Dalton Transactions

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Journal:	*Dalton Transactions*
Manuscript ID	DT-COM-11-2015-004466.R1
Article Type:	Communication
Date Submitted by the Author:	13-Jan-2016
Complete List of Authors:	Telfer, Shane; Massey University, IFS - Chemistry Perl, David; IFS - Massey University, Bisset, Sean; Massey University,

Journal Name

COMMUNICATION

Postcomplexation Synthetic Routes to Dipyrrin Complexes

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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We report a postfunctionalization synthetic route to dipyrrin complexes that gives access to a broad range of new complexes. This route involves the coordination of a 5-methylthiodipyrrinato ligand to a metal centre followed by displacement of the thiomethyl moiety by a nucleophile. Using rhenium(I) as a platform and amine nucleophiles, we show how complexes that would be difficult or impossible to synthesize via traditional methods can now be accessed.

The coordination chemistry of dipyrrinato and azadipyrrinato ligands continues to be an active field of research.[1, 2] Because dipyrrins have a conjugated π system between two pyrrole rings, analogous to half of a porphyrin, they typically have intense absorption bands in the visible region of the electromagnetic spectrum. This has led to exploration of their applications in light harvesting for dye-sensitised solar cells[3-6] and in functional materials such as photoactive metal organic frameworks.[7] They are also used as dyes and fluorescent markers, with BF_2 dipyrrin complexes (BODIPYs) being particularly well-studied for these applications.[8-10] Furthermore, transition metal complexes of dipyrrin complexes are often fluorescent.[11, 12]

In this light, synthetic routes to dipyrrin ligands are of considerable interest. The prevalent methodology involves the synthesis of a preformed dipyrrin ligand[13-15] followed by its deprotonation and coordination to a metal centre. All known transition metal complexes of dipyrrin ligands bear either a hydrogen atom or, more typically, a unsaturated cyclic substituent such as a phenyl or pyridyl ring at the meso position of the dipyrrin. Synthetic access to complexes with a more diverse range of functional groups at the meso position would broaden the structural and functional characteristics of dipyrrin complexes. Such functional groups may include recognition motifs for analytes, supramolecular synthons for crystal engineering, or biomolecules such as proteins and peptides. However, traditional synthetic routes to that involve the use of pre-formed dipyrrin ligands are often incompatible with ligands that bear interesting and/or delicate functional groups. The reasons for this include (i) the ligand being impossible to prepare or isolate, (ii) the ligand being unstable under the conditions required to achieve coordination to the target metal (e.g. high temperature, base), or (iii) the ligand bearing a functional group that will compete with the dipyrrin for coordination to the metal centre.

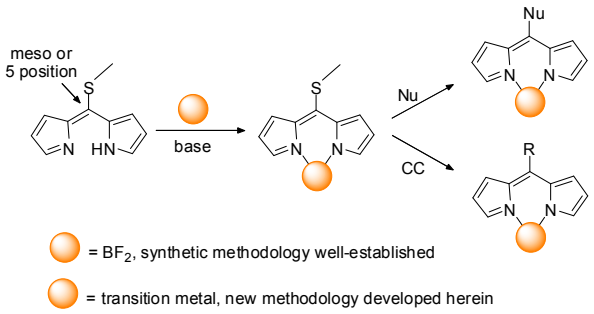

Figure 1. Our strategy is to extend the known postcomplexation reactivity of 5-thiomethylBODIPY to transition metal complexes. Nu = nucleophile, CC = cross-coupling.

We postulated that a recently-established method for synthesising heteroatom- and alkyl-substituted BODIPYs,[9, 16, 17] which uses a dipyrrin with an appropriate leaving group at the *meso* position, could be adapted to transition metal complexes. As shown in Figure 1, 5-thiomethylBODIPY is known to undergo nucleophilic substitution and Liebeskind-Srögl cross-coupling reactions to introduce various substituents at the *meso* position. We envisaged that a novel postcomplexation synthetic route to dipyrrin complexes could be developed from a 5-thiomethyldipyrrinato complex intermediate. An additional advantage of this approach is that modification of the ligand subsequent to complexation enables delicate substituents to be introduced. The general strategy of modifying dipyrrin ligands postcomplexation has been used, for example, to diversify cobalt(III) complexes of meso-aryl

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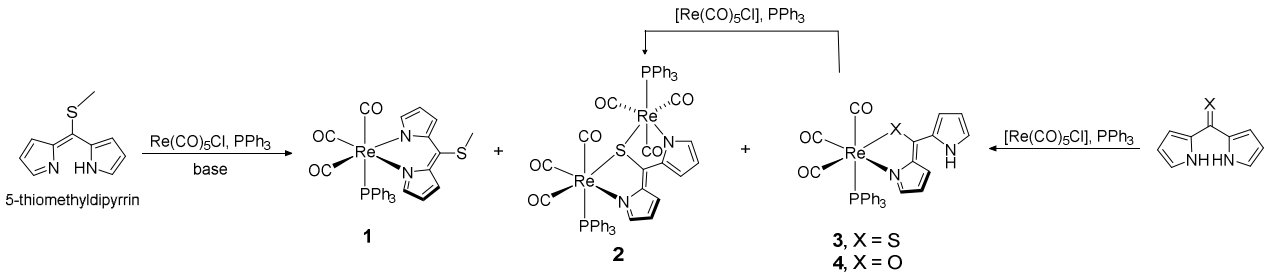
Electronic Supplementary Information (ESI) available: synthetic procedures, characterization details, and CCD deposition numbers. See DOI: 10.1039/x0xx00000x



Scheme 1. Synthetic routes to complexes **1** – **4**.

dipyrrinato complexes,[18-20] and to oxidatively couple dipyrrin ligands.[21] Rhenium(I) was a pragmatic choice for this proof-of-concept study since it is a d^6 ion which forms inert and diamagnetic complexes that are amenable to ^{1}H NMR spectroscopy. Further, Re(I)-dipyrrin complexes have interesting photophysical properties[22] and they may find use in devices and as photocatalysts.[23]

The reaction of 5-methylthiodipyrrin, $Re(CO)_5Cl$ and PPh_3 in the presence of base produces complex **1** in 45% yield (Scheme 1). Compound **1** was targeted in preference to the direct product of the reaction between 5-methylthiodipyrrin and $Re(CO)_5Cl$, $[Re(CO)_3(5\text{-methyldipyrrinato})Cl]^+$, since such complexes are rather unstable and are not amenable to column chromatography.[22] To our knowledge, this is the first report of a 5-heteroatom substituted dipyrrinato transition metal complex. We note that 2,2'-dipyrrolylthione, the synthetic precursor to 5-methylthiodipyrrin, was first reported in 1969,[24] and its coordination chemistry with Ni(II), Co(III), and Hg(II) was reported in 2000[25] with a view to developing radioimaging agents based on Re and Tc, which are described in the patent literature.[26]

We employed NMR spectroscopy and single-crystal X-ray crystallography to characterize **1**. As anticipated,[22] the three carbonyl ligands adopt a facial arrangement around the metal centre and the dipyrrinato ligand is slightly bowed (Fig. 2).

By employing column chromatography, we isolated two noteworthy side-products from the reaction used to produce **1**. Complex **3** (~35% yield) results from the loss of the methyl group from 5-methylthiodipyrrin and subsequent coordination via sulfido and pyrrole nitrogen donor groups. Varying the base used in this reaction (various alkyl amines, K_2CO_3) did not suppress its formation. Complex **2** is a dinuclear complex in which the sulfide ligand bridges the two rhenium(I) centres. It is produced in yields of up to 10%, presumably by via a pathway involving **3**. In an independent reaction, we verified that **3** can be transformed into **2** by reaction with $[Re(CO)_5Cl]$ and PPh_3. In exploring the coordination chemistry of 2,2'-dipyrrolylthione we established that it produces **3** in almost quantitative yield upon reaction with $[Re(CO)_5Cl]$ and PPh_3. We also found that 2,2'-dipyrrolylketone[17] delivers an related complex (**4**) in which the sulphur atom is replaced by an oxygen. The structures of complexes **2** – **4** were determined by X-ray crystallography.

With **1** in hand we set out to explore the postcomplexation reactivity of the thiomethyldipyrrin unit with nucleophiles and in the Liebeskind–Srogl coupling reaction. However, it soon became apparent that this complex is significantly less reactive than the related BODIPY.[16] No reaction of **1** with amine nucleophiles was observed under typical conditions. Experiments in neat benzylamine, demonstrated that the displacement of the triphenylphosphine ligand takes place in preference to reaction at the meso carbon. We ascribe the greater reactivity of 5-thiomethyl BODIPY to the electron withdrawing nature of the BF_2 group, which renders the meso carbon more electrophilic. Consistent with this, difficulties in performing the nucleophillic substitution of a thiomethyl group on a closely related metalloporphyrin have been reported.[27]

Speculating that that steric hindrance by the bulky phosphine ligand may also partly underlie the reduced postcomplexation reactivity of **1**, we turned our attention to **5**, which features a less bulky pyridyl ligand (Scheme 2A). Complex **5** was synthesized using similar conditions to **1**, with the PPh_3 being replaced by pyridine. It was characterized by NMR spectroscopy and X-ray crystallography, which showed that its molecular structure closely parallels that of **1** (Fig. 3).

We successfully realized our postcomplexation synthetic strategy using complex **5** as an intermediate. We found that its thiomethyldipyrrin group can be displaced by nucleophiles provided that the nucleophile is present in high concentration. The versatility of this method is highlighted by the range of complexes shown in Scheme 2A, and its utility is underscored

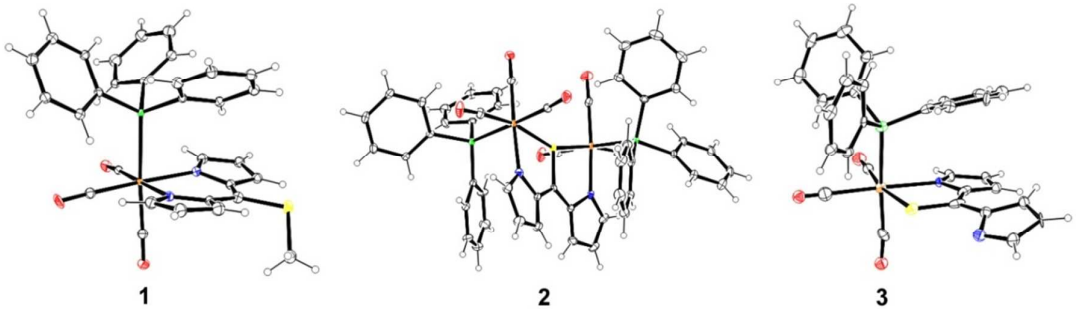
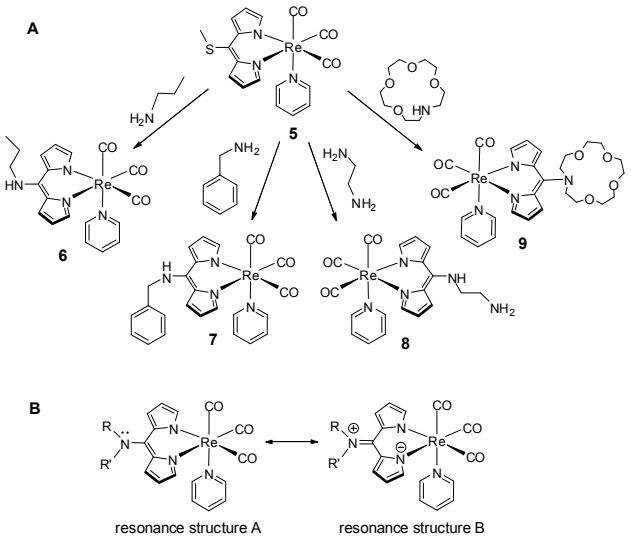


Figure 2. The structures of **1** – **3** as deduced by X-ray crystallography. Ellipsoids are set at the 30% level. Orange = Re, blue = N; red = O; yellow = S; green = P; black = C. The H atoms are represented as small black spheres.

by noting that complexes **6** - **9** cannot be accessed by conventional synthetic routes that involve 5-amino substituted dipyrrin precursors since such compounds are unstable and/or synthetically inaccessible.



Scheme 2. A) Postcomplexation synthetic routes from complex **5** to complexes **6** – **9**. B) Two resonance structures of the 5-amino functionalised complexes.

Using neat primary amines as nucleophiles results in yields of complexes **6** - **8** that are close to quantitative. The synthesis of **9** was carried out in neat 1-aza-15-crown-5, the unreacted portion of which can be easily recovered from the reaction mixture. All complexes could be purified by column chromatography except for **8**, which resisted all attempts at purification by chromatography or crystallization. However, the purity of the crude product was relatively good, thus we could ascertain its structure with a high degree of certainty. The free amino group of this complex is an attractive feature since it enables this complex to be used as a building block for functional materials such as polynuclear complexes, bioconjugates, or covalently-modified surfaces.

Complexes **5**, **6**, **7**, and **9** were characterized by NMR spectroscopy and single-crystal X-ray diffraction. Their molecular structures are presented in Figure 3. While the dipyrrin unit is nearly planar in **5**, it is noticeably bowed in **6**, **7**, and **9**. This nonplanarity correlates with a short bond (1.33 – 1.35 Å) between the meso carbon atom and the nitrogen of the amino group, which suggests that resonance structure B (Scheme 2) contributes strongly to the electronic distribution in these complexes. In keeping with this, UV-vis spectra of this series of compounds (Fig. 4) show that the π–π^* transition typical of planar dipyrrin ligands[28] is observed only for **1**, and **5** since resonance structure 2 inhibits the delocalization of electrons between the pyrrole units.

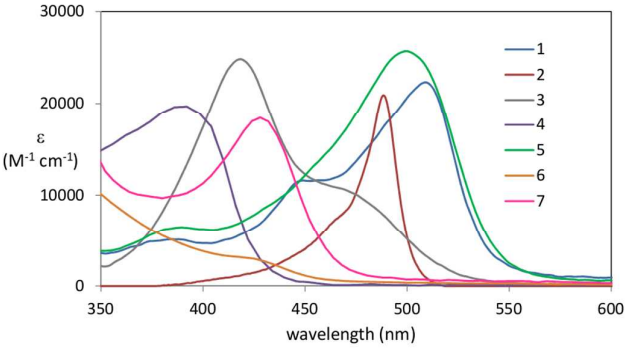


Figure 4. UV-vis spectra of complexes **1** – **7**.

None of the complexes described in this work has detectable luminescence. This includes complex **9**, which we had hoped may exhibit a fluorescent response to the binding of metal ions to its crown ether macrocyle. However, even in the presence of a range of metal ions, including K^+, no fluorescence was observed. We ascribe the quenching of radiative relaxation processes in these complexes to photoinduced intramolecular charge transfer processes involving the lone pair on the meso nitrogen atom, as observed for related BODIPYs.[29]

In summary, we have developed a new and widely-applicable postcomplexation synthetic route to complexes of dipyrrin ligands. This route provide access to complexes that cannot be synthesized by traditional means. We have established this methodology by using 5-thiomethyldipyrrinato complexes of rhenium(I) in proof-of principle experiments. Nucleophilic displacement of the thiomethyl group at the meso position of the dipyrrin chelate occurs in high yield and with a broad range of substrates. In this way, moieties that modulate the functional properties of this important class of materials can be incorporated. We predict that the future implementation of 5-chlorodipyrrin in place of 5-thiomethyldipyrrin in postcomplexation synthetic routes will offer a complementary synthetic pathway. The chloro group will have little propensity to coordinate to the metal centre (unlike the thiomethyl group) and it is known to be highly reactive in substitution and coupling reactions.[16]

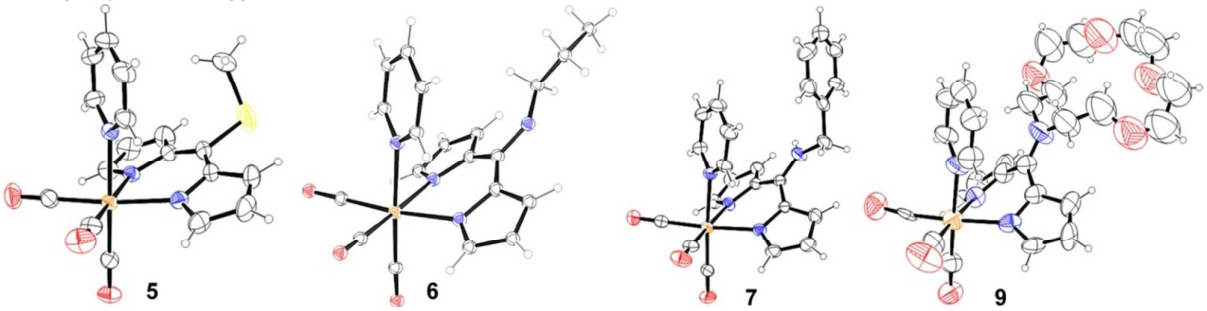


Figure 3. The structures of complexes **5**, **6**, **7**, and **9** deduced by X-ray crystallography. Ellipsoids are set at the 30% level. Orange = Re, blue = N; red = O; yellow = S; black = C. The H atoms are represented as small black spheres.

Notes and references

‡ We thank Janice Moody for preliminary experimental work.

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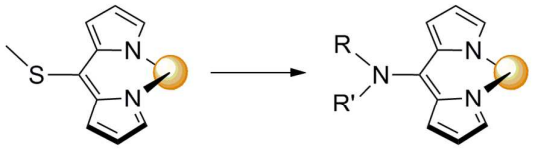

synthetic intermediate

new dipyrrin complexes

The postcomplexation reactivity of 5-thiomethyldipyrrin complexes provides a synthetic route to hitherto inaccessible dipyrrin complexes.