

Axial Butadiynyl Adducts on a Tetrakis-(di(*m*-methoxyphenyl)formamidinato)diruthenium Core: First Examples of M–M Bonded Complexes Containing σ -Poly-ynyl Ligand

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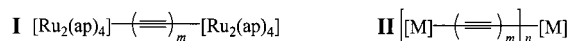
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Interest in the synthesis and characterization of M–M bonded species bearing σ -alkynyl ligands continues from the first such example reported by Cotton in 1986,¹ [Ru₂(ap)₄](C≡CPh), where ap is 2-anilinyridinate and the phenylethynyl group is axially bonded to the Ru(II,III) core. Subsequent work by Bear et al. demonstrated that a variety of axial alkynyl complexes of both dirhodium and diruthenium cores can be isolated,^{2,3} and both the mono adduct and bis adduct may be obtained with a diruthenium core. Coordination of alkynyls at equatorial positions of the M₂ core has been demonstrated by Hopkins et al.,⁴ where a significant $\delta(\text{MM})-\pi(\text{CC})$ conjugation was noted.

Our contributions to this field include the elucidation of the linear free-energy relationship in Ru₂(DArF)₄(C≡CR)_n compounds (DArF = diarylformamidinate and *n* = 1 and 2)⁵ and the syntheses and characterization of Ru₂(ap)₄(C≡CR) with R = SiMe₃, H, and CH₂OCH₃.⁶ More recently, we published the first examples of a carbyne chain capped by bimetallic termini, [Ru₂(ap)₄]₂(μ -(C≡C)_m) (**I** in Scheme 1),⁷ where the degree of electronic delocalization across the carbyne bridges is comparable with the highest degree of electronic delocalization reported for carbyne chains capped with mononuclear termini.⁸ The diruthenium terminus is advantageous over the mononuclear termini as a result of its extraordinary redox flexibility and the availability of an open axial site trans to the existing carbyne

Scheme 1^a



^a **I**, simple rods with [Ru₂(ap)₄] termini, *m* = 1 and 2. **II**, oligometallayne rigid rods; *m* and *n* = integers.

chain in **I**, a desirable feature for the construction of an oligometallayne (**II** in Scheme 1). However, our synthetic effort toward **II** was hampered by the low solubility of [Ru₂(μ -ap)₄]⁺-containing species. In the search for more soluble diruthenium species that retain the essential structural features of **I**, we investigated the reactivity of Ru₂(DArF)₄Cl toward Li(C≡C)_mSiR₃ reagents. Details of the isolation and characterization of both mono- and bisbutadiynyl adducts of the tetrakis(di(*m*-methoxyphenyl)formamidinato)diruthenium core (Ru₂(DmAniF)₄, DmAniF = di-*m*-methoxyphenylformamidinate) are presented.

Results and Discussion

Treating Ru₂(DmAniF)₄Cl⁹ with 3 equiv of LiC₄SiMe₃ and exposing the reaction mixture to air afforded Ru₂(DmAniF)₄-(C₄SiMe₃) (**1**) and Ru₂(DmAniF)₄(C₄SiMe₃)₂ (**2**) in a combined yield of 70%. As elaborated in earlier work on phenylethynyl adducts,^{3,5} there exists an equilibrium between the mono adduct and the anionic form of the bis adduct ([Ru₂(DmAniF)₄-(C₄SiMe₃)₂]¹⁻ in this study) when the reaction mixture is maintained under an inert atmosphere. The anion of the bis adduct is subsequently converted to the neutral form when the reaction mixture is exposed to air. While the yields of mono-phenylethynyl adducts and bisphenylethynyl adducts of a Ru₂(DArF)₄ core are dependent on the postsynthesis treatment of the reaction mixture,^{3,5} the yields of **1** and **2** are independent of the workup procedure. Unlike the phenylethynyl analogues,^{3,5} both compounds **1** and **2** are thermally stable under aerobic conditions. Molecule **1** has an effective magnetic moment of 4.09 μ_B at room temperature, indicative of the *S* = 3/2 ground state common to this class of Ru₂(II,III) species.¹⁰ Molecule **2**, a Ru₂(III,III) species, displays a well-resolved ¹H NMR spectrum and is diamagnetic. Formulation of monobutadiynyl adduct and bisbutadiynyl adduct is confirmed by the study of crystal and molecular structures of **1** and **2**, as shown in Figures 1 and 2, respectively. The relevant topological parameters for molecules **1** and **2** are listed in Tables 1 and 2.

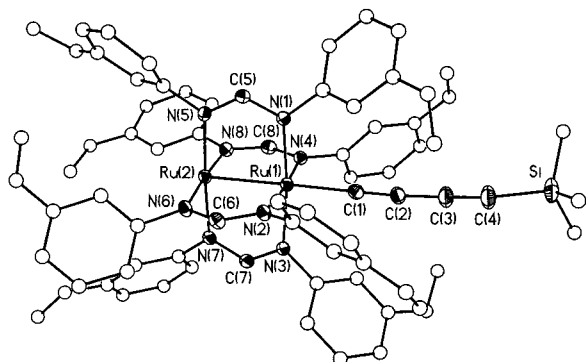
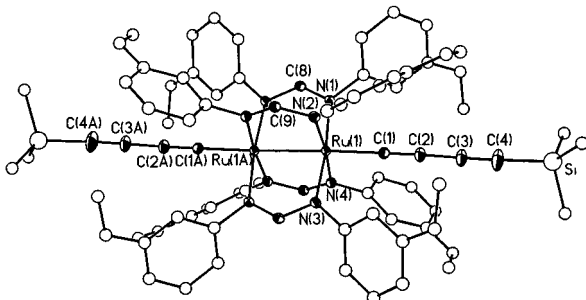
While the coordination geometry of the bridging formamidinates around the Ru₂ core in **1** is similar to that in the parent compound Ru₂(DmAniF)₄Cl,⁹ the Ru–Ru bond distance (2.5060(5) Å) is increased by 0.12 Å from that of the parent compound (2.3855(8) Å).⁹ In contrast, the elongation of the Ru–Ru bond upon formation of Ru₂(DArF)₄(C≡CPh)^{3,5} and Ru₂(ap)₄-(C≡CR) (R = Ph and SiMe₃)^{1,6} is generally less than 0.04 Å. The significant elongation of the Ru–Ru bond length in **1** is attributed to the strong electron-withdrawing nature of the additional C≡C bond, which siphons the σ -bonding electron density away from the Ru₂ core and hence weakens the σ (Ru–Ru) bond.

In the bis adduct of **2**, the Ru–Ru distance is 2.5990(3) Å, a slight increase from that in Ru₂(DArF)₄(C≡CPh)₂ (2.55–2.56

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Figure 1. ORTEP plot of **1** at 20% probability level.Figure 2. ORTEP plot of **2** at 20% probability level.Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compounds **1** and **2**

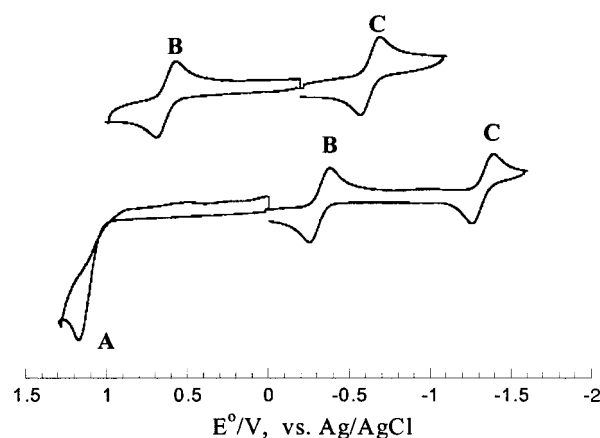
| 1 | | 2 | |
|------------------|------------|-------------------|------------|
| Ru(1)–Ru(2) | 2.5060(5) | Ru(1)–Ru(1A) | 2.5990(3) |
| Ru(1)–N(1) | 2.054(3) | Ru(1)–C(1) | 1.947(2) |
| Ru(1)–N(2) | 2.065(3) | Ru(1)–N(2) | 2.0062(18) |
| Ru(1)–N(3) | 2.060(3) | Ru(1)–N(3) | 2.027(2) |
| Ru(1)–N(4) | 2.064(3) | Ru(1)–N(1) | 2.0709(19) |
| Ru(2)–N(5) | 2.039(3) | Ru(1)–N(4) | 2.1203(18) |
| Ru(2)–N(6) | 2.019(3) | C(1)–C(2) | 1.206(3) |
| Ru(2)–N(7) | 2.032(4) | C(2)–C(3) | 1.371(4) |
| Ru(2)–N(8) | 2.031(3) | C(3)–C(4) | 1.196(4) |
| Ru(1)–C(1) | 2.027(5) | | |
| C(1)–C(2) | 1.207(6) | | |
| C(2)–C(3) | 1.377(7) | | |
| C(3)–C(4) | 1.205(7) | | |
| N(1)–Ru(1)–Ru(2) | 88.33(9) | N(1)–Ru(1)–Ru(1A) | 82.59(5) |
| N(2)–Ru(1)–Ru(2) | 88.10(9) | N(2)–Ru(1)–Ru(1A) | 95.10(5) |
| N(3)–Ru(1)–Ru(2) | 86.00(9) | N(3)–Ru(1)–Ru(1A) | 90.66(5) |
| N(4)–Ru(1)–Ru(2) | 85.13(9) | N(4)–Ru(1)–Ru(1A) | 78.55(5) |
| N(5)–Ru(2)–Ru(1) | 86.84(9) | C(1)–Ru(1)–Ru(1A) | 164.34(7) |
| N(6)–Ru(2)–Ru(1) | 86.96(10) | C(2)–C(1)–Ru(1) | 175.2(2) |
| N(7)–Ru(2)–Ru(1) | 89.43(10) | C(1)–C(2)–C(3) | 177.3(3) |
| N(8)–Ru(2)–Ru(1) | 90.39(10) | C(4)–C(3)–C(2) | 179.2(5) |
| C(1)–Ru(1)–Ru(2) | 175.34(12) | | |
| C(2)–C(1)–Ru(1) | 175.9(4) | | |
| C(1)–C(2)–C(3) | 176.4(6) | | |
| C(4)–C(3)–C(2) | 178.5(7) | | |

Å).^{3,5} The Ru–C_α bond length (1.947(2) Å) is decreased from that of the phenylethynyl analogues (1.99(1) Å). These structural changes are consistent with an enhancement of Ru–C_α bonding at the expense of Ru–Ru bonding. Since trimethylsilylbutadiynyl is a weaker nucleophile than phenylethynyl, the stronger Ru–C_α bonding in **2** is likely due to a significant filled π – π interaction.¹¹ As additional evidence of the presence of filled π – π interactions, **2** exhibits a very intense C≡C stretch in the IR spectrum. Since most σ -alkynyl complexes exhibit only a weak C≡C stretch,¹² the observed intense C≡C stretch implies a constructive interference between two trans butadiynyls

Table 2. Crystallographic Data for Compounds **1** and **2**

| | 1 | 2 |
|--|---|---|
| chemical formula | C ₆₇ H ₆₉ N ₈ O ₈ SiRu ₂ | C ₇₄ H ₇₈ N ₈ O ₈ Si ₂ Ru ₂ |
| fw | 1344.53 | 1465.7 |
| space group | <i>Pbca</i> (No. 61) | <i>P1</i> (No. 2) |
| <i>a</i> , Å | 25.7964(13) | 10.8663(4) |
| <i>b</i> , Å | 16.4755(8) | 10.8991(4) |
| <i>c</i> , Å | 30.6770(15) | 16.0803(6) |
| α , deg | 90 | 92.728(1) |
| β , deg | 90 | 90.921(1) |
| γ , deg | 90 | 103.121(1) |
| vol, Å ³ | 13038(1) | 1851.9(1) |
| <i>Z</i> | 8 | 1 |
| <i>T</i> , °C | 27 | 27 |
| λ (Mo K α), Å | 0.71073 | 0.71073 |
| D_{calcd} , g/cm ^{–3} | 1.370 | 1.314 |
| μ , cm ^{–1} | 5.41 | 4.98 |
| R1, wR2 ^a (<i>I</i> > 2 σ (<i>I</i>)) | 0.0385, 0.0892 | 0.0296, 0.0732 |
| R1, wR2 (all data) | 0.0733, 0.1197 | 0.0366, 0.0764 |

$$^a R1 = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}, wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

Figure 3. Cyclic voltammograms of compounds **1** and **2** recorded at a scan rate of 100 mV/s in 0.20 M (*n*-Bu)₄NPF₆ solution (THF, N₂-degassed) with a glassy carbon working electrode, a Pt-wire auxiliary electrode, and an Ag/AgCl reference electrode.

mediated by the filled π – π interaction across the Ru–Ru bond. Similar to the phenylethynyl analogues, the arrangement of the bridging formamidinate ligands around the Ru₂ core is severely distorted, which was attributed to a second-order Jahn–Teller effect.⁵ The butadiynyl ligands are bent away from the Ru–Ru vector, but the Ru–Ru–C_α angle (164°) is closer to 180° than that found in phenylethynyl adducts (ca. 159°).

The rich redox characteristics of compounds **1** and **2** were revealed with the measurement of cyclic voltammograms (CV, Figure 3). The bis adduct of **2** undergoes two reversible one-electron reductions at –0.32 V (B) and –1.32 V (C) and one irreversible oxidation at 1.17 V (A). When the potential range is limited within 1.20 V, the mono adduct of **1** displays two reversible one-electron processes, an oxidation at 0.63 V (B) and a reduction at –0.63 V (C). However, the reversible waves disappear when the range of potential sweep is extended beyond 1.2 V, indicating an oxidative degradation of **1** in the high potential range. The observed redox couples in both **1** and **2** are assigned to the formal oxidation states of the Ru₂ core as follows:

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