



Synthesis and characterization of redox active cyrhetrene–triazole click products



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ABSTRACT

We report the synthesis and characterization of two new cyclopentadienyl tricarbonyl rhenium(I) (cyrhetrene) complexes modified with a 1,4-disubstituted 1,2,3-triazole moiety. The two compounds, (η^5 -[4-phenyltriazol-1-yl]cyclopentadienyl) tricarbonyl rhenium(I), and (η^5 -[4-(4-aminophenyl)triazol-1-yl]cyclopentadienyl) tricarbonyl rhenium(I), were structurally characterized using ^1H and ^{13}C NMR, ATR-IR spectroscopy, UV–vis spectroscopy, mass spectrometry and X-ray crystallography where appropriate. The electrochemical behaviour of these two cyrhetrene–triazole complexes was explored using cyclic voltammetry, whereupon we observed that irreversible oxidation of the pendant 4-substituted-triazole moiety occurs before any electron transfer at the metal centre. This redox behaviour is in stark contrast to that of the analogous manganese(I) cymantrene–triazole derivatives, recently reported by our group.

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Introduction

The chemistry of half-sandwich complexes has been of recent interest in the literature [1], with complexes such as cyclopentadienyl tricarbonyl manganese(I) illustrating versatility with its introduction into a wide array of research areas, including exploiting the photo-labile carbonyl ligands [2], modification of the cyclopentadienyl moiety to generate new organometallic species [3], and even incorporating the cymantrene moiety into drug molecules [4].

Cyclopentadienyl tricarbonyl rhenium (I), **1**, is the next commercially available complex in the group 7 series (with the technetium analogue being radioactive) [5], that we wished to focus our attention upon. The applications of cyclopentadienyl rhenium(I) tricarbonyl, **1**, have recently been reported in a wide array of research areas, including examples that have shown the photolysis of CO ligands allowing the coordination of new ligands (CS_2 , PPh_3) [6], utilizing the CO ligands of **1** as non-natural labels for probing protein electrostatics [7], and modification of the cyclopentadienyl moiety to allow the formation of new cyrhetrene complexes with bidentate ligands, capable of forming new palladacycles [8].

Geiger has previously investigated the anodic behaviour of cyclopentadienyl tricarbonyl rhenium(I) **1**, and has shown that the half-cell potential for the cyclopentadienyl tricarbonyl rhenium(I) redox couple $+1/+2$ is +1.16 V vs the ferrocene/ferrocenium couple [9]. Interestingly, this oxidation is only partly reversible in CH_2Cl_2 (with [*n*-Bu₄N][B(C₆F₅)₄] as the supporting electrolyte) [10], due to the formation of the dimer, $[\text{Re}_2\text{Cp}_2(\text{CO})_6]^{2+}$, which shows an irreversible cathodic wave around *ca.* 0.55 V vs the ferrocene/ferrocenium couple. Furthermore, the use of $[\text{ReCp}(\text{CO})_3]^+$, **1**⁺, as a strong one-electron oxidant proved to be an excellent electron-transfer mediator in the case of coupling unactivated olefin substrates [11].

We herein report the synthesis and structural modification of cyclopentadienyl tricarbonyl rhenium(I) (cyrhetrene) complexes modified with a 1,4-disubstituted 1,2,3-triazole moiety *via* the copper-catalysed variant of the Huisgen 1,3-dipolar cycloaddition [12]. The copper catalysed azide–alkyne “click” reaction (CuAAC) has been extensively reviewed, and the use of this methodology would adhere to stringent criteria as set by Nobel laureate, Barry Sharpless [13]. Previous relevant examples of ‘click’ reactions within the coordination chemistry of metal complexes include the formation of various new transition-metal coordination complexes incorporating 2-pyridyl-1,2,3-triazole ligands as shown by Crowley and Schubert [14,15], Gladysz’s synthesis of permetalated rhenium–platinum alkyne–azide ‘click’ cycloadducts [3], and Sarkar’s incorporation of tripodal-triazole ligands into various transition-metal complexes [16]. Molina has reported click reactions applied

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to organometallic sandwich complexes such as ferrocene [17], whilst the work conducted by Astruc has shown dendrimers can be modified with metallocenes and organometallics via a click chemistry reaction [18].

In contrast to the behaviour of **1**, and the manganese(I) cymantrene–triazole derivatives reported previously by our group [19], the two new cyrhetrene–triazole complexes reported herein are found to exhibit redox active behaviour of the triazole ligand moiety that prevents them acting as metal-based electron-transfer mediators.

Results and discussion

Synthesis and structural characterization of 4-substituted cyrhetrene–triazole complexes

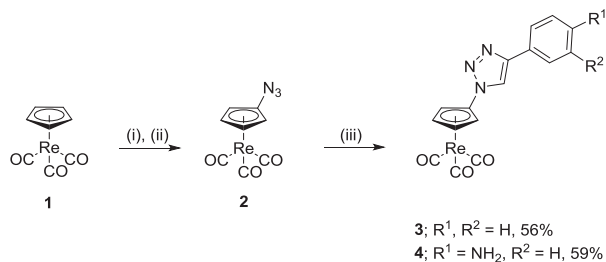
Following the procedure reported by Gladysz and co-workers, we report the synthesis of **2** as an off-white solid (after purification via flash column chromatography) in good yield {Scheme 1(i) and (ii)}. Confirmation of the structure of **2** was provided by ¹H, ¹³C NMR and IR spectroscopy {Supporting information Figs. 2 and 5b, (ν N=N azide/cm⁻¹) 2124} [3].

Our first attempt at the copper-catalysed azide/alkyne cycloaddition of **3** was achieved using the conditions we have previously reported for the manganese variant of cyrhetrene {Scheme 1, (iii)} [3,19,20]. Reassuringly, the transformation of **2** into **3** was complete in 8 h under these mild conditions; purification of **3** via silica gel flash column chromatography afforded **3** as a white crystalline solid in good yield and high purity (Scheme 1).

The ¹H NMR spectrum of **3** allows us to assign the key areas of the complex, confirming that our product was indeed the desired (η^5 -[4-phenyltriazol-1-yl]cyclopentadienyl tricarbonyl rhenium(I)) product. We observe a characteristic splitting of the five protons in the cyclopentadienyl ligand observed as a singlet in **1**, into two equivalent triplets integrating to two protons each for the cyclopentadienyl protons of complex **3** (chemical shifts in the range δ 5.6–6.5 ppm), formed by the introduction of a single triazole moiety. ¹H COSY NMR experiments have shown the aromatic protons of the phenyl substituent attached to the triazole moiety can couple to one another around the region of δ 7.3–8.0 ppm. The proton at the 5-position of the triazole moiety is observed as a characteristic singlet at δ 8.86 ppm (see Supporting information Fig. 3).

The UV–vis spectra of the parent molecule, [CpRe(CO)₃] **1**, can be directly compared with click-product **3**, and we show that in both cases, we observe MLCT bands around the region of 250–280 nm (see Supporting information, Fig. 6) [21].

The infra-red spectral data recorded for compounds **1–4**, with band assignments, are tabulated below {Table 1, See Supporting information Fig. 5(a)–(d) for IR spectra of compounds **1–4**}.



Scheme 1. Reagents and conditions: (i) **1** (1 equiv), *n*-BuLi (1 equiv), THF, –78 °C, 2 h; (ii) *p*-toluenesulfonylazide (1 equiv), THF, –78 °C – rt, 14 h. (iii) **2** (1 equiv), phenylacetylene (1 equiv for **3**), or 4-ethynylaniline (1 equiv for **4**), Cu(OAc)₂·H₂O (0.1 equiv), CH₃CN, 8 h.

Table 1
(ν /cm⁻¹) Bands for complexes **1–4**.

Complex	$\nu(\text{C}\equiv\text{O})/\text{cm}^{-1}$		$\nu(\text{C}=\text{C})$ (triazole)/cm ⁻¹
	Sym	Asym	
1	2014	1888	n/a
2	2019	1907	n/a
3	2021	1949, 1927, 1907 ^a	1530
4	2025	1939, 1908, 1897 ^a	1621, 1565, 1498

^a An extra band is observed in the asymmetric region for samples run in the solid state as a result of hindered rotation about the Re–Cp centroid and a subsequent descent in symmetry.

In the case of compounds **3** and **4** we observe both symmetric and asymmetric (C≡O) stretches at ~2020 cm⁻¹ and 1900–1950 cm⁻¹ respectively [9,22], in addition to characteristic C=C stretches of the triazole group in the region of 1500–1600 cm⁻¹ [19,23].

Single crystals of **3** were grown by diffusion of petroleum ether into a saturated CH₂Cl₂ solution of the compound at room temperature and a X-ray crystal structure obtained (Fig. 1, bond lengths and angles detailed in Tables S1 and S2). The structure is comparable to our previously reported manganese analogue [19] with two molecules in the asymmetric unit related by a non-crystallographic pseudo-inversion centre. The cyclopentadienyl–triazole–phenyl rings of each molecule are approximately co-planar (the triazole ring is twisted by ca. 12° from the co-planar cyclopentadienyl and phenyl rings), with the aromatic ring systems of each molecule approximately parallel, separated by ca. 3.5 Å; together this suggests the possibility of not only a conjugated π -system in each molecule but also a degree of π – π interaction between the molecules. Compound **4** exhibits the same crystallographic behaviour as its manganese analogue [19], and resisted all our exhaustive attempts to grow single crystals suitable for X-ray crystallographic characterisation (Table 2).

Electrochemical characterization

We first investigated the electrochemical properties of **3** (2 mM), in dichloromethane containing 0.1 M [ⁿBu₄N][B(C₆F₅)₄] as supporting electrolyte, using cyclic voltammetry (CV, Fig. 2(a) and (b)).

The oxidation of **3** shows only a single, irreversible oxidation wave at ca. 1.20 V vs ferrocene at all scan rates studied. The oxidation wave is stable over repeat voltammetric cycles at a gold macroelectrode, whilst fouling and passivation of the working electrode was observed at platinum and glassy carbon working electrodes. By comparison with the voltammetry observed for the parent cyrhetrene, **1** [9], the observed voltammetry of **4** is not characteristic of the oxidation of the rhenium metal centre, and is instead likely due to the oxidation of the pendant 4-substituted triazole moiety [19]. This finding contrasts with our earlier studies of the triazole-derivatised cymantrene analogue, (η^5 -[4-phenyltriazol-1-yl]cyclopentadienyl tricarbonyl manganese(I)), where oxidation of the manganese centre occurred before any oxidation of the triazole ligand, and likely reflects the difference in the relative redox potentials of cymantrene and cyrhetrene, the latter of which is oxidised at more positive potentials [19].

The voltammetric behaviour of **4** recorded under identical conditions as described above is shown in Fig. 3 and Fig. S7.

Upon scanning in an oxidative direction an irreversible oxidation wave is observed at ca. 0.64 V vs ferrocene. No oxidation wave corresponding to oxidation of the Re metal centre is observed beyond this first oxidation peak up to the limit of the solvent window. Instead the voltammogram exhibits a rectangular wave

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