

Synthesis and characterization of wire-like $\text{Ru}_2(\text{ap})_4$ - $[\sigma$ -oligo(phenylene ethynyl)] compounds

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Abstract

Reported herein are the synthesis, electrochemical and structural characterization of wire-like Ru_2 -alkynyl compounds, $\text{Ru}_2(\text{ap})_4(\text{Ln})_x$, where ap is 2-anilinopyridinate, and Ln is $-(\text{C}\equiv\text{CC}_6\text{H}_4)_n\text{SCH}_2\text{CH}_2\text{SiMe}_3$ with $n = 1$ (**1**) and 2 (**2**), and x can be 1 (**a**) and 2 (**b**). Reactions between $\text{Ru}_2(\text{ap})_4\text{Cl}$ and one equiv. of LiLn yielded the mono-alkynyl compound only, while the use of 4–5 equiv. of LiLn resulted in a mixture of both the mono and bis-alkynyl species. Single crystal X-ray diffraction studies of compounds **1a** and **1b** revealed structural similarities to $\text{Ru}_2(\text{ap})_4(\text{C}_2\text{Ph})$ and $\text{Ru}_2(\text{ap})_4(\text{C}_2\text{Ph})_2$, respectively. Magnetic, spectroscopic and voltammetric measurements also revealed a minimal perturbation on electronic structures due to the functionalization of OPE ligands with thiol-TMSE group ($-\text{SCH}_2\text{CH}_2\text{SiMe}_3$). Most significantly, it can be estimated based on the structure of **1a** that the Ru–OPE2–S– linkage in **2a** is significantly longer than the depth of C11 thiol SAM and hence enables the insertion of **2a** into the latter.

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Keywords: Diruthenium; OPE complexes; Molecular wires; Synthesis; Crystal structures

1. Introduction

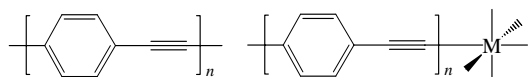
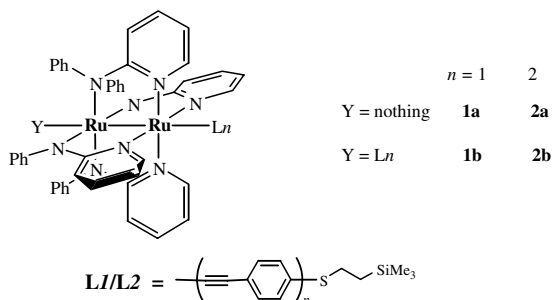
Synthesis of active materials for *molecular electronic devices* is an exciting and challenging area of current materials research, where conjugated organic compounds, especially oligo(phenylene ethynylene)s (OPEs, **Scheme 1**), have played a prominent role [1,2]. The interest in OPE goes beyond molecular electronic applications: it is an excellent scaffold for the construction of *shape-persistent* linear and cyclic supramolecules [3–5];

and OPE and its OArE (oligo(arylene ethynylene)) surrogates are ideal molecular photonic wires and have been employed as the key component in highly sensitive and selective sensors for exotic volatiles (TNT) [6], toxic metal ions (Pb^{2+}) [7] and proteins (lectins) [8].

Metal- σ -phenylacetylide complexes are the most commonplace motifs in metal-alkynyl chemistry [9–11]. Aiming at further improvement of materials properties via extended π -conjugation, transition metal-OPE hybrids (**Scheme 1**) with OPE functioning as σ -arylacetylide ligand has emerged as a new direction of metal-acetylide chemistry. Humphrey et al. [12–15] have reported the synthesis and NLO properties of OPE2 complexes of Au(I), Ni(II) and Ru(II) complexes, and observed the substantial enhancement of the third-order

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Scheme 1. OPE n and metal- σ -OPE n complex.Scheme 2. Ru $_2$ (ap) $_4$ - σ -OPE n -STMSE compounds.

optical nonlinearity (γ) in comparison with the phenylacetylide homologs. Intensely emissive complexes of Pt(II) and coinage metal monocations have also been reported [16–18] and the attenuation of $^3(\pi\pi^*)$ excited states in both Au(I)–OPE n and Pt(II)–OPE n complexes by the variation of chain length n is noteworthy [19,20]. We reported recently the series of *trans*-Ru $_2$ (DMBA) $_4$ (OPE n -S-TMSE) $_2$ compounds with $n = 1$ –3 (DMBA is *N,N'*-dimethylbenzoamidinate and TMSE is $-\text{CH}_2\text{CH}_2\text{SiMe}_3$), which, upon the removal of TMSE groups, link Au nano-particles into dimers and chains [21]. A more significant advance would be the improvement of molecular conductance on incorporating transition metal centers into the backbone of OPEs. Unfortunately, the *trans*-Ru $_2$ (DMBA) $_4$ (OPE n -S) $_2$ type compounds failed to form self-assembled monolayer (SAM) on Au substrate that is essential for nano-junction measurement [22]. We disclosed very recently that Ru $_2$ (ap) $_4$ (OPE n -S) (*ap* = 2-anilino-pyridinate) molecules inserted into a SAM matrix of C11-thiol exhibit a electronic decay constant (β) 15–40% smaller than that of OPE molecules of comparable lengths [23]. The reduction in β or the enhancement of molecular transconductance is clearly the result of the E_g (energy gap) reduction on the insertion of Ru $_2$ unit. Reported in this contribution are the details of synthesis, voltammetric and structural characterization of Ru $_2$ (ap) $_4$ (OPE n -S-TMSE) $_x$ shown in Scheme 2, where $n = 1$ and 2, and $x = 1$ and 2.

2. Results and discussion

Syntheses of compounds **1** and **2** are very similar to the previously developed protocols for Ru $_2$ (ap) $_4$ (CCR) $_x$ ($x = 1$ and 2) [24–26]: reactions between Ru $_2$ (ap) $_4$ Cl and one equiv. of LiLn in THF yielded Ru $_2$ (ap) $_4$ (Ln) (**1a/2a**, Ru $_2$ (II,III) species) as the only product, while that with LiLn in excess (4–5 equiv.) resulted in a mixture of

Ru $_2$ (ap) $_4$ (Ln) and Ru $_2$ (ap) $_4$ (Ln) $_2$ (**1b/2b**, Ru $_2$ (III,III) species) in ca. 1:1 ratio. The separation of mono- and bis-alkynyl compounds is very tedious and required several rounds of column chromatography and recrystallizations due to both similar polarities of two compounds and the low solubility of the bis-compounds. Purified mono-functional compounds **1a** and **2a** are reddish brown, and paramagnetic with effective magnetic moments corresponding to a $S = 3/2$ ground state. The di-functional compounds **1b** and **2b** are deep blue and diamagnetic, and the latter enables the recording of ^1H NMR spectra. Compounds **1** and **2** are indefinitely stable towards ambient atmosphere when stored as solids. The TMSE group is clearly robust toward BuLi and remained intact during the synthesis of **1/2**, but can be readily removed with Bu $_4$ NF in wet THF.

Both compounds **1** and **2** readily crystallize from common organic solvents as thin plates, which are unfortunately very fragile and often twinned. Single crystals of X-ray quality were obtained for both **1a** and **1b**, and the structures were determined through diffraction studies. Molecule **1a**, shown in Fig. 1, has an overall feature very similar to that of Ru $_2$ (ap) $_4$ (C $_2$ Ph) [27]. The *ap* ligands adopt the (4,0)-arrangement around the Ru $_2$ center, where all pyridine N centers bond to Ru1 and all anilino N centers bond to Ru2. The Ru–Ru bond length in **1a** (Ru1–Ru2, 2.3225(3) Å) is identical to that in Ru $_2$ (ap) $_4$ (C $_2$ Ph) (2.319(3) Å) [27] within the experimental errors. The Ru1–C1 bond in **1a** (Ru1–C1, 2.125(3) Å), however, is longer than those of Ru $_2$ (ap) $_4$ (C $_2$ Ph) and other Ru $_2$ (ap) $_4$ (C $_2$ R) type compounds (ca. 2.08(1) Å) [28]. The C1–C2 distance is substantially shorter than 1.20 Å expected for a typical C \equiv C bond. The cause of abnormal Ru–C and C \equiv C distances is unclear presently, but it is unlikely due to crystallographic artifacts since the structure of **1a** was refined to convergence with excellent figures of merit.

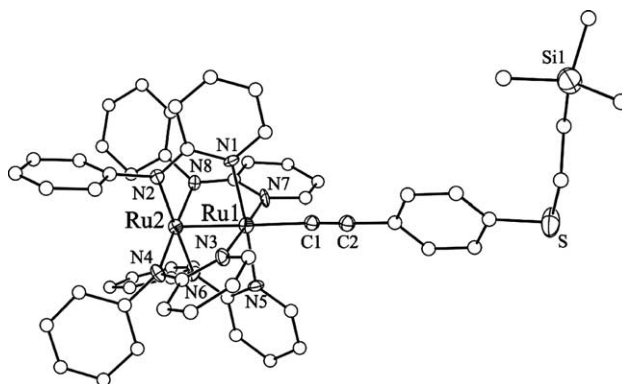


Fig. 1. Structural plot of **1a** at 30°C, all *non-acetylenic* carbons were shown as open circles and hydrogen atoms were omitted. Selected bond lengths (Å) and angles ($^\circ$): Ru1–Ru2, 2.3225(3); Ru1–C1, 2.125(3); C1–C2, 1.159(4); Ru1–N(av.), 2.096(2); Ru2–N(av.), 2.045(2); Ru2–Ru1–C1, 178.88(8); Ru1–C1–C2, 175.5(3).

The molecular structure of **1b** is shown in Fig. 2, and bears close resemblance to that of $\text{Ru}_2(\text{ap})_4(\text{C}_2\text{Ph})_2$ [26]. The Ru–Ru bond length in **1b** (2.4407(6) Å) is slightly shorter than that in $\text{Ru}_2(\text{ap})_4(\text{C}_2\text{Ph})_2$ (2.4707(3) Å) but consistent with the designation of a Ru–Ru single bond [29]. Compared with **1a**, the Ru–C bond lengths are significantly shorter in **1b**, which is due to both a much enhanced Ru–C bond strength and the increased formal oxidation state of the Ru_2 core. It is safe to conclude that the modification of phenylethynyl with trimethylsilylethylsulfanyl ($\text{SCH}_2\text{CH}_2\text{SiMe}_3$) has induced very minimal structural changes around the Ru_2 core.

With the precisely determined bond lengths for **1a** and **1b** in hand, some topological parameters can be calculated or estimated for the wire-like molecules **1** and **2**. The $\text{Ru1}\cdots\text{S}$ distance is 9.26 Å in **1a**, and that of **2a** is ca. 16.26 Å based on a length of 6.90 Å for one phenylene ethyne unit ($-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4$). The latter $\text{Ru}\cdots\text{S}$ distance is sufficiently long to ensure the doping of **2a** into the SAM of C11-thiol with a thickness of ca. 14 Å, and this has been verified through the doping and subsequent interfacial CV studies [23]. The $\text{S1}\cdots\text{S2}$ distance of the complete wire **1b** is 20.69 Å, and that of **2b** is similarly estimated to be 34.49 Å.

Voltammetric properties of compounds **1** and **2** were investigated in THF solution and their cyclic voltammograms (CV) are shown in Fig. 3. All compounds exhibit single one-electron oxidation and two one-electron reduction couples, and their assignments are given in Scheme 3. As shown by the data in Table 1, the mono-functionalized compounds **1a** and **2a**, formally $\text{Ru}_2(\text{II,III})$, display reversible oxidation (B) and first reduction (C), and irreversible second reduction (D). The di-functionalized compounds **1b** and **2b**, formally $\text{Ru}_2(\text{III,III})$, are reversible on the oxidation (A) and first reduction (B), and quasireversible on the second reduction (C). Similarity between phenylethynyl (OPE1) and OPE2 compounds in both the electrode potentials and over-all behaviors is clear from Fig. 3 and Table 1. The main contrast between the mono- and di-function-

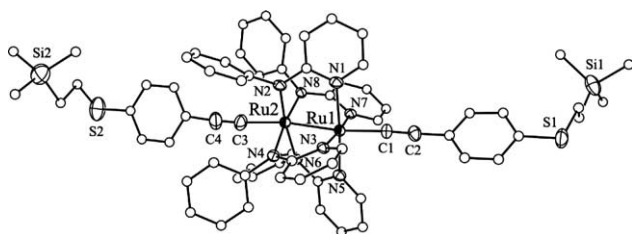


Fig. 2. Structural plot of **1b** at 30clarity, all non-acetylenic carbons were shown as open circles and hydrogen atoms were omitted. Selected bond lengths (Å) and angles (°): Ru1–Ru2, 2.4407(6); Ru1–C1, 1.992(5); Ru2–C3, 1.981(6); C1–C2, 1.180(8); C3–C4, 1.171(9); Ru1–N(av.), 2.102(5); Ru2–N(av.), 2.074(4); Ru2–Ru1–C1, 171.23(19); Ru1–Ru2–C3, 171.5(2); Ru1–C1–C2, 176.3(6); Ru2–C3–C4, 174.4(7).

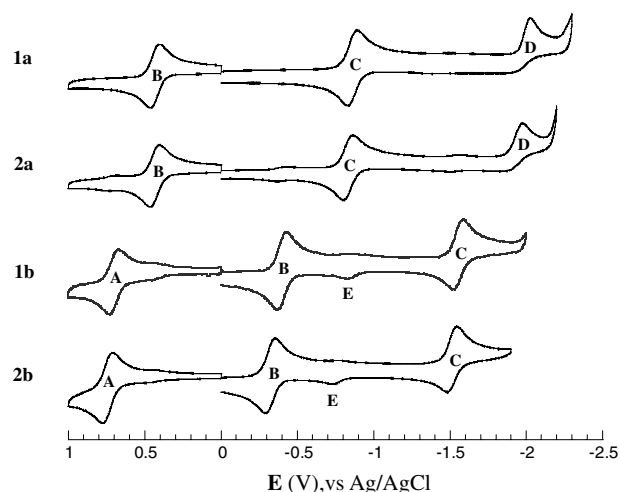
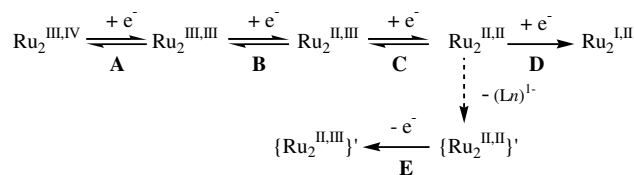


Fig. 3. Cyclic voltammograms of compounds **1** and **2** recorded in 0.20 M THF solution of Bu_4NPF_6 at a scan rate of 0.10 V/s.



Scheme 3. Assignment of redox couples in **1** and **2**. Loss of axial ligand L indicated by dashed arrow and associated step apply to bis-compounds.

alized compounds is the behavior on second reductions: the mono-species lose the axial alkynyl ligand completely upon reduction and hence renders D irreversible, while the di-species only partially dissociates to yield mono-ligated species $\{\text{Ru}_2\}'$ that is reoxidized on backward sweep (E). While the rationale for Ds irreversibility is based on our experiences with other Ru_2 -alkynyl species [28,30], that for the appearance of E is easily verified by the fact that $E_{\text{pa}}(\text{E})$ is nearly identical to $E_{\text{pa}}(\text{C})$ of mono-alkynyl species. It is clear on comparing data acquired for **1** and **2** with those of $\text{Ru}_2(\text{ap})_4(\text{C}_2\text{Ph})_x$ ($x = 1$ and 2) that the $-\text{SCH}_2\text{CH}_2\text{SiMe}_3$ substitution did not change the redox behaviors of Ru_2 -alkynyls. Most importantly, the feature of small energy gaps (E_g) has been preserved in both mono- (1.30 eV) and di-functionalized (1.10 eV) compounds [28].

In summary, we have prepared and characterized a family of Ru_2 -OPE n complexes with TMSE-protected thiol termini. Voltammetric behaviors and structural features of these compounds agree well with $\text{Ru}_2(\text{ap})_4(\text{C}_2\text{Ph})_x$ compounds, indicating minimal alteration of electronic structures. Preliminary STM study of **2a** in free thiol form, a “half wire”, revealed substantial enhancement in molecular conductance [23]. The study of conductances of the complete wire molecule **2b** is under the way.

Table 1
Voltammetric and spectral data for compounds **1** and **2**

	Ru ₂ (ap) ₄ (C ₂ Ph)	1a	2a	Ru ₂ (ap) ₄ (C ₂ Ph) ₂	1b	2b
<i>E</i> (+1/0)/V (ΔE_p /mV, $i_{back}/i_{forward}$)	0.44 (66, 0.96)	0.43 (55, 0.97)	0.43 (62, 0.99)	0.72 (68, 0.83)	0.70 (57, 0.93)	0.74 (67, 0.78)
<i>E</i> (0/−1)/V (ΔE_p /mV, $i_{back}/i_{forward}$)	−0.88 (69, 0.95)	−0.86 (58, 0.93)	−0.83 (65, 0.96)	−0.42 (59, 0.64)	−0.40 (62, 0.89)	−0.32 (59, 0.90)
<i>E</i> (−1/−2)/V (ΔE_p /mV, $i_{back}/i_{forward}$)	Na	−2.02 ^a	−1.98 ^a	−1.58 (75, 0.38)	−1.55 (59, 0.88)	−1.51 (64, 0.73)
<i>E</i> _g , eV ^b	1.32	1.29	1.26	1.14	1.10	1.06

^a *E*_{pc} of irreversible reductions.

^b *E*_g = *e*{*E*(1/0) − *E*(0/−1)}.

3. Experimental section

Ru₂(ap)₄Cl [31], HL1 [32] and HL2 [33] were prepared according to the literature procedures. 2-Anilino-pyridine and *n*-BuLi were purchased from Aldrich and silica gel from Merck. ¹H NMR spectra were recorded in CDCl₃ on either a Bruker AVANCE300 or a Bruker DRX400 NMR spectrometer, and chemical shifts (δ) were referenced to the residual CHCl₃. Infrared spectra were recorded on a Perkin–Elmer 2000 FT-IR spectrometer using KBr disks. UV–Vis–NIR spectra in THF were obtained with a Perkin–Elmer Lambda-900 UV–Vis–NIR spectrophotometer. Magnetic susceptibility was measured at 293 K with a Johnson Matthey Mark-I Magnetic Susceptibility Balance. Cyclic voltammograms (CVs) were recorded in 0.20 M (*n*-Bu)₄NPF₆ solution (THF, N₂-degassed) on a CHI620A voltammetric analyzer with a glassy carbon working electrode (\varnothing = 3 mm), a Pt-wire auxiliary electrode, a Ag/AgCl reference electrode for non-aqueous solution (Cypress), and a concentration of diruthenium species about 1.0 mM. Ferrocenium/ferrocene couple was observed at 0.576 V under the experimental conditions.

3.1. Synthesis of Ru₂(ap)₄(L1) (**1a**)

To a 20 mL THF solution of HL1 (0.030 g, 0.13 mmol) was added 0.10 mL BuLi (1.6 M in hexanes, 0.16 mmol) at liquid nitrogen temperature, which resulted in a light brown solution on warming to room temperature. The resultant LiL1 solution was added to a THF solution of Ru₂(ap)₄Cl (0.12 g, 0.13 mmol), and the solution changed from green to brownish red upon the completion of the addition. Ru₂(ap)₄Cl was consumed in 1 h and the reaction mixture was filtered through a 2-cm silica gel pad (deactivated with Et₃N). Solvent removal from the filtrate yielded a dark brown solid, which was recrystallized from CH₂Cl₂/hexanes to afford 0.11 g **1a** (76% based on Ru). Data of **1a**: Anal. for C₅₄H₅₃N₈Ru₂SSi, Found (Calc.): C, 61.76 (61.57); H, 4.88 (4.77); N, 9.95 (10.08). MS-FAB (*m/z*, based on ¹⁰¹Ru): 1113 [MH⁺]; Vis–NIR in THF (λ , nm (ϵ , M^{−1} cm^{−1})): 486 (6510), 752 (4460); ν (C≡C) (cm^{−1}, KBr disk): 1935(w), 1948(w). μ_{eff} (293 K): 3.80 μ_B .

3.2. Synthesis of Ru₂(ap)₄L1 (**1a**) and trans-Ru₂(ap)₄(L1)₂ (**1b**)

LiL1 (3.0 mmol in 15 mL THF) prepared as above was added to a solution of Ru₂(ap)₄Cl (0.69 g, 0.75 mmol, 100 mL THF) and the mixture changed from green to brownish red upon the completion of the addition. Ru₂(ap)₄Cl was fully consumed in 1 h based on TLC and the reaction was terminated after 2 h by gently bubbling air through the solution. TLC revealed the presence of approximately equal amounts of a reddish brown compound (**1a**, *R*_f = 0.72, ethyl acetate/hexanes/Et₃N = 1/8/1; the same solvent combination was used for other TLCs and column purifications as well) and a royal blue compound (**1b**, *R*_f = 0.66). Silica column purification resulted in 0.31 g of pure **1a** (37% based on Ru) and crude **1b** contaminated with small amount of **1a**, and the latter was recrystallized three times from warm ethyl acetate/hexanes to yield pure **1b** (0.17 g, 17% based on Ru). Data of **1b**: Anal. for C₇₀H₇₂N₈ORu₂S₂Si₂ (**1b** · H₂O): Found (Calc.): C, 61.70 (61.67); H, 5.16 (5.29); N, 8.35 (8.22). ¹H NMR (CDCl₃): 9.31 (q, 4H), 7.44 (d, 2H), 7.37 (d, 2H), 7.19 (m, 6H), 6.99 (q, 12H), 6.37 (d, 4H), 6.28 (t, 4H), 6.11 (d, 2H), 5.87 (s, 8H), 3.01 (m, 4H), 0.99 (m, 4H), 0.10 (s, 18H). MS-FAB (*m/z*, based on ¹⁰¹Ru): 1347 [MH⁺]; Vis–NIR in THF (λ , nm (ϵ , M^{−1} cm^{−1})): 440 (5560), 482 (5770), 628 (7150), 1028 (3730); ν (C≡C)(cm^{−1}, KBr disk): 2099(w), 2075(m).

3.3. Synthesis of Ru₂(ap)₄(L2) (**2a**)

To a 20-mL THF solution of HL2 (0.47 g, 0.15 mmol) was added 0.1 mL of 1.6 M BuLi in hexanes at liquid nitrogen temperature, which yielded a deep green solution on warming to room temperature. The presumed LiL2 solution was transferred via cannula to a Schlenk flask containing 0.14 g of Ru₂(ap)₄Cl (0.15 mmol) in 40 mL THF, and the color of the solution changed from olive green to dark brown upon the completion of transfer. Ru₂(ap)₄Cl disappeared from the mixture in 2 h as indicated by TLC and the reaction mixture was filtrated through a 2-cm silica gel pad (deactivated with Et₃N). The crude product from the filtrate

was purified by column chromatography (ethyl acetate/hexanes/Et₃N = 20/100/10) to yield 0.115 g **2a** (65% based on Ru). Data of **2a**. Anal. for C₆₈H₆₄N₈Ru₂SSi (**2a** · 0.5C₆H₁₄): Found (Calc.): C, 65.10 (65.05); H, 5.07 (5.14); N, 8.54 (8.92). MS-FAB (*m/z*, based on ¹⁰¹Ru): 1213 [MH⁺]; Vis-NIR in THF (λ , nm (ϵ , M⁻¹ cm⁻¹)): 465 (8590), 748 (4870); ν (C≡C) (cm⁻¹, KBr disk): 1958(w), 1921(w). μ_{eff} (293 K): 3.74 μ_{B} .

3.4. Synthesis of Ru₂(*ap*)₄L2 (**2a**) and trans-Ru₂(*ap*)₄(L2)₂ (**2b**)

LiL2 (1.0 mmol in 10 mL THF) prepared as above was transferred to a Schlenk flask containing 0.182 g of Ru₂(*ap*)₄Cl (0.20 mmol) dissolved in 30 mL THF. The reaction mixture was stirred under N₂ overnight to yield a burgundy solution, which was quenched by bubbling air through for 15 min to yield a bluish green solution. TLC analysis revealed the complete consumption of Ru₂(*ap*)₄Cl and presence of **2a** (*R_f* = 0.64) and bluish green **2b** (*R_f* = 0.52). Silica column purification resulted in 0.10 g of pure **2a** (42% based on Ru), while column fractions of **2b** were still contaminated with **2a**. Further purification was effected with three successive recrystallizations from warm ethyl acetate/hexanes to afford 0.045 g **2b** (15% based on Ru). Data of **2b**: Anal. for C₉₀H₈₆N₈O₂Ru₂S₂Si₂ (**2b** · C₄H₈O₂), Found (Calc.): C, 66.28 (66.15); H, 5.64 (5.30); N, 6.66 (6.86). ¹H NMR (CDCl₃): 9.28 (4H), 7.47 (d, 2H), 7.41 (d, 2H), 7.40–7.36 (m, 6H), 7.30–7.25 (m, 4H), 7.18–7.10 (m, 4H), 6.98 (q, 12H), 6.41 (d, 4H), 6.34 (t, 4H), 6.16 (d, 2H), 5.87 (s, 8H), 3.04–2.98 (m, 4H), 0.99–0.94 (m, 4H), 0.08 (s, 18H); MS-FAB (*m/z*, based on ¹⁰¹Ru): 1546 [MH⁺]; Vis-NIR in THF (λ , nm (ϵ , M⁻¹ cm⁻¹)): 480(sh), 621(5770), 1027(2960); ν (C≡C)(cm⁻¹, KBr disk): 2092(w), 2066(m).

3.5. X-ray data collection, processing, and structure analysis and refinement

Single crystals of both compounds **1a** and **1b** were grown via slow evaporation of fractions from column purification. Both data sets were collected on a Bruker three-circle platform diffractometer equipped with a SMART6000 CCD detector using graphite-monochromated Cu K α radiation. Crystals were cooled using a Bruker LT2 low temperature device. Data collection was performed and the unit cell was initially refined using SMART (v5.625) [34]. Data reduction was performed using SAINT (v6.36A) [35] and XPREF (v6.12) [36]. Corrections were applied to the integrated structure factors for Lorentz, polarization, and absorption effects using SADABS (v2.03) [37] for **1a** and TWINABS (v1.05) [38] for **1b**. The structures were solved and refined with the aid of the programs in the SHELXTL-PLUS (v6.10) [39] system of programs. While the data processing and structure solution

Table 2
Crystal data for compounds **1a** and **1b**

	1a	1b · 0.25C ₆ H ₁₄
Formula	C ₅₇ H ₅₃ N ₈ SSiRu ₂	C _{71.5} H _{73.5} N ₈ S ₂ Si ₂ Ru ₂
Formula weight	1112.36	1367.32
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.411(1)	10.875(1)
<i>b</i> (Å)	16.530(1)	18.532(1)
<i>c</i> (Å)	17.004(1)	18.792(2)
α (°)	68.432(2)	99.746(2)
β (°)	83.805(2)	100.772(6)
γ (°)	71.927(2)	102.720(6)
<i>V</i> (Å ³)	2587.0(3)	3540.6(6)
<i>Z</i>	2	2
ρ_{calc} (g cm ⁻³)	1.428	1.283
μ (mm ⁻¹)	5.681	4.674
<i>T</i> (°C)	-75(2)	-75(2)
λ (Cu K α) (Å)	1.54178	1.54178
Reflections collected	21,306	17,787
Independent reflections	7222 [<i>R</i> _{int} = 0.034]	17,787 [<i>R</i> _{int} = 0.000]
Final <i>R</i> indices	<i>R</i> ₁ = 0.029, [<i>I</i> > 2 σ (<i>I</i>)] <i>wR</i> ₂ = 0.077	<i>R</i> ₁ = 0.062, <i>wR</i> ₂ = 0.165

of **1a** were quite routine, preliminary data collection on the crystal **1b** indicated that it was non-merohedrally twinned. The structure of **1b** was solved using the data from one of the components, while both components were used in the refinement using the HKLF 5 format. Final analysis revealed that there were two components with the approximate ratio of 52:48. The full-matrix least-squares refinement on *F*² included atomic coordinates and anisotropic thermal parameters for all non-H atoms except those of the solvent molecule. The solvent molecule is disordered over a special position and was refined with isotropic thermal parameters only. All hydrogen atoms were included using a riding model. Relevant information on the data collection and the figures of merit of final refinement are listed in Table 2.

4. Supporting information available

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC 275966 and 275965 for compounds **1a** and **1b**, respectively. Copies of this information may be obtained free of charge from, The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (Fax: +44 1233 336033; deposit@ccdc.cam.ac.uk or www: <http://ccdc.cam.ac.uk>).

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