

Synthesis of a Ferrocenyl-Capped Ruthenium(II) Bis(acetylide) Complex: A Model for Organometallic Molecular Wires

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Summary: *trans*-Ru(dppm)₂(C≡CFc)₂ (**1**, dppm = Ph₂PCH₂PPh₂, Fc = ferrocenyl) was prepared by the CuI-catalyzed coupling of FcC≡CSn(*n*-Bu)₃ with *cis*-RuCl₂(dppm)₂. We have demonstrated by cyclic voltammetry that the ruthenium(II) bis(acetylide) bridge, -C≡C-Ru(dppm)₂-C≡C-, of **1** enhances the ground-state electronic communication between terminal ferrocenyl groups compared to the all-carbon butadiynyl bridge of 1,4-diferrocenylbutadiyne, Fc-C≡C-C≡C-Fc.

Polymers and oligomers containing -C≡C- bonds are of interest as candidates for "molecular wires" because of the possibility of charge transfer along a conjugated backbone.^{1,2} Oligoacetylide chains have been stabilized with redox-active organometallic terminal groups, and charge transfer along such capped chains has been probed by cyclic voltammetry.^{3–5} In several such systems, a significant interaction between terminal groups separated by acetylide bridges up to 11 carbon atoms in length has been reported.^{3–5} We are interested in the effect a metal bis(acetylide) bridge has on the electronic interaction between the capping groups. Molecules of this type would be useful models for conducting polymers that have metal centers incorporated into their backbones. Although a number of metal-containing conjugated polymers are known,^{6–30} there are very few reports of conductivities in these materials.^{8,17} A series of platinum bis(acetylides) was

prepared recently with terminal redox-active ruthenium and osmium bipyridyl groups.³¹ In these complexes, cyclic voltammetry showed that the terminal groups remained electronically isolated despite the platinum bis(acetylide) bridge. In this communication, we report the first example of a metal bis(acetylide) which allows a significant ground-state interaction between terminal redox-active groups.

Complex **1** was synthesized by the reaction of *cis*-RuCl₂(dppm)₂ (dppm = Ph₂PCH₂PPh₂) and FcC≡CSn(*n*-Bu)₃ (Fc = ferrocenyl)^{32,33} in 1,2-dichloroethane in the presence of catalytic copper(I) iodide, Scheme 1.³⁴

When the reaction is carried out in methylene chloride at reflux, bis(acetylide) **1**, the previously reported mono(acetylide) *trans*-RuCl(dppm)₂(C≡CFc) (**2**),³⁵ and *trans*-RuCl₂(dppm)₂ are all identified as products by ¹H and ³¹P NMR spectroscopy. It is likely that in methylene chloride solution at reflux, *cis*-RuCl₂(dppm)₂ not only reacts to form acetylides **1** and **2** but also photochemically isomerizes to the less reactive *trans* form.³⁶ To prevent isomerization, the higher boiling 1,2-dichloroethane was used as the solvent and **1** was obtained in higher yield. Complex **1** was recrystallized from a methylene chloride–diethyl ether two-layered system

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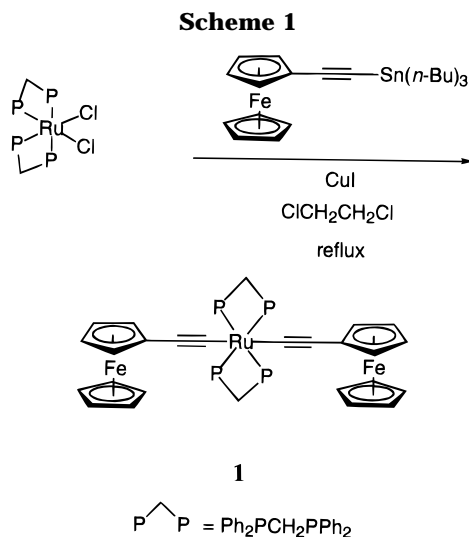
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to give orange rodlike crystals whose structure was determined by single-crystal X-ray diffraction (Figure 1).³⁷ The structure shows that the ruthenium center is in an octahedral environment and that the ferrocenylacetylide ligands are in a trans orientation, with bond lengths and angles similar to those reported for related metal acetylide complexes.^{35,38,39} The ruthenium-containing carbon chain connecting the two ferrocenyl centers is only slightly distorted from linear, with Ru–C≡C bond angles of 174.9° and C≡C–Cp angles of 173.6° (Figure 1).

(33) Preparation of $\text{FcC}\equiv\text{CSn}(n\text{-Bu})_3$: To ethynylferrocene (353 mg, 1.68 mmol) in THF solution (20 mL) at -78°C was added *n*-butyllithium (1.10 mL, 1.6 M in hexanes). The solution was stirred for a period of 2 h, after which time tributyltin chloride (0.48 mL, 1.77 mmol) was added and the dry ice–acetone bath removed. The mixture was stirred overnight at room temperature. Ether (100 mL) was then added, and the mixture was washed with water (4×75 mL) before being dried over anhydrous MgSO_4 and filtered. The filtrate was then reduced to a red-black oil by rotary evaporation, and purified by vacuum distillation. Yield = 0.626 g (75%). ^1H NMR (400 MHz, CDCl_3): δ 0.92 (t, 9H), 0.99 (m, 6H), 1.37 (m, 6H), 1.61 (m, 6H), 4.12 (t, 2H, $J_{\text{HH}} = 1.9$ Hz), 4.16 (s, 5H), 4.39 (t, 2H, $J_{\text{HH}} = 1.9$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, CDCl_3): δ 108.5, 88.9, 71.7, 70.0, 68.3, 66.1, 29.0, 27.6, 14.8, 11.2. Anal. Calcd for $\text{C}_{24}\text{H}_{36}\text{FeSn}$: C, 57.76; H, 7.27. Found: C, 57.81; H, 7.19%.

(34) Preparation of *trans*- $\text{Ru}(\text{dppm})_2(\text{C}\equiv\text{CFC})_2$ (**1**): To a solution of $\text{FcC}\equiv\text{CSn}(n\text{-Bu})_3$ (250 mg, 0.50 mmol) in 1,2-dichloroethane (20 mL) was added solid *cis*- $\text{RuCl}_2(\text{dppm})_2$ (188 mg, 0.20 mmol) and copper(I) iodide (10 mg, 0.05 mmol). The mixture was heated at reflux with stirring for 2 h. After this period, the mixture was cooled to 0°C and filtered through Celite 545. The volume of the filtrate was then reduced *in vacuo* to approximately 3 mL, and the product was afforded as a fine orange powder by addition of ether. This powder was isolated by filtration and washed with ether (2×20 mL). Yield = 93 mg (36%). ^1H NMR (400 MHz, CDCl_3): δ 3.46 (t, 4H, C_5H_4), 3.67 (s, 10H, Cp), 3.76 (t, 4H, C_5H_4), 4.85 (t, 4H, CH_2 , $J_{\text{HP}} = 3.8$ Hz), 7.1–7.6 (m, 40H, phenyl). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 136.4 (m), 133.6 (t), 128.9 (s), 127.3 (s), 122.0 (m), 108.8 (s), 68.8 (s), 68.6 (s), 65.8 (s), 65.3 (s), 52.3 (t). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, CDCl_3): δ -5.79 (s, 4P). IR (KBr): 2067 cm^{-1} . UV–vis (CH_2Cl_2): 434 nm, ϵ 2000 $\text{M}^{-1}\text{cm}^{-1}$ (shoulder); 334 nm, ϵ 20 000 $\text{M}^{-1}\text{cm}^{-1}$. Mp 245–255 $^\circ\text{C}$ (dec). Anal. Calcd for $\text{C}_{74}\text{H}_{62}\text{Fe}_2\text{P}_4\text{Ru}$: C, 69.01; H, 4.85. Found: C, 68.63; H, 4.76.

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(37) Crystallographic data for **1**: $\text{C}_{74}\text{H}_{62}\text{Fe}_2\text{P}_4\text{Ru}$, orthorhombic, space group *Pccn*; $a = 26.841(3)$ Å, $b = 25.088(3)$ Å, $c = 9.749(2)$ Å; $V = 6564.8(7)$ Å³; $Z = 4$; ρ (calcd) = 1.303 g cm^{-3} . Primary atoms were located using direct methods (SHELXS-86). Refinement was conducted using a full-matrix calculation (SHELXS-93). A total of 3056 reflections were measured at 293 K using Mo $K\alpha$ radiation on an Enraf-Nonius Diffractis 586 diffractometer. $R1 = 0.0394$, $wR2 = 0.0785$.

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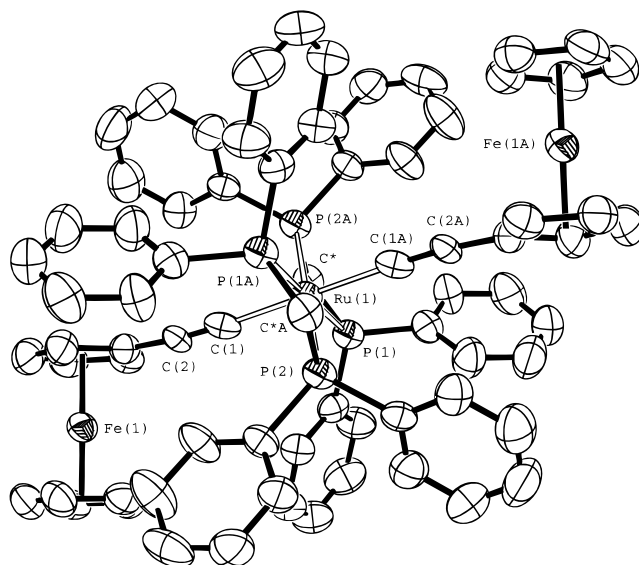


Figure 1. ORTEP diagram of the solid-state structure of **1** (50% probability ellipsoids shown). Hydrogen atoms are omitted for clarity. Key bond lengths (Å) and angles (deg): Ru(1)–C(1) = 2.078(7); C(1)–C(2) = 1.184(8); C(2)–C(11) = 1.434(9); Ru(1)–P(1) = 2.320(2); Ru(1)–P(2) = 2.336(2); Ru(1)–C(1)–C(2) = 174.9(5); C(1)–C(2)–C(11) = 173.6(6); Ru(1)–P(1)–C* = 94.1(2); P(1)–C*–P(2A) = 94.2(3); P(1)–Ru(1)–P(2) = 108.72(6).

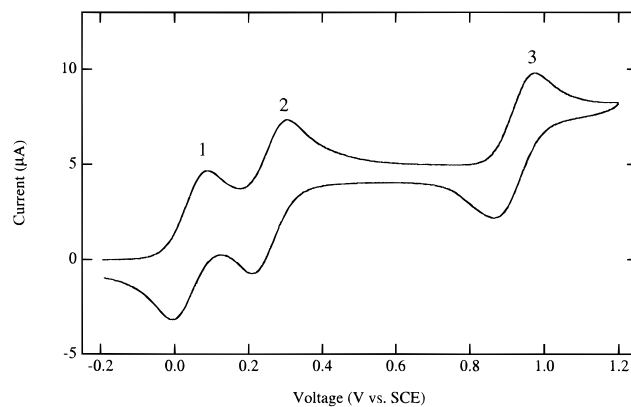


Figure 2. Cyclic voltammogram of **1** in methylene chloride containing 0.1 M $[(n\text{-Bu})_4\text{N}]\text{PF}_6$ as supporting electrolyte (scan rate 100 mV/s). Wave assignments are discussed in the text.

The cyclic voltammogram (CV) of complex **1** in methylene chloride containing 0.1 M $[(n\text{-Bu})_4\text{N}]\text{PF}_6$ is shown in Figure 2.⁴⁰ The CV contains three quasireversible waves of equal area ($E_{1/2}^1 = 0.04$ V, $E_{1/2}^2 = 0.26$ V, $E_{1/2}^3 = 0.92$ V vs SCE). We assign the waves at 0.04 V and 0.26 V to oxidation of the two ferrocenyl centers in bis(acetylide) **1** (*vide infra*). These centers are more easily oxidized than ferrocenylacetylene (0.61 V vs SCE). This is consistent with the results observed for related complexes $\text{CpRu}(\text{C}\equiv\text{CFC})\text{L}$, in which the ferrocene oxidation occurs at 0.00 V ($\text{L} = (\text{PPh}_3)_2$) or -0.03 V vs SCE ($\text{L} = \text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$),⁴¹ and for $\text{RuCl}(\text{dppm})_2(\text{C}\equiv\text{CFC}\equiv\text{C})\text{-RuCl}(\text{dppm})_2$, in which the first ferrocene oxidation is at 0.06 V vs SCE.⁴²

(40) Cyclic voltammetry was carried out in dry methylene chloride solutions containing 0.1 M $[(n\text{-Bu})_4\text{N}]\text{PF}_6$ as the supporting electrolyte and using a Pt working electrode, Pt wire counter electrode, and SCE reference electrode (ferrocene = 0.43 V vs SCE).

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In order to assign unambiguously the oxidation waves observed in the CV of complex **1**, [*trans*-Ru(dppm)₂-(C≡CfC)₂][PF₆]₂ (**3**) was prepared via oxidation of **1** by 2 equiv of ferrocenium hexafluorophosphate in methylene chloride.⁴³ The molar conductivity of a methanol solution of **3** is in the expected range for a 2:1 electrolyte. The IR spectrum of **3** contains a single, strong band at 1997 cm⁻¹. This band is lower in energy than the acetylide stretch in **1** (2067 cm⁻¹) and similar to that observed for the monocation of CpRu(C≡CfC)(PPh₃)₂ (1986 cm⁻¹).⁴¹ The presence of a single band suggests that **3** is a symmetrical species, as would be expected by oxidation of the two ferrocenyl centers. The resonances assigned to the ferrocenyl protons in the ¹H NMR spectrum of **3** are broadened compared to the phosphine phenyl and methylene resonances, consistent with the presence of diamagnetic Ru^{II} and two paramagnetic Fe^{III} centers. Only one set of resonances is observed for the ferrocenyl protons, indicating the overall symmetry in the molecule. The X-ray photoelectron spectra (XPS) of **1** and **3** powder samples were compared.⁴⁴ Both spectra contained peaks corresponding to the expected elemental composition. The spectra of both compounds **1** and **3** show only a single Ru 3d_{5/2} peak (280.6 eV) corresponding to Ru^{II}. The Fe 2p_{1/2} and 2p_{3/2} peaks in the spectrum of **3** are shifted to higher binding energy than the corresponding peaks in the spectrum of **1**, consistent with the presence of Fe^{III} in **3**. The absence of Ru^{III} in the XPS spectrum of **3** indicates that the waves at 0.04 and 0.26 V in the CV of complex **1** correspond to ferrocenyl-based oxidations.

The effect of increasing the number of oxidized ferrocenylacetylide ligands on the ruthenium is to increase the oxidation potential of the ruthenium center. The redox wave at 0.92 V vs SCE in the cyclic voltammogram of complex **1** is assigned to oxidation of the ruthenium center. This oxidation is 0.13 V more positive than the corresponding wave in the cyclic voltammogram of complex **2** ($E_{1/2}^1 = 0.08$ V, $E_{1/2}^2 = 0.79$

V vs SCE) and 0.46 V more positive than the Ru^{III/II} oxidation wave for *trans*-RuCl₂(dppm)₂ (0.46 V vs SCE). This is consistent with the oxidized ferrocenylacetylide ligands donating less electron density to the ruthenium center than the chloride ligands.

Dissolving equimolar masses of **1** and **3** in methylene chloride yielded a blue solution, which is likely due to the formation of the monocation [Ru(C≡CfC)₂(dppm)₂]⁺. Attempts to isolate the monocation as a solid were unsuccessful, yielding only **1** and **3**. The near infrared (NIR) spectrum of this solution displays a broad band ($\lambda_{\text{max}} = 2190$ nm; $\epsilon = 8000$ M⁻¹ cm⁻¹) with a shoulder at 1645 nm ($\epsilon = 4700$ M⁻¹ cm⁻¹). The presence of these bands is indicative of electron delocalization in the monocation;⁴⁵ however, it was not possible to assign these bands conclusively to specific intervalence transfer transitions because of the possibility of both Ru^{II} → Fe^{III} and Fe^{II} → Fe^{III} transfers.

The difference between the first and second ferrocenyl oxidation waves in complex **1**, $\Delta E_{1/2}$, is 0.22 V ($\Delta E_{1/2} = E_{1/2}^2 - E_{1/2}^1$). Larger $\Delta E_{1/2}$ values have been observed for bimetallic complexes in which the two capping metal atoms are linked directly via a common acetylide ligand.³⁻⁵ For example, $\Delta E_{1/2}$ is 0.53 V for (C₅Me₅)-Re(NO)(PPh₃)(C≡C)₂(C₅Me₅)Re(NO)(PPh₃).⁴ However, **1** is the first example of a complex for which a metal bis(acetylide) bridge enhances a ground state interaction between terminal redox-active groups. In comparison, $\Delta E_{1/2}$ is 0.10 V for diferrocenylbutadiyne (Fc-C≡C-C≡C-Fc) and 0.13 V for diferrocenylacetylene (Fc-C≡C-Fc),⁴⁶ complexes in which the terminal ferrocenyl groups are linked by all-carbon bridges. This suggests that conjugated polymers which incorporate metal moieties such as Ru(dppm)₂ may act as better electronic conductors than their all-carbon analogs.

Note Added in Proof. An independent report describing the characterization and an alternate synthesis of **1** has recently appeared: Colbert, M. C. B.; Lewis, J.; Long, N. J.; Raithby, P. R.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1997**, 99–104.

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Supporting Information Available: Tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters and XPS spectra for **1** and **3** (25 pages). Ordering information is given on any current masthead page.

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(43) Preparation of [*trans*-Ru(Ph₂PCH₂PPh₂)₂(C≡CfC)₂][PF₆]₂ (**3**): To a solution of **1** (15.0 mg, 0.0116 mmol) in methylene chloride (10 mL) was added ferrocenium hexafluorophosphate (7.7 mg, 0.023 mmol). The mixture was stirred at 25 °C for 1 h. Hexanes (50 mL) was added to the solution, affording the product as a fine purple powder. This powder was isolated by filtration and washed with hexanes (2 × 50 mL). Yield = 9.2 mg (50%). ¹H NMR (400 MHz, CD₂Cl₂): δ 44.93 (s, broad, 4H, C₅H₄), 41.62 (s, broad, 4H, C₅H₄), 19.39 (s, broad, 10H, Cp), 7.96 (s, 8H, phenyl), 6.40 (s, 16H, phenyl), 4.92 (s, 16H, phenyl), -2.24 (s, 4H, CH₂). IR (KBr): 1997 cm⁻¹. Λ_M (MeOH) = 211 Ω^{-1} mol⁻¹ cm². UV-vis (CH₂Cl₂): 420 nm, ϵ 5500 M⁻¹ cm⁻¹ (shoulder); 560 nm, ϵ 13 000 M⁻¹ cm⁻¹. Anal. Calcd for C₇₄H₆₂Fe₂F₁₂P₆Ru: C, 56.33; H, 3.96. Found: C, 56.32; H, 4.09.

(44) XPS analyses on powder samples were performed with a Leybold MAX200 spectrometer using an unmonochromatized Al K α source operated at 10 kV, 20 mA. The emitted photoelectrons were collected from a 2 × 4 mm² area, and high-resolution spectra were performed at the 96 eV pass energy. The binding energy of the Au 4f_{7/2} peak at 84.0 eV was used to reference all other photoemission peaks.