Heterotrimetallic complexes of iron and ruthenium based on vinyliminium dithiocarboxylate ligands

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The diiron vinyliminium compounds [Fe2(μ-η1:η2-C(R)) = C(H)C=NN(Me)R](μ-CO)(CO)(Cp)2]OSO2CF3
(R = Xyl = 2,6-C6H3Me2, R = Me; R = Me, R = CO2Me) provide a versatile entry point for many subsequent transformations, such as their reaction with carbon disulfide to provide zwitterionic dithiocarboxylate products. These compounds react with the coordinatively-unsaturated ruthenium vinyl precursors [Ru(CH=CHR)(CO)(PPh3)2] (R = C6H4Me-4, 1-Pyrenyl) to yield heterotrimetallic Fe2Ru compounds, exhibiting vinyl moieties at both iron and ruthenium centres. The emission associated with the pyrenyl unit is enhanced in the diiron vinyliminium ruthenium pyrenyl complex compared to the diethyldithiocarbamate analogue.

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1. Introduction

The ability to bring multiple metals together within the same molecular framework opens up the possibility of many fascinating interactions. These have been exploited in many areas, including catalysis [1], sensing [2] and imaging [3]. In particular, diiron assemblies are very well known and heavily investigated due to their important role in nature [4], such as hemerythrin, which reversibly binds dioxygen [5] and [FeFe] hydrogenases [6]. Many pioneering investigations have employed diiron units in the cleavage of challenging C-H and O-H bonds [7], oxidation of methane [8] or to form ammonia as a nitrogenase mimic [9]. In many examples, the accessibility of different oxidation states is fundamental to the action of these diiron systems [10], which once again relies on the redox potential of the two iron centres in order to function. This has been used by Gibson and Long to modulate the lactide polymerisation behaviour of a ferrocenyl-derivatised salen-based ligand bonded to a titanium centre [11]. In oxidised form, the resulting positively charged complex is found to be a significantly less effective catalyst due to the electron withdrawing effect, allowing block copolymers to be prepared through sequential addition of monomers.

The potential for diiron units to be used themselves as ligands was indicated by the work of Busetto and Marchetti and coworkers, who prepared a series of vinyliminium diiron complexes (1 and 2 in Scheme 1), which are susceptible to a variety of nucleophilic additions [12,13]. Furthermore, these μ-vinyliminium ligands undergo deprotonation of the α-C–H proton [14], which has been exploited to introduce a variety of substituents and functionalities into the diiron frame [15]. In particular, the C–H activation in the presence of the heteroallene, CSS, leads to the zwitterionic dithiocarboxylates shown in Scheme 1 [16].

In recent years, our investigations have concentrated on the additional functionality provided to metal complexes and gold nanoparticles by the addition of dithiocarbamate [17] and xanthate [18] ligands. In particular, their application in the formation of multimetallic assemblies is noteworthy [19]. These studies on 1,1′-dithio ligands have been extended to dithiocarbamate betaines based on N-heterocyclic carbenes (NHCs) [20].

In this contribution, the dithiocarbamate betaines shown in Scheme 1 are employed to form multimetallic complexes with other group 8 metals, forming heterotrinuclear assemblies. In contrast to previous work, the availability of a 1,1′-dithio ligand with intimate connection to the diiron unit offers the possibility of
influencing the behaviour of the metal to which the dithiocarboxylate is attached.

2. Results and discussion

Ruthenium vinyl compounds of the form \([\text{Ru}(\text{CHR})\text{Cl}](\text{CO})(\text{L})(\text{PPh}_3)_2\) [21] and \([\text{Ru}(\text{CHR})\text{Cl}](\text{CO})(\text{BTD})(\text{PPh}_3)_2\) (BTD = 2,13-benzothiadiazole) [22] are readily accessible through hydronitrogenation of alkynes by hydride precursors (R = alkyl or aryl substituents). These vinyl compounds have proved versatile precursors for many further transformations, including the addition of mono- and polydentate ligands [23]. The BTD compounds \([\text{Ru}(\text{CHR})\text{Cl}](\text{CO})(\text{L})(\text{PPh}_3)_2\) (L = BTD, thiényl-BTD) have recently been employed as highly selective and sensitive probes for carbon monoxide [24].

The two zwitterionic dithiocarboxylate complexes used in this study were chosen on the basis of their differing steric profiles. The diiron compound, \([\text{Fe}_2(\mu-\text{C}(\text{CO}_2\text{Me})(\text{Me})\text{XYlyl})](\mu-\text{CO})(\text{CO})(\text{Cp})_2\) (3), has been reported previously [16], whereas the analogues, \([\text{Fe}_2(\mu-\text{C}(\text{CO}_2\text{Me})(\text{C}(\text{CS}_2)\text{NMe}_2))](\mu-\text{CO})(\text{CO})(\text{Cp})_2\) (4), was prepared for this study, in a moderate yield. Compound 4 has a less pronounced steric profile due to the less bulky NMe2 group. The presence of the CO2Me ester group also renders 4 less soluble in common organic solvents compared to 3. The \(^1\text{H} \text{NMR} \) spectrum of 4 displayed three methyl singlet resonances in the higher field region, at 3.28, 3.80 and 4.08 ppm. The former were attributed to the NMe2 group and the latter to the CO2Me ester unit. The spectrum was completed by two singlets at 5.12 and 5.25 ppm for the two cyclopentadienyl ligands.

Reaction of \([\text{Fe}_2(\mu-\eta^1-\eta^1-\text{C}(\text{Me})(\text{Me})\text{XYlyl})(\mu-\text{CO})(\text{CO})(\text{Cp})_2]\) (3) with coordinatively unsaturated \([\text{Ru}(\text{CH})\text{Cl}](\text{CO})(\text{BTD})(\text{PPh}_3)_2\) and NH4PF6 in dichloromethane led to an immediate darkening of the solution. While anaerobic conditions were used as a precaution, the dark brown product isolated appeared to be indefinitely stable in air and light. The solid state infrared spectrum proved particularly diagnostic as the absorptions for the terminal and bridging carbonyl ligands of the diiron unit were retained in the product at 1982 and 1820 cm\(^{-1}\) respectively, alongside a new band at 1929 cm\(^{-1}\), due to the CO2Me ester unit. The spectrum was completed by the molecular ion at m/z 1440 in the electrospray mass spectrum (+ve mode). Given the presence of the well-known pyrenyl fluorophore in compound 7, it was decided to investigate its emission properties compared to a compound bearing a 1,1’-dithio ligand without a diiron unit, \([\text{Ru}(\text{CH})\text{Cl}](\text{CO})(\text{S}_2\text{CNEt}_2)(\text{CO})(\text{PPh}_3)_2\) (Fig. 1) [25]. Spectra were also recorded for the precursor \([\text{Ru}(\text{CH})\text{Cl}](\text{CO})(\text{PPh}_3)_2\) and 1-ethylnylpyrene.

Excitation of dichloromethane solutions (100 \(\mu\text{M}\)) of the four compounds at 450 nm revealed that the emission of the pyrenyl unit in 7 was far more intense than in the precursor compound, \([\text{Ru}(\text{CH})\text{Cl}](\text{CO})(\text{PPh}_3)_2\), even exceeding that of 1-ethynylpyrene itself. It was also shown that, at this excitation wavelength, \([\text{Ru}(\text{CH})\text{Cl}](\text{CO})(\text{S}_2\text{CNEt}_2)(\text{CO})(\text{PPh}_3)_2\) produced a modest emission, almost half that displayed by 7. This suggested a quenching of the fluorescence in \([\text{Ru}(\text{CH})\text{Cl}](\text{CO})(\text{PPh}_3)_2\) and \([\text{Ru}(\text{CH})\text{Cl}](\text{CO})(\text{S}_2\text{CNEt}_2)(\text{CO})(\text{PPh}_3)_2\) relative to the trinuclear complex containing the diiron core. Computational studies are

**Scheme 1. Preparation of diiron dithiocarboxylate betaine complexes 3 and 4.**

**Scheme 2. Preparation of heterotrimetallic group 8 complexes 5–7.**
3. Conclusions

This report illustrates how multimetallic compounds can be constructed in a controlled, stepwise manner by exploiting the reliable reactivity of 1,1'-dithio units. Heterotrimetallic Fe2Ru compounds are formed from the reaction of zwitterionic diiron vinyliminium dithiocarboxylate units, [Fe2(μ-η1,1-n3-C(R2)=C(S2)C=O)(μ-CO)(CO)(Cp)2] (R1 = Xyl, R2 = Me; R1 = Me, R2 = CO3(Me)), acting as effective organometallic L2-ligands, with the versatile five-coordinate ruthenium vinyl precursors [Ru(CH=CHR3)Cl(CO)(PPh3)2] (R3 = C6H4Me-4, 1-Pyrenyl). The novel products contain two group 8 metals with vinyl moieties at both iron and ruthenium centres. Compared to the analogous dithiocarbamate complex, the trimetallic pyrenyl complex, [Fe2(μ-η1,1-n3-C(Me)=C(S2)Ru(CH=CHPy1)(μ-CO)(PPh3)2)C=O] (Xylyl[μ-CO](CO)(Cp)2)PF6 (7) shows enhanced emission associated with the pyrenyl unit.

Declarations of interest

None.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.02.003.

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