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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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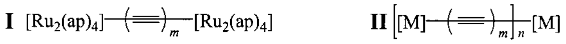
Interest in the synthesis and characterization of M−M bonded species bearing *σ*-alkynyl ligands continues from the first such example reported by Cotton in 1986,[1] $[Ru_2(ap)_4](C{\equiv}CPh)$, where ap is 2-anilinopyridinate and the phenylethynyl group is axially bonded to the Ru(II,III) core. Subsequent 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 M_2 core has been demonstrated by Hopkins et al.,[4] where a significant $\delta(MM)-\pi(CC)$ conjugation was noted.

Our contributions to this field include the elucidation of the linear free-energy relationship in $Ru_2(DArF)_4(C{\equiv}CR)_n$ compounds (DArF = diarylformamidinate and $n = 1$ and 2)[5] and the syntheses and characterization of $Ru_2(ap)_4(C{\equiv}CR)$ with R = $SiMe_3$, H, and CH_2OCH_3.[6] More recently, we published the first examples of a carbyne chain capped by bimetallic termini, $[Ru_2(ap)_4]_2(\mu\text{-}(C{\equiv}C)_m)$ (**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 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 $[Ru_2(\mu\text{-ap})_4]^+$-containing species. In the search for more soluble diruthenium species that retain the essential structural features of **I**, we investigated the reactivity of $Ru_2(DArF)_4Cl$ toward $Li(C{\equiv}C)_mSiR_3$ reagents. Details of the isolation and characterization of both mono- and bisbutadiynyl adducts of the tetrakis(di(*m*-methoxyphenyl)formamidinato)diruthenium core ($Ru_2(DmAniF)_4$, D*m*AniF = di-*m*-methoxyphenylformamidinate) are presented.

Scheme 1[a]



[a] **I**, simple rods with $[Ru_2(ap)_4]$ termini, $m = 1$ and 2. **II**, oligometallayne rigid rods; m and n = integers.

Results and Discussion

Treating $Ru_2(DmAniF)_4Cl$[9] with 3 equiv of LiC_4SiMe_3 and exposing the reaction mixture to air afforded $Ru_2(DmAniF)_4(C_4SiMe_3)$ (**1**) and $Ru_2(DmAniF)_4(C_4SiMe_3)_2$ (**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 ($[Ru_2(DmAniF)_4(C_4SiMe_3)_2]^{1-}$ 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 monophenylethynyl adducts and bisphenylethynyl adducts of a $Ru_2(DArF)_4$ 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 Ru_2(II,III) species.[10] Molecule **2**, a Ru_2(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 Ru_2 core in **1** is similar to that in the parent compound $Ru_2(DmAniF)_4Cl$,[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 $Ru_2(DArF)_4(C{\equiv}CPh)$[3,5] and $Ru_2(ap)_4(C{\equiv}CR)$ (R = Ph and $SiMe_3$)[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 Ru_2 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 $Ru_2(DArF)_4(C{\equiv}CPh)_2$ (2.55−2.56

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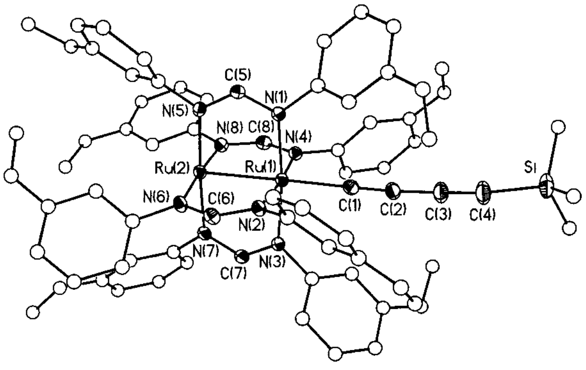

Figure 1. ORTEP plot of **1** at 20% probability level.

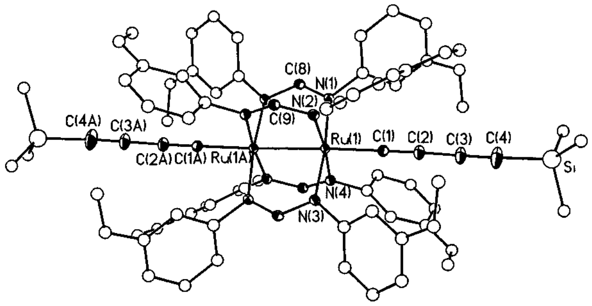

Figure 2. ORTEP plot of **2** at 20% probability level.

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)		

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

	1	2
chemical formula	$C_{67}H_{69}N_8O_8SiRu_2$	$C_{74}H_{78}N_8O_8Si_2Ru_2$
fw	1344.53	1465.7
space group	*Pbca* (No. 61)	$P\bar{1}$ (No. 2)
a, Å	25.7964(13)	10.8663(4)
b, Å	16.4755(8)	10.8991(4)
c, 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)
Z	8	1
T, °C	27	27
λ(Mo Kα), Å	0.71073	0.71073
D_{calcd}, g/cm^{-3}	1.370	1.314
μ, cm^{-1}	5.41	4.98
R1, wR2[a] ($I > 2\sigma(I)$)	0.0385, 0.0892	0.0296, 0.0732
R1, wR2 (all data)	0.0733, 0.1197	0.0366, 0.0764

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

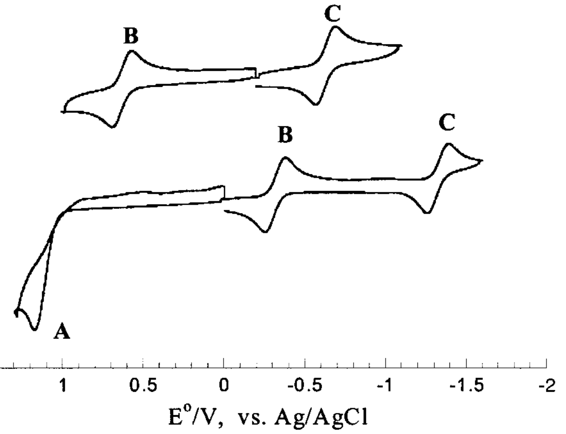

Figure 3. Cyclic voltammograms of compounds **1** and **2** recorded at a scan rate of 100 mV/s in 0.20 M (*n*-Bu)$_4$NPF$_6$ solution (THF, N$_2$-degassed) with a glassy carbon working electrode, a Pt-wire auxiliary electrode, and an Ag/AgCl reference electrode.

Å).[3,5] The Ru−C$_\alpha$ 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$_\alpha$ bonding at the expense of Ru−Ru bonding. Since trimethylsilylbutadiynyl is a weaker nucleophile than phenylethynyl, the stronger Ru−C$_\alpha$ 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 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 Ru$_2$ 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$_\alpha$ 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 Ru$_2$ core as follows:

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$$\mathrm{Ru_2(II,II)} \underset{\text{C}}{\xrightleftharpoons[+\,e^-]{-\,e^-}} \mathrm{Ru_2(II,III)} \underset{\text{B}}{\xrightleftharpoons[+\,e^-]{-\,e^-}} \mathrm{Ru_2(III,III)} \underset{\text{A}}{\xrightarrow{-\,e^-}} \mathrm{Ru_2(IV,III)}$$

It is clear that the potentials of the B and C couples in molecule **2** have been cathodically shifted by about 0.95 and 0.69 V from that of **1**, and the cathodic shifts reflect the further stabilization of the Ru_2 core by an additional butadiynyl ligand, a strong nucleophile. It is noteworthy that the first reduction potential of **2** is nearly zero, indicating a high electron affinity in solution. As pointed out by Michl et al.,[13] high electron affinity is an essential prerequisite for the modules of type II rods as molecular wires.

Molecules **1** and **2** represent the first examples of M−M bonded compounds bearing poly-ynyl ligands and exhibit significant differences from alkynyl analogues in both structure and thermal stability. Synthetic methodologies for **1** and **2** may be extended to analogues bearing longer poly-ynyls, such as 1,3,5-hexatriynyl and 1,3,5,7-octatetraynyl, which are being explored in our laboratory. Preliminary studies indicate that the terminal trimethylsilyl groups in both **1** and **2** can be easily removed to yield the unprotected terminal alkyne (≡C−H), which may undergo further oxidative coupling to yield extended rods (**II** in Scheme 1) under the Glaser−Hay−Eglinton conditions.[14]

Experimental Section

n-Butyllithium (1.6 M in hexane) and 1,4-bis(trimethylsilyl)-1,3-butadiyne were purchased from Aldrich. Syntheses were generally performed in a dry argon atmosphere using standard Schlenk-line techniques. NMR (^{1}H and ^{13}C), IR, and UV/Vis spectra were recorded on a Bruker AVANCE300 NMR spectrometer, a Perkin-Elmer 2000 FT-IR spectrometer (using KBr disks), and a Perkin-Elmer Lambda900 UV/Vis/NIR spectrophotometer, respectively. Magnetic susceptibility was measured with a Johnson Matthey MarkII magnetic susceptibility balance. Cyclic voltammograms were recorded on a CHI620A voltammetric analyzer with a glassy carbon working electrode, a Pt wire auxiliary electrode, and a Ag/AgCl reference electrode in 0.2 M n-Bu_4NPF_6 in THF. Single crystals of X-ray quality were obtained for both **1** and **2** by slow evaporation of fractions from column chromatography purification (hexanes/ethyl acetate). Diffraction data were collected on a Bruker SMART1000 CCD diffractometer at ambient temperature, and the structures were solved and refined using the Bruker SHELXTL (Version 5.1) software package.[15]

Synthesis of Compounds 1 and 2. To a solution of 0.291 g (1.5 mmol) of bis(trimethylsilyl)butadiyne in 20 mL of THF at −78 °C was added 0.63 mL of Li*n*Bu (1.6 M in hexane). The reaction was allowed to warm to room temperature to yield an off-white solution, which was transferred to a 40-mL THF solution of $Ru_2(DmAniF)_4Cl$ (0.630 g, 0.5 mmol). The reaction mixture was stirred at room temperature overnight and became a clear deep purple solution. TLC analysis (4:1 hexane/ethyl acetate) revealed the formation of two major products: **1** ($R_f = 0.60$) and **2** ($R_f = 0.80$) and the absence of the starting ruthenium compound. After being exposed to air for 20 min. the solvent was removed in vacuo, and the residue was purified by flash column chromatography using a linear gradient eluent (hexanes/ethyl acetate, 95:5−5:1, v/v) to yield **1** (0.283 g, 42% based on Ru) and **2** (0.205 g, 28%) as purple crystalline solids.

Data for 1. Anal. Calcd for $C_{67}H_{69}N_8O_8SiRu_2$: C, 59.73; H, 5.13; N, 8.32. Found: C, 59.47; H, 5.25; N, 8.07. MS−FAB (*m*/*z*): [M^+] calcd for ^{101}Ru, 1346. UV−vis λ_{max}, nm (ϵ): 771.0 (sh), 564.9 (7682.5). IR (cm^{-1}, KBr disk): 2154.5 (w), 2103.9 (m).

Data for 2. Anal. Calcd for $C_{74}H_{78}N_8O_8Si_2Ru_4$: C, 60.53; H, 5.35; N, 7.63. Found: C, 60.33; H, 5.41; N, 7.42. MS−FAB (*m*/*z*): [M^+] calcd for ^{101}Ru, 1467. ^{1}H NMR δ: 8.19 (s, 4H, −NC*H*N), 7.13 (t, 8H, Ph-*H*), 6.70 (q, 8H, Ph-*H*), 6.56 (t, 8H, Ph-*H*), 6.19 (d, 8H, Ph-*H*), 3.48 (s, 24H, C*H*$_3$O), 0.09 (s, 18H, (C*H*$_3$)$_3$Si). UV−vis λ_{max}, nm (ϵ): 920.03 (sh), 575.42(11 089), 516.19 (12 053). IR (cm^{-1}, KBr disk): 2183.5 (m), 2118.7 (s).

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determination of both **1** and **2**. This material is available free of charge via the Internet at http:/pubs.acs.org.

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