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Nanoscale molecular organometallo-wires containing diruthenium cores

Ken-Tsung Wong,[a,b] Jean-Marie Lehn,*[a] Shie-Ming Peng[b] and Gene-Hsiang Lee[b]

[a] *ISIS, Université Louis Pasteur, 4, rue Blaise Pascal, Strasbourg 67000, France. E-mail: lehn@chimie.u-strasbg.fr*
[b] *Department of Chemistry, National Taiwan University, Taipei 106, Taiwan, R.O.C.*

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A conjugated linear molecule 3 of nanometric size containing two diruthenium units as redox active linkers has been synthesised; its electrochemical properties indicate molecular wire-type delocalization.

Linear systems with extended π-conjugation are of interest as candidates for 'molecular wires', which might operate as a connector permitting electron flow to occur between different elements of a molecular electronic system.[1] Among different approaches to construct such entities, conjugated organic chains capped with redox-active metals as their terminal groups allow electron transfer along the backbone.[2] In several systems, a significant interaction between terminal groups has been revealed by electrochemical data. Hybrid systems incorporating redox-active metal centers in the conjugated organic backbone, could be useful models for potential molecular wires. For example, a Ru(II) containing bis(acetylide) bridge (–C≡C–Ru–C≡C–) has been found to enhance the ground state electronic communication between terminal ferrocenyl groups.[3] Electrons delocalize through the Ru center over the whole system more efficiently compared to the all-carbon butadiynyl bridge. It is well documented that there is a barrier to efficient charge transfer between the redox-active terminal groups if a d^8 metal such as Pd is used as a bridging unit inside the conjugated chain.[4] Proper selection of the metal center linkage may allow the enhancement of the ground state electron delocalization along the π-conjugated organic system. Along these lines, it is of interest to investigate the effect of introducing units containing metal–metal bonds into conjugated chains. Organic conjugated oligomers linked by Pt–Pt single bonds have been reported.[5] We describe herein some of our work on a new type of carbon-rich molecular wire incorporating a redox-active diruthenium unit as linker.

Treatment of 1,4-bistrimethylsilylbuta-1,3-diyne with 1 equiv. of MeLi/LiBr in THF at room temperature yielded selectively the monolithium acetylide.[6] To the solution obtained, a green powder of $Ru_2(dpf)_4Cl$ (dpf = *N,N′*-diphenylformamidine, 0.045 equiv.) was added under argon. The connection of the bisacetylide to the Ru–Ru core was completed in 3 days. Subsequent oxidation with air gave **1** which was isolated by chromatography on Al_2O_3 as a reddish-black solid in 70% yield. Under carefully controlled conditions, removal of one trimethylsilyl group from **1** with K_2CO_3 in THF–MeOH (3:1) in 3 h at 0 °C afforded **2** (51%), which was found to decompose slowly even when stored at −4 °C. However, in the presence of CuCl in pyridine,[7] homodimerization of the terminal acetylene of **2** was accomplished, giving **3** in 76% yield as a black solid by chromatographic purification (Scheme 1).[8]

The crystal structure of complex **3**[8,9] revealed a unit cell containing four toluene molecules and two hexane molecules; two of the toluene molecules have their methyl group directed towards the main carbon chain and fill the empty space between the two Ru–Ru cores.[9] The crystal structure shows that **3** is a bent linear molecule of total length up to *ca.* 3.5 nm [C(9) to C(9′)] (Fig. 1). The diruthenium core bond lengths and angles are comparable to those of $Ru_2(dpf)_4(–C≡CPh)_2$,[10] with a Ru–Ru distance of 2.5586 Å, which lies in the range of a single Ru–Ru σ bond. Complex **3** possesses two different Ru–C distances, Ru^{III}(1)–C(4) 1.939(12) Å, Ru^{III}(2)–C(5) 1.977 Å, both of which are shorter than the Ru^{II}–C bond (2.078 Å) in Fc–C≡C–$Ru(dppm)_2$C≡C–Fc (Fc = ferrocenyl),[3] probably as a result of the higher oxidation state of the Ru center. The molecular structure deviates significantly from linearity with a Ru(2)–Ru(1)–C(4) bond angle of 163.1°. The Ru–Ru coordination is

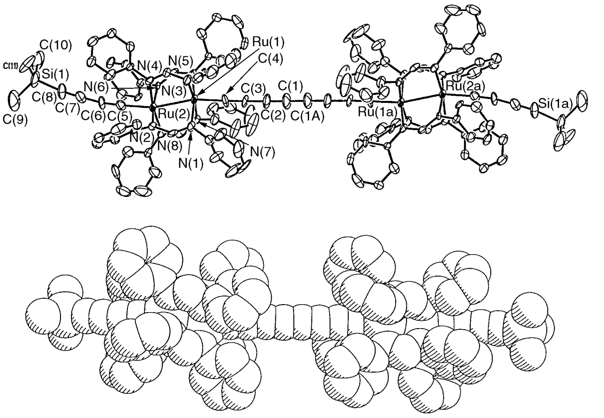
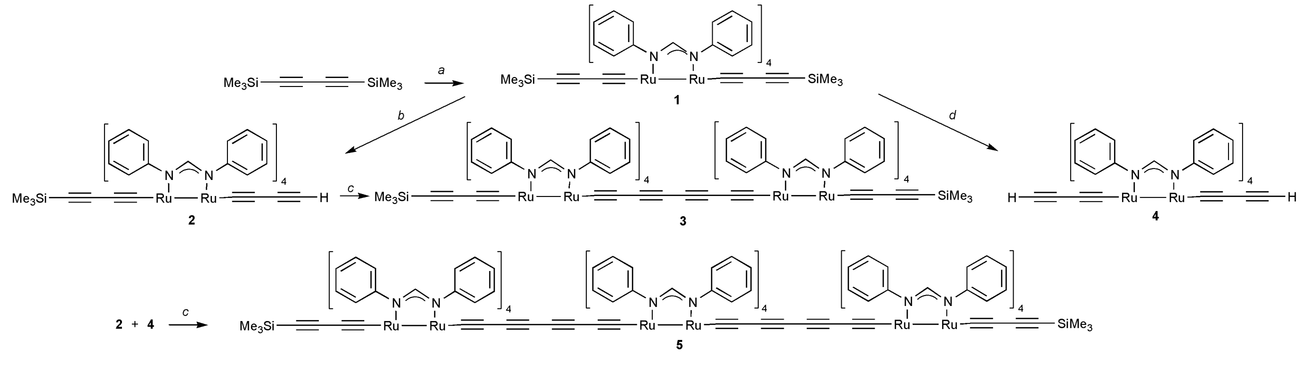


Fig. 1 Crystal structure of compound **3**: (top) ORTEP representation; thermal ellipsoids drawn at 50% probability; (bottom) space-filling representation.



Scheme 1 *Reagents and conditions*: (a) 1. MeLi/LiBr 2. $Ru_2(dpf)_4Cl$; (b) K_2CO_3, THF–MeOH (3:1), 0 °C; (c) CuCl, pyridine, O_2; (d) K_2CO_3, THF–MeOH (3:1), room temperature.

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basically octahedral, four equatorial dpf ligands with eight phenyl rings extending helically over the rod-like carbon-rich chain. A space-filling representation (Fig. 1, bottom) shows that these phenyl groups cover up the conjugated core, thus providing an efficient insulating sheath protecting the wire type chain.

Cyclic voltammetry measurements on **1** and **3** were performed in 0.1 M NBu_4ClO_4 (TBAP) in CH_2Cl_2 using an Ag/$AgNO_3$ reference (Fig. 2). Complex **1** undergoes two quasi-reversible reductions at $E_{1/2} = -1.68$ V ($\Delta E = 0.18$ V) and -0.74 V ($\Delta E = 0.12$ V) and one irreversible oxidation at $E_{pc} = 0.72$ V. Complex **3** also shows two reductions at the same potentials as **1**, but two irreversible oxidations were observed at $E_{cp} = 0.50$ and 0.81 V. The conjugation through the carbon rod in **3** makes the first oxidation more accessible, and the large ΔE (310 mV) demonstrates that the first radical cation is efficiently delocalized over the system. However, **3** is not stable during the cyclic voltammetry experiment, the third cycle indicating that the reduction at $E_{1/2} = -0.74$ V becomes irreversible.

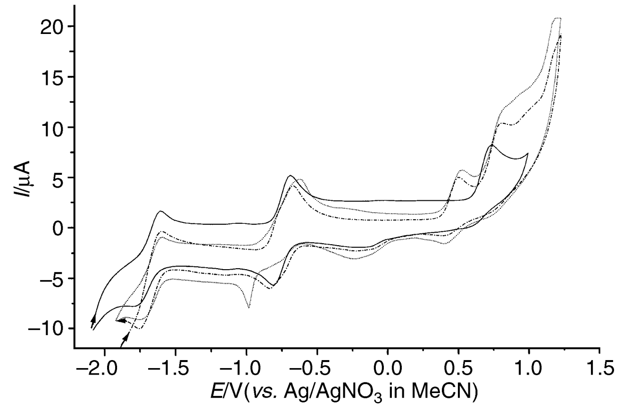

Fig. 2 Cyclic voltammograms of **1** (solid, scan rate 0.15 V s^{-1}) and **3** (first cycle, dash-dot; third cycle, dot, scan rate 0.1 V s^{-1}) in CH_2Cl_2, 0.1 M TBAP at 25 °C (*E*/V *vs.* Ag/$AgNO_3$ 0.1 M in MeCN).

In order to synthesize a longer homologue of **3**, freshly prepared complex **4** was condensed with **2** (ratio: **4**:**2** = 1:6) in the presence of a catalytic amount of CuCl in pyridine to afford **3** (58%) and **5** (46%) (Scheme 1). Attempts to characterize **5** by FAB-MS were not successful. However, the ^{1}H NMR spectrum shows two partially overlapping singlets at δ 8.23 and 8.22 with integration ratio = 1:2, which may be attributed respectively to the four protons attached to the formamidinate carbon of the internal Ru–Ru core, and to the eight protons of the external Ru–Ru units. Species **5** has an overall length of *ca.* 45–50 Å. Further characterization is in progress.

In conclusion, complex **3** represents a new type of conjugated molecular chain having a total length of *ca.* 3.5 nm, in which a Ru–Ru bond is inserted as a redox-active connector. The ground state electronic delocalization was confirmed by the electrochemical properties. This represents an approach to the construction of molecular wire type devices incorporating dimetallic centers. It extends our earlier work on the design[11] and transmembrane electron transfer properties[12] of purely organic entities to the metallo-wire domain. Further efforts are directed in particular towards derivatives of push–pull wire type.

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8 *Experimentals*: anhydrous LiBr (3.82 g, 44.0 mmol) and 1,4-bis-(trimethylsilyl)buta-1,3-diyne (8.55 g, 44.0 mmol) were dissolved in THF (250 mL). This solution was treated dropwise with MeLi (27.5 ml, 1.6 M in hexane, 44.0 mmol) at room temperature and stirred under argon for 3 h. Well ground green powder of $Ru(dpf)_4Cl$ (2.04 g, 2.0 mmol) was added in one portion. The mixture was stirred at room temperature for 3 days, during which time it changed from yellowish green to reddish purple. The latter solution was then exposed to air and stirred for 1 h. The mixture was concentrated *in vacuo* and the residue was chromatographed twice on neutral Al_2O_3, eluting with CH_2Cl_2–hexane (50/50). The red purple band was collected and concentrated to afford the adduct **1** as a reddish black solid (1.71 g, 70%). IR (KBr, cm^{-1}) 2215, 1486, 1209. δ_H($CDCl_3$, 400 MHz) 0.12 (s, 18H), 6.72–6.75 (m, 8H), 7.13–7.19 (m, 12H), 8.21 (s, 4H). δ_C($CDCl_3$, 100 MHz) 0.93, 47.47, 78.61, 89.93, 119.51, 125.23, 125.74, 128.05, 154.95, 168.67. FAB-MS: 1226.4, 1105.3, 1030.3, 983.3, Anal. Calc. for $C_{66}H_{62}N_8Ru_2Si_2$: C, 64.68; H, 5.10; N, 9.14. Found C, 64.75; H, 5.21; N, 9.12%.

Compound **1** (0.5 g) was dissolved in THF–MeOH (21 ml:7 ml) and K_2CO_3 (200 mg) was added to this red–purple solution. The mixture was stirred at 0 °C for 3 h and the solvent then was removed *in vacuo*. The resulting residue was chromatographed on neutral Al_2O_3, eluting with CH_2Cl_2–hexane (40/60) to afford compound **2** (240 mg, 51%) which is not very stable at room temperature. IR (KBr, cm^{-1}) 3298, 2118, 2059, 1486, 1212. δ_H($CDCl_3$, 400 MHz) 0.13 (s, 9H), 6.74–6.78 (m, 8H), 7.14–7.20 (m, 12H), 8.22 (s, 4H), δ_C($CDCl_3$, 100 MHz) 0.91, 44.29, 46.68, 61.88, 68.66, 78.70, 89.89, 117.08, 119.57, 125.21, 125.28, 125.76, 125.81, 127.97, 128.05, 154.86, 154.95, 168.62. FAB-MS: 1154.4, 1105.4, 984.3.

Compound **2** (115.4 mg, 0.1 mmol) dissolved in pyridine (15 mL) was treated with CuCl (3.6 mg, 0.036 mmol). The mixture was stirred under oxygen for 2 h. The solvent was removed *in vacuo* and the residue chromatographed on neutral Al_2O_3 eluting with CH_2Cl_2–hexane (60/40) to afford compound **3** (93.1 mg, 76%). Single crystals suitable for structure determination were grown by carefully layering hexane above a toluene solution of **3**. IR (KBr, cm^{-1}) 2118, 1488, 1212. δ_H($CDCl_3$, 400 MHz) 0.12 (s, 18H), 6.73–6.75 (m, 16H), 7.15–7.21 (m, 24H), 8.21 (s, 8H), δ_C($CDCl_3$, 100 MHz) 0.91, 47.11, 49.16, 61.06, 63.27, 78.78, 89.86, 119.75, 120.66, 125.20, 125.23, 125.76, 125.82, 128.06, 128.13, 154.93, 155.09. 168.75.

9 *Crystal data* for **3**: $C_{166}H_{166}N_{16}Ru_4Si_2$, $M = 2845.61$, monoclinic, space group $C2/c$, $a = 46.3326(12)$, $b = 13.6260(4)$, $c = 27.5394(7)$ Å, $\beta = 118.194(1)°$, $U = 153323.5(7)$ Å^3, $Z = 4$, $D_c = 1.233$ Mg m^{-3}, $\mu = 0.457$ mm^{-1}, $F(000) = 5912$, $T = 150$ K, wavelength 0.71073 Å, crystal size 0.35 × 0.08 × 0.04 mm, θ_{max} 25.00°, 28842 reflections measured, Final R [$I > 2\sigma(I)$] = 0.1122. CCDC 182/1813. See http://www.rsc.org/suppdata/cc/b0/b005679k/ for crystallographic files in .cif format.

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