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Note

Heterotrimetallic complexes of iron and ruthenium based on vinyliminium dithiocarboxylate ligands

Lorenzo Mognon [a], Samuel Richardson [a], Gabriele Agonigi [b], Tamzin Bond [a],
Fabio Marchetti [b, **], James D.E.T. Wilton-Ely [a, *]

[a] Department of Chemistry, Imperial College London, Molecular Sciences Research Hub, White City Campus, London, W12 0BZ, UK
[b] Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Moruzzi 13, 56124, Pisa, Italy

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A B S T R A C T

The diiron vinyliminium compounds $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(R^2)=C(H)C=N(Me)R^1\}(\mu\text{-}CO)(CO)(Cp)_2]OSO_2CF_3$ ($R^1 = Xyl = 2,6\text{-}C_6H_3Me_2$, $R^2 = Me$; $R^1 = Me$, $R^2 = CO_2Me$) 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 $[Ru(CH{=}CHR^3)Cl(CO)(PPh_3)_2]$ ($R^3 = C_6H_4Me\text{-}4$, 1-Pyrenyl) to yield heterotrimetallic Fe_2Ru 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.

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, CS_2, 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 dithiocarboxylate betaines based on *N*-heterocylic carbenes (NHCs) [20].

In this contribution, the dithiocarboxylate betaines shown in Scheme 1 are employed to form multimetallic compounds 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

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* Corresponding author.
** Corresponding author.
E-mail addresses: fabio.marchetti1974@unipi.it (F. Marchetti), j.wilton-ely@imperial.ac.uk (J.D.E.T. Wilton-Ely).

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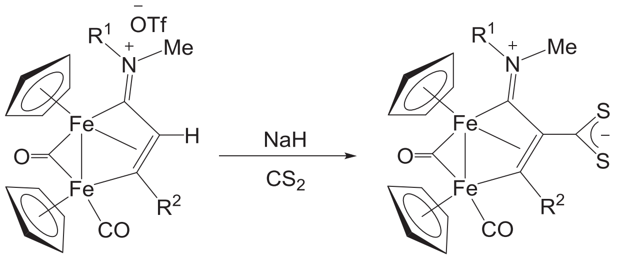


R^1 = Xyl, R^2 = Me **1**
R^1 = Me, R^2 = CO_2Me **2**

R^1 = Xyl, R^2 = Me **3**
R^1 = Me, R^2 = CO_2Me **4**

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

influencing the behaviour of the metal to which the dithiocarboxylate is attached.

2. Results and discussion

Ruthenium vinyl compounds of the form [Ru(CH=CHR)Cl(CO)$(PPh_3)_2$] [21] and [Ru(CH=CHR)Cl(CO)(BTD)$(PPh_3)_2$] (BTD = 2,1,3-benzothiadiazole) [22] are readily accessible through hydroruthenation 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 [Ru(CH=CHR)Cl(CO)(L)$(PPh_3)_2$] (L = BTD, thienyl-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, [Fe_2{μ-η^1:η^3-C(Me) = C(CS_2)C=N(Me)Xylyl}(μ-CO)(CO)$(Cp)_2$] (**3**), has been reported previously [16], whereas the analogue, [Fe_2{μ-η^1:η^3-C(CO_2Me) = C(CS_2)C=NMe_2}(μ-CO)(CO)$(Cp)_2$] (**4**), was prepared for this study, in a moderate yield. Compound **4** has a less pronounced steric profile due to the less bulky NMe_2 group. The presence of the CO_2Me ester group also renders **4** less soluble in common organic solvents compared to **3**. The ^{1}H 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 NMe_2 group and the latter to the CO_2Me ester unit. The spectrum was completed by two singlets at 5.12 and 5.25 ppm for the two cyclopentadienyl ligands.

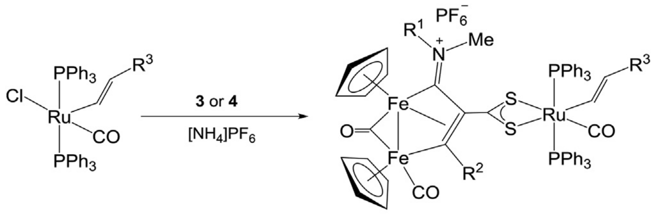
Reaction of [Fe_2{μ-η^1:η^3-C(Me) = C(CS_2)C=N(Me)(Xyl)}(μ-CO)(CO)$(Cp)_2$] (**3**) with coordinatively-unsaturated [Ru(CH=CHC_6H_4Me-4)Cl(CO)$(PPh_3)_2$] and NH_4PF_6 in dichloromethane led to an immediate darkening of the solution. While anaerobic conditions were used as a precaution, the dark brown 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}, attributed to the Ru-CO ligand. In contrast to the singlet at 30.9 ppm observed for the precursor, the $^{31}P\{^1H\}$ NMR spectrum of the product showed a pair of doublets at 37.2 and 39.6 ppm ($^2J_{PP} = 282$ Hz), exhibiting substantial roofing effects. This indicated the inequivalence of the two phosphorus nuclei due to the orientation of the diiron unit. The ^{1}H NMR spectrum displayed the expected features for the diiron unit with resonances attributed to the Cp ligands at 4.58 and 5.23 ppm as well as the methyl groups of the vinyliminium and xylyl substituents between 1.80 and 3.36 ppm. It was not possible to unequivocally assign the methyl protons of the tolyl substituent, however, the presence of the ruthenium-bound vinyl ligand was confirmed by resonances for the Hβ at 5.71 ppm ($^3J_{HH} = 16.0$ Hz). The resonance for the Hα proton was obscured by the aromatic protons of the triphenylphosphine ligands. A molecular ion at *m/z* 1330 in the electrospray mass spectrum (+ve mode) confirmed the overall composition for **5** as that shown in Scheme 2:

The analogous reaction of the new diiron compound, [Fe_2{μ-η^1:η^3-C(CO_2Me) = C(CS_2)C=NMe_2}(μ-CO)(CO)$(Cp)_2$] (**4**), with [Ru(CH=CHC_6H_4Me-4)Cl(CO)$(PPh_3)_2$] in the presence of NH_4PF_6 led to the formation of compound **6**. Similar features were observed as for **5** with the exception of a new feature at 1703 cm^{-1} in the solid state infrared spectrum for the C=O of the methyl ester group and additional resonances in the ^{1}H NMR spectrum corresponding to the CO_2Me and NMe_2 protons. The similarity in reactivity between **3** and **4**, despite their differing steric profiles, led to the more synthetically accessible **3** being used in the subsequent reactions.

The 1-pyrenyl vinyl complex, [Ru(CH=CHPyr-1)Cl(CO)$(PPh_3)_2$], was investigated partly due to the photophysical properties arising from the pyrenyl substituent. The closely-related precursor, [Ru(CH=CHPyr-1)Cl(CO)(BTD)$(PPh_3)_2$], reacts with CO to afford the 36-times more fluorescent complex, [Ru(CH=CHPyr-1)Cl$(CO)_2(PPh_3)_2$], allowing CO to be detected in amounts as low as 1 ppb [24a]. This behaviour is partly attributed to the quenching effect of the BTD ligand but the possible effects of adding a dithiocarboxylate ligand were unknown. Reaction of [Ru(CH=CHPyr-1)Cl(CO)$(PPh_3)_2$] with **3** in the presence of ammonium hexafluorophosphate led to isolation of [Fe_2{μ-η^1:η^3-C(Me) = C(CS_2{Ru(CH=CHPyr-1)(CO)$(PPh_3)_2$} C=N(Me)Xylyl](μ-CO)(CO)$(Cp)_2$]PF_6 (**7**). Similar spectroscopic data were observed as for compound **5** apart from new features due to the pyrenyl unit (doublet at 6.86 ppm, $^3J_{HH} = 8.1$ Hz) in the ^{1}H NMR spectrum. The overall formulation was supported 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, [Ru(CH=CHPyr-1)(S_2CNEt_2)(CO)$(PPh_3)_2$] (Fig. 1) [25]. Spectra were also recorded for the precursor [Ru(CH=CHPyr-1)Cl(CO)$(PPh_3)_2$] and 1-ethynylpyrene.

Excitation of dichloromethane solutions (100 μM) 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, [Ru(CH=CHPyr-1)Cl(CO)$(PPh_3)_2$], even exceeding that of 1-ethynylpyrene itself. It was also shown that, at this excitation wavelength, [Ru(CH=CHPyr-1)(S_2CNEt_2)(CO)$(PPh_3)_2$] produced a modest emission, almost half that displayed by **7**. This suggested a quenching of the fluorescence in [Ru(CH=CHPyr-1)Cl(CO)$(PPh_3)_2$] and [Ru(CH=CHPyr-1)(S_2CNEt_2)(CO)$(PPh_3)_2$] relative to the trimetallic complex containing the diiron core. Computational studies are



R^1 = Xyl, R^2 = Me, R^3 = C_6H_4Me-4 **5**
R^1 = Me, R^2 = CO_2Me, R^3 = C_6H_4Me-4 **6**
R^1 = Xyl, R^2 = Me, R^3 = Pyr-1 **7**

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

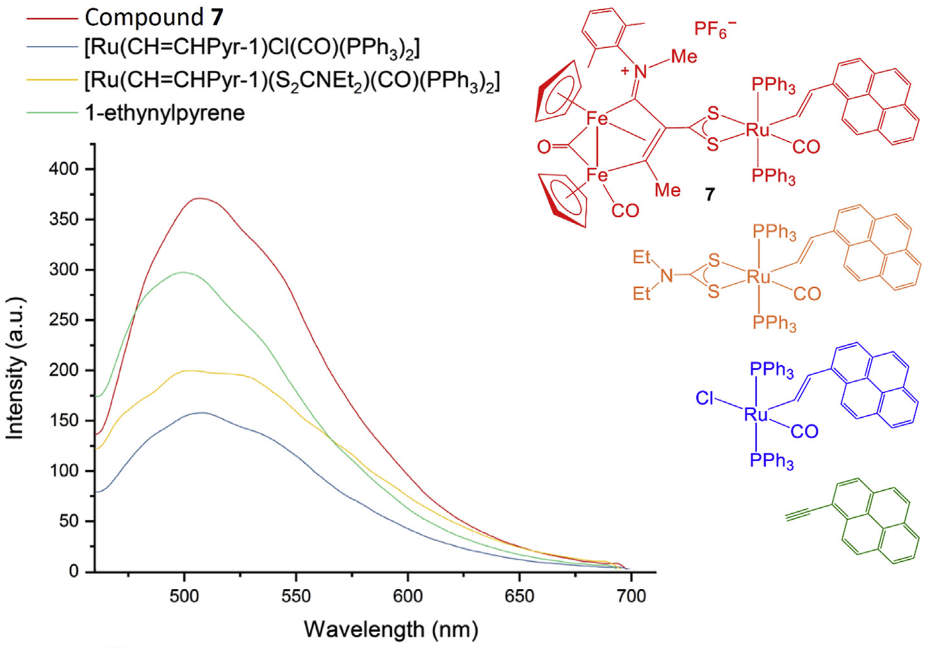


Fig. 1. Emission spectra of **7**, [Ru(CH=CHPyr-1)(S$_2$CNEt$_2$)(CO)(PPh$_3$)$_2$], [Ru(CH=CHPyr-1)Cl(CO)(PPh$_3$)$_2$] and 1-ethynylpyrene ($\lambda_{exc} = 450$ nm) in dichloromethane solution (100 μM).

currently being used to probe this phenomenon further.

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 Fe$_2$Ru compounds are formed from the reaction of zwitterionic diiron vinyliminium dithiocarboxylate units, $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(R^2)=C(CS_2)C=N(Me)R^1\}(\mu\text{-}CO)(CO)(Cp)_2]$ ($R^1 = Xyl$, $R^2 = Me$; $R^1 = Me$, $R^2 = CO_2Me$), acting as effective organometallic k^2S-ligands, with the versatile five-coordinate ruthenium vinyl precursors $[Ru(CH=CHR^3)Cl(CO)(PPh_3)_2]$ ($R^3 = C_6H_4Me\text{-}4$, 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, $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(Me)=C(CS_2\{Ru(CH=CHPyr\text{-}1)(CO)(PPh_3)_2\}C=N(Me)Xylyl](\mu\text{-}CO)(CO)(Cp)_2]PF_6$ (**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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