New Families of Coordinated Carbon: Oxidative Coupling and Cross-coupling of a Transition Metal Butadiynyl Complex to Bimetallic M–C≡CC≡CC≡CC≡C–M and M–C≡CC≡CC≡C–M Adducts

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$[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}C)(Ph_3P)(ON)Re(\eta^5\text{-}C_5Me_5)]$ and $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}CC{\equiv}C)(Ph_3P)(ON)Re(\eta^5\text{-}C_5Me_5)]$, which contain the longest chains of elemental carbon tethered between two transition metals to date, are prepared by $Cu(OAc)_2$ coupling of $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}CH)]$, or cross-coupling with the corresponding ethynyl complex; unusual spectroscopic and redox properties are described.

Compounds in which unsaturated chains of elemental carbon span two metals, $L_nMC_xM'L'_{n'}$,[1] constitute one of the most fundamental classes of one-dimensional molecular wires.[2] Particular attention is being focused on the synthesis of adducts of longer carbon chains, which are expected to exhibit a number of interesting properties. Several species with C_4 linkages have been isolated,[3,4] and we recently prepared the first complex with a C_5 chain.[5] In this communication, we report oxidative coupling and cross-coupling reactions that give adducts with C_6 and C_8 chains—the longest characterized to date‡—and preliminary data on their spectroscopic and redox properties.

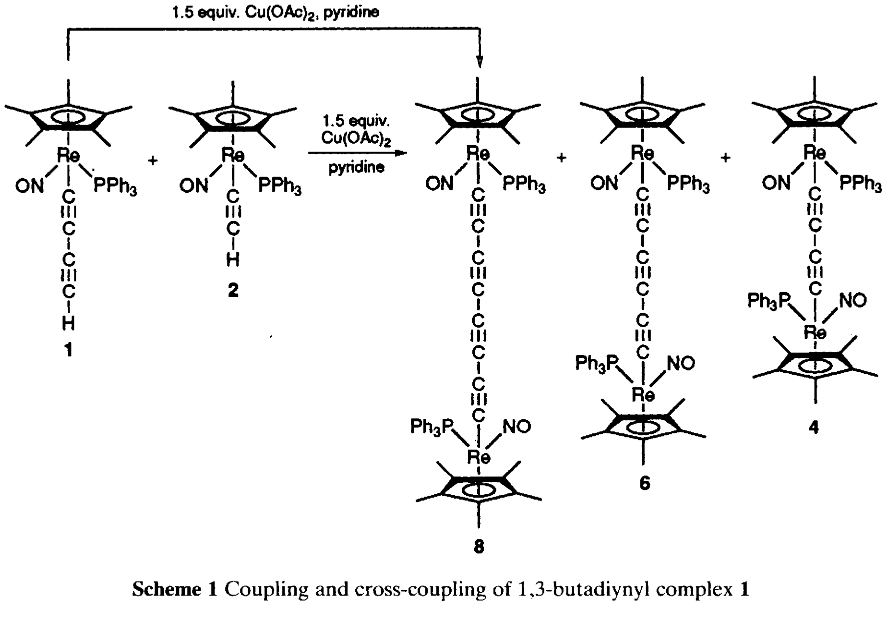
The chiral, racemic rhenium butadiynyl or C_4H complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}CH)]$ **1**[5] and $Cu(OAc)_2$ (1.5 equiv.) were combined in pyridine at 80 °C (Scheme 1). Similar conditions were previously used to convert the corresponding C_2H complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CH)]$ **2**[7] to the μ-butadiynediyl or C_4 complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}C)(Ph_3P)(ON)Re(\eta^5\text{-}C_5Me_5)]$ **4**.[4a] Workup gave the air-stable, orange μ-octatetraynediyl or C_8 complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}C)(Ph_3P)(ON)Re(\eta^5\text{-}C_5Me_5)]$ **8** in 70% yield.

A 50:50 mixture of C_4H and C_2H complexes **1** and **2** was treated similarly. Subsequent silica gel column chromatography easily separated the desired cross-coupling product, μ-hexatriynediyl or C_6 complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(C{\equiv}CC{\equiv}CC{\equiv}C)(Ph_3P)(ON)Re(\eta^5\text{-}C_5Me_5)]$ (**6**, 44%), from **4** (14%) and **8** (15%). Complexes **6** and **8** gave correct microanalyses and mass spectral parent ions, and were stable in the solid state below 175 °C.§ Low temperature ^{13}C and ^{31}P NMR spectra of **6** showed two closely spaced sets of resonances (50:50), which were assigned to *meso* and (±) diastereoisomers. Complex **8** was similarly assumed to be a 50:50 mixture of diastereoisomers, but gave a single set of NMR resonances under all conditions assayed, presumably due to the greater separation of the stereocentres.

We found earlier that the diastereoisomers of **4** are separable by crystallization.[4a] However, attempts to enrich samples of **6** in one diastereoisomer (including analytical HPLC) have been unsuccessful to date. Importantly, each diastereoisomer of **4** gave identical IR, ESR, UV–VIS and CV data.[4] Thus, **6** and **8** were characterized as mixtures. Several conspicuous trends were apparent.

Perhaps most strikingly, **4**, **6** and **8** exhibited strong UV maxima that shifted to longer wavelengths and intensified as the carbon chain lengths increased [Fig. 1; λ/nm (ε/dm^3 mol^{-1} cm^{-1}): **4**, 350 (17000); **6**, 328 (39000), 354 (37000); **8**, 360 (67000), 390 (60000)]. These were red-shifted ≥35 nm from those of analogous methylated polyalkynes, and were 100–500 times more intense.[8] Also, the IR ν_{NO} values of **4**, **6** and **8** increased monotonically (ν/cm^{-1}, CH_2Cl_2: 1623, 1640, 1648), indicating reduced backbonding into the nitrosyl ligand. The IR $\nu_{C\equiv C}$ bands showed regular increases in frequency and intensity (1964 w, 2061 m, 2108/1956 s/m cm^{-1}). The ^{13}C NMR signals shifted progressively downfield as the $^2J_{CP}$ values increased (**4**/**6**/**8**,¶ $^2H_8$-THF: 96.6/104.2–103.3/109.7 d/d/d, $^2J_{CP}$ 12.7/15.7–16.0/16.9 Hz; Re$C{\equiv}C$ 116.4/114.3–113.9/113.3 s/s/s).

The redox properties of **4**, **6** and **8** were probed by CV. As shown in Fig. 2, each compound exhibited two one-electron oxidations with high degrees of chemical reversibility (**4** > **6** > **8**) at 100 mV s^{-1} in CH_2Cl_2 at room temperature ($E_{p,a}$/V 0.15,



Scheme 1 Coupling and cross-coupling of 1,3-butadiynyl complex **1**

0.68/0.24, 0.62/0.37, 0.66; $E_{p,c}$/V 0.06, 0.59/0.17, 0.55/0.30, 0.59; E^0/V 0.11, 0.64/0.20, 0.58/0.34, 0.62; ΔE/mV 90, 90/70, 70/70, 70). Reversibility improved at −45 or −80 °C, and no reductions were observed at the cathodic limit (−1.0 V). Under analogous conditions in MeCN, only **4** gave reversible oxidations.[4b] Hence, the cation radicals become progressively less stable as the carbon chains and distances between the bulky rhenium termini lengthen. We speculate that the diminished congestion facilitates coupling or solvent reactions.

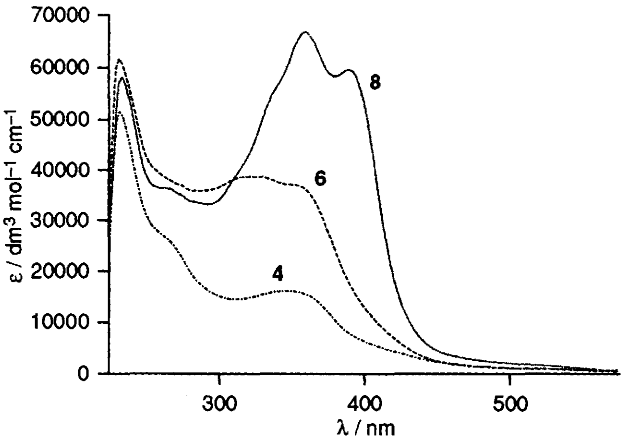


Fig. 1 UV-VIS spectra of **4**, **6** and **8** (1.6–3.3×10^{-5} mol dm^{-3} in CH_2Cl_2 at ambient temperature)

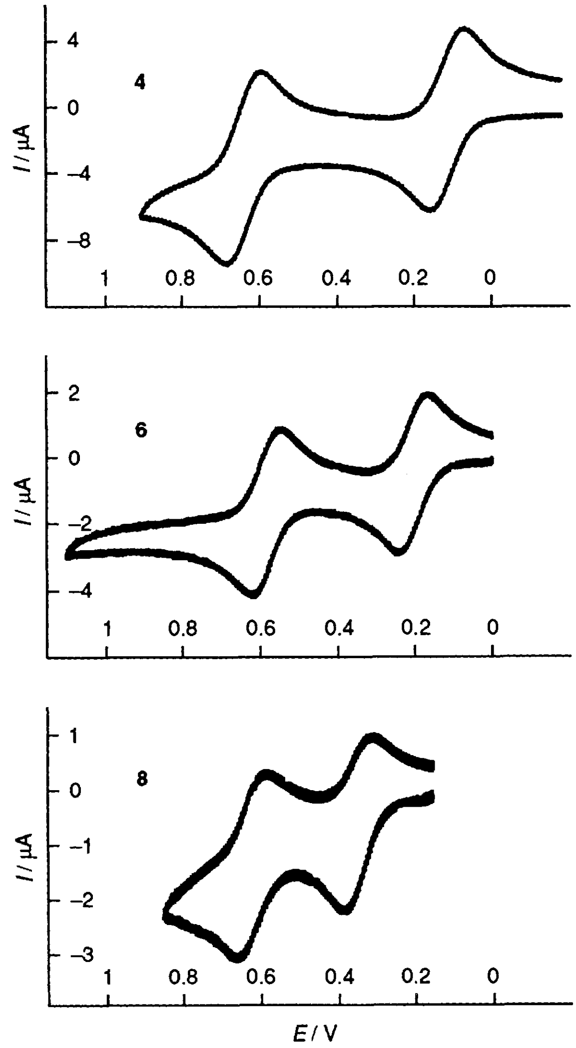


Fig. 2 Cyclic voltammograms of **4**, **6** and **8** (7–8×10^{-5} mol dm^{-3} in 0.1 mol dm^{-3} $Bu_4N^+BF_4^-$–CH_2Cl_2 at ambient temperature; Pt working and counter electrodes, ferrocene standard, potential *vs.* Ag wire pseudoreference; scan rate 100 mV s^{-1})

Curiously, the first oxidation becomes thermodynamically less favourable with longer carbon chains. In contrast, Hückel MO theory predicts increased HOMO energies for higher organic poly(enes) and poly(ynes). This suggests that the HOMOs are predominantly metal centred, in accord with PES studies of ethynyl and butadiynyl complexes.[9] One rationale would be that repulsive interactions between occupied orbitals on each metal are enhanced in shorter chains, giving higher ionization potentials and facilitating oxidation.

In summary, we have established efficient routes to bimetallic C_6 and C_8 complexes consisting of C≡C linkages—robust species that exhibit unusual spectroscopic and redox properties. Higher homologues will probably be available by simple extensions of our methodology. Such efforts, and further characterization of the oxidation products of **6** and **8**, will be the focus of future reports.

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Footnotes

† Formerly Monika Jaeger.

‡ Compounds containing C_6 and C_8 chains may have been prepared in 1970, but were only partially characterized.[6]

§ Full details of the preparation and characterization of **6** and **8** have been furnished to the referees of this communication and are available from the authors upon request.

¶ Data for **4** are from the $^{13}C_4$ labelled *meso* diastereoisomer.[4a] The ranges given for **6** correspond to both diastereoisomers. Other ^{13}C NMR data: **6**, 65.7–65.2 brs (ReC≡C*C*); **8**, 66.6 d, $^4J_{CP}$ 2.72 Hz and 64.5 s (ReC≡CC≡*C*).

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