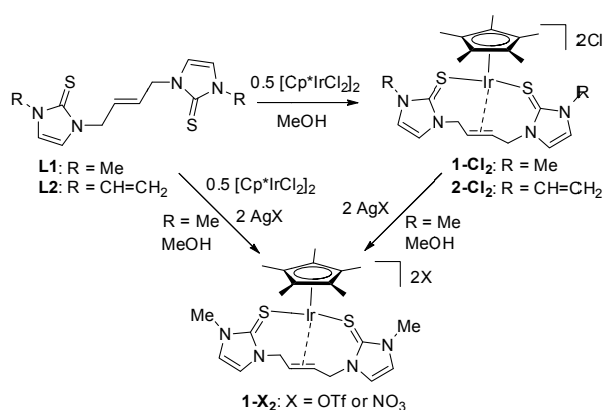
Scheme 1 Alkene-coordinating tridentate $S(\eta^2-C=C)S$ ligands.

chemistry. This is surprising considering such ligands are easily accessible, highly tailorable, and their metal complexes generally exhibit good stability.⁵ Indeed, imidazole-based thiones are an exciting class of structures with utility in antithyroid drugs.⁶

Imidazolin-2-thiones have also been synthesized during the capture of highly-reactive N-heterocyclic carbene species.⁷ Studies of thione metal complexes have led to many important discoveries related to their fundamental chemistry,⁸ their applications in catalysis,⁹ and their use as potential materials.¹⁰ Very recently, we found that organometallic complexes featuring thione ligands have potential applications in the activation of small molecules.¹¹ However, in general, the chemistry of thione-based ligands and their metal complexes is a relatively underdeveloped field.

Herein we report a novel alkene-bridged thione-based ligand family and complexes of these ligands with iridium, rhodium and palladium. The structures formed represent a new class of complexes containing metal-alkene π -bonding (Scheme 1).

Imidazolin-2-thiones **L1** and **L2** were synthesized by treating 1,4-dibromo-2-butene with appropriate N-substituted imidazoles to produce the corresponding imidazole salts, followed by their reactions with element sulfur to afford the corresponding thiones.^{9a} The metal-alkene coordinated complex **1-Cl₂** was obtained in 92% yield from the reaction of $[Cp^*IrCl_2]_2$ with two equimolar amounts of **L1** in methanol at room temperature (Scheme 2). Complex **1-Cl₂** was characterized by multi-nuclear NMR spectroscopy, ESI-MS and elemental analysis. The ¹H NMR spectrum of complex **1-Cl₂** shows significant upfield shift of the olefinic protons compared to those of the free ligand **L1**. This shift is consistent with a π -bound olefinic unit and a considerable amount of π backbonding from the metal center.⁴



Scheme 2 Synthesis of iridium complexes from alkene-coordinating tridentate SCS ligands.

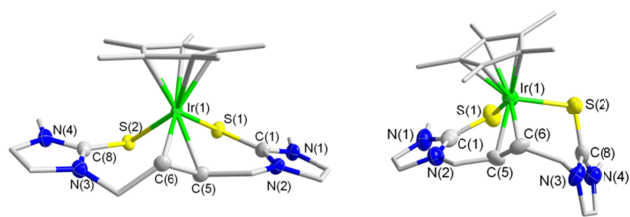


Fig. 1 Molecular structures and numbering schemes of **1-Cl₂** (left) and **1-(OTf)₂** (right); thermal ellipsoids shown at 50% probability. Hydrogen atoms, anions and solvent molecules are omitted for clarity.

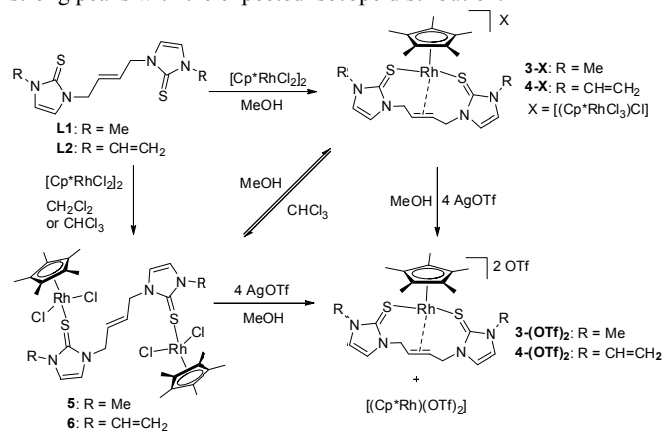
η^2 -Coordination of the olefinic carbons to the iridium atom in complex **1-Cl₂** was established by X-ray crystallographic analysis. As shown in Fig. 1 (left), the ligand **L1** is bound to the iridium atom in a tridentate manner to generate a $S(\eta^2-C=C)S$ olefin-type structure. The olefinic C=C bond length (1.411(5) Å) is obviously longer than that of the free ligand (1.325(5) Å), indicating the existence of an interaction between the metal center and the C=C bond.

The alkene-chelating complex **1-Cl₂** was converted to complexes **1-(OTf)₂** or **1-(NO₃)₂** in quantitative yield by abstraction of the chloride with silver salts. Complexes **1-(OTf)₂** and **1-(NO₃)₂** can also be synthesized in excellent yields by reaction of **[Cp*IrCl₂]₂** with excess AgOTf or AgNO₃ in methanol, followed by addition of **L1**. All spectroscopic data are consistent with the proposed structures for **1-X₂** (X = OTf or NO₃). The ¹H NMR spectra of **1-(OTf)₂** and **1-(NO₃)₂** also exhibit significant upfield shifts of the olefinic protons, similar to that observed in **1-Cl₂**, indicating that the olefin remains bound to the metal center. Each ¹H NMR spectrum of **1-X₂** (X = Cl⁻, OTf⁻ or NO₃⁻) shows four different signals of the methylene-arm resonances, attributed to the asymmetric structure of cation (see ESI).

The molecular structures of **1-(OTf)₂** and **1-(NO₃)₂** in the solid states were determined by single-crystal X-ray diffraction methods. The examples of **1-Cl₂** and **1-(OTf)₂** are shown in Fig. 1. Each of the molecules has a mononuclear structure composed of one Cp*Ir unit with the metal atom being surrounded by two S atoms and one η^2 -coordinated alkene. The nature of the counteranion was observed to affect the coordination between the metal center and the alkene

group. The olefinic bond length (1.407(12) Å) in **1-(OTf)₂** is slightly shorter than that in **1-Cl₂**, but longer than that in **1-(NO₃)₂** (1.392(10) Å, see ESI). The average Ir-S bond length (ca. 2.38 Å) in each of the complexes is in the range of typical distances of reported mononuclear half-sandwich iridium complexes bearing thione-based ligands.¹¹ In each of complexes, the olefin in the backbone approaches a perpendicular orientation to the plane defined by S(1), Ir(1), and S(2). It is worth noting that the two thione rings were found to be in different geometries after exchange of anion from chloride to triflate or nitrate.

In a further investigation of the interaction of transition metals with alkenes, a new ligand **L2** was introduced containing terminal vinyl groups at the nitrogen atoms. Formation of **2-Cl₂** was confirmed by ¹H and ¹³C{¹H} NMR spectroscopy, the former showing the significantly upfield-shifted resonances for the central olefinic protons, however the signals for the protons on the terminal vinyl groups are shifted only slightly. ESI-MS also showed the formation of the mononuclear iridium cations **[2]²⁺** and **[2-Cl]⁺** as strong peaks with the expected isotope distribution.



Scheme 3 Synthesis of rhodium complexes from alkene-coordinating tridentate SCS ligands and their reactivity.

Complexes **1-X₂** (X = Cl⁻, OTf⁻ or NO₃⁻), and **2-Cl₂** are air- and moisture-stable. Even in the presence of H₂ or CO, no reaction with iridium complex **1-(OTf)₂** was observed after 24 h.

In order to investigate whether the coordination mode is affected by the metal center, the reaction of **L1** with **[Cp*RhCl₂]₂** was performed (Scheme 3). Examining the reaction mixture by ¹H NMR spectroscopy indicated that the reaction is solvent dependent (Fig. 2). When methanol is used as solvent, the chemical shifts of olefinic protons in ¹H NMR indicated the formation of metal-alkene coordination (Fig. 2c). However, unlike in complex **1-Cl₂**, the formation of a mononuclear rhodium complex **3-[Cp*RhCl₃]Cl** containing one **[Cp*RhCl₃]⁻** and one chloride counteranions was established by ESI-MS in methanol.

In contrast, when the same reaction was performed in CDCl₃, the coordination of the olefinic backbone was not observed (Fig. 2b). Red crystals which recrystallized from CDCl₃ were identified as the dinuclear complex **5**. To our surprise, although the complex **3-[Cp*RhCl₃]Cl** is stable in methanol solution, only red crystals of complex **5** were obtained in quantitative yield upon diffusion of diethyl ether into this solution. The X-ray structure of **5** was also

obtained, further confirming the presence of an uncoordinated olefin group as shown in Fig. 3 (left). This suggests that the rhodium-alkene coordination of **3**-[Cp***RhCl**₃]**Cl** is unstable and rearranged

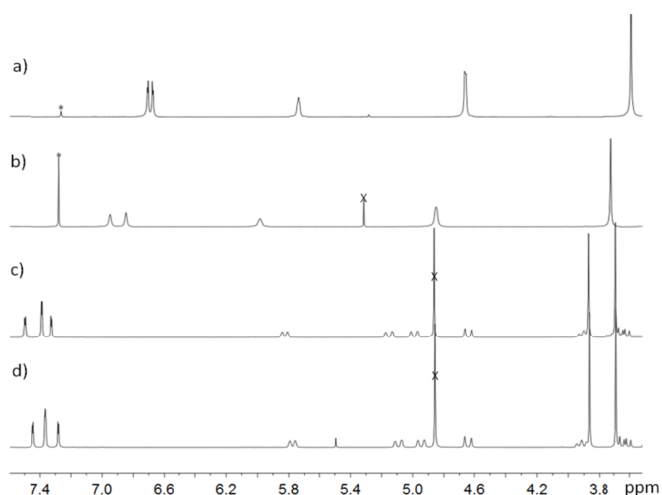


Fig. 2 Partial ¹H NMR spectra (400 MHz, 300K) of a) ligand **L1** (CDCl₃), b) the mixture of **L1** and [Cp***RhCl**₂]₂ (1:1 ratio) in CDCl₃, c) the mixture of **L1** and [Cp***RhCl**₂]₂ (1:1 ratio) in CD₃OD, and d) complex **3**-(**OTf**)₂ (CD₃OD). (* and x represent CDCl₃ and H₂O, respectively.)

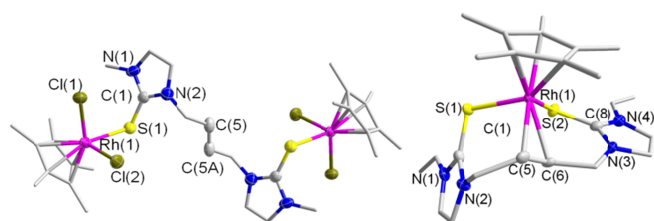


Fig. 3 Molecular structures and numbering schemes of **5** (left) and **4**-(**OTf**)₂ (right); thermal ellipsoids shown at 50% probability. Hydrogen atoms, anions and solvent molecules are omitted for clarity.

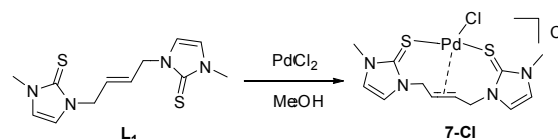
to complex **5** after removal of methanol. In contrast, when crystals of **5** were dissolved in CD₃OD, very similar ¹H NMR spectroscopic data indicated the presence of **3**-[Cp***RhCl**₃]**Cl**. The results imply that polar solvents such as methanol could strongly favour ionic species in this case.¹² By changing the ligand from **L1** to **L2**, a similar reversible phenomenon between complex **6** and **4**-[Cp***RhCl**₃]**Cl** was also observed.

Reaction of the dimetallic complexes **5** or **6** with excess AgOTf results in the formation of monometallic complexes **3**-(**OTf**)₂ or **4**-(**OTf**)₂ in high yield, respectively. The monometallic complexes **3**-(**OTf**)₂ or **4**-(**OTf**)₂ can also be obtained from the reaction of **3**-[Cp***RhCl**₃]**Cl** or **4**-[Cp***RhCl**₃]**Cl**, respectively, and AgOTf. The monometallic complexes **3**-(**OTf**)₂ and **4**-(**OTf**)₂ are stable both in the solution and solid states (Fig. 2d and ESI). For example, the formation of monometallic complex **4**-(**OTf**)₂ was confirmed by ¹H, ¹³C, ¹H-¹H COSY and ¹H-¹³C HSQC spectroscopy and mass spectrometry. Rearrangement to a dimetallic complex was not observed even in chloroform solution (see ESI).

An X-ray diffraction analysis of single crystals of **4**-(**OTf**)₂ established the presence of a mononuclear η²-alkene-rhodium(III)

complex (Fig. 3, right). No coordination with either of the terminal vinyl groups was observed.

The reaction of **L1** with PdCl₂ in methanol was carried out and resulted in the formation of a red solution (Scheme 4). Again, the significant upfield shifts of the olefinic protons were observed. The pseudo-square-planar structure of the metal center in complex **7**-**Cl** was unambiguously confirmed by single-crystal X-ray diffraction (Fig. 4). Again, an elongated C(5)-C(6) distance of 1.385(5) Å was observed due to π-bonding. The olefin in the backbone approaches a perpendicular orientation to the plane defined by S(1), Pd(1), and S(2), similarly to that observed for the rhodium analogue. The structure of **7** looks very similar to Zeise's salt.



Scheme 4 Synthesis of palladium complex **7**-**Cl** from alkene-coordinating tridentate SCS ligands.

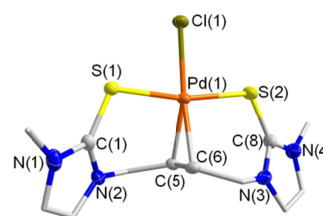


Fig. 4 Molecular structure and numbering scheme of **7**-**Cl**; thermal ellipsoids shown at 50% probability. Hydrogen atoms, one chloride anion and solvent molecules are omitted for clarity.

In conclusion, we present here a novel type of tridentate metal complex containing a chelating *E*-alkene unit bound in an η²-fashion. The interaction was established in the solid state by the elongated C-C bond distance in the olefinic backbone. We have found that the reaction of such SCS ligands with [Cp***RhCl**₂]₂ is solvent dependent. When dichloromethane or chloroform is used as the solvent instead of methanol, the coordination of the olefinic backbone with metal center was not observed. The stability of these SCS pincer-style alkene-chelating complexes makes them potentially attractive for catalytic reactions and material science, and this work is in progress in our laboratories.

The authors thank the National Science Foundation of China (21371036, 91122017, 21001029), PCSIRT (IRT1117), Shanghai Pujiang Program (14PJD006) and Shanghai Rising-Star Program (11QA1400300) for funding.

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