ELSEVIER

Journal of Organometallic Chemistry 660 (2002) 1–5

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Short communication

Synthesis, characterization and electrochemistry of diruthenium complexes linked by aryl acetylide bridges

Stephanie K. Hurst, Tong Ren *

Department of Chemistry, University of Miami, 1301 Memorial Dr., Coral Gables, FL 33124, USA

Received 12 July 2002; received in revised form 6 August 2002; accepted 7 August 2002

Abstract

The reactions between $Ru_2(ap)_4Cl$ and the appropriate lithiated aryl acetylene resulted in the complexes $Ru_2(ap)_4(C{\equiv}C{-}4{-}C_6H_4C{\equiv}CX)$ with X as $SiMe_3$ (**1**), H (**2**) and $Ru_2(ap)_4$ (**3**), 1,3-$[Ru_2(ap)_4(C{\equiv}C)]_2(C_6H_4)$ (**4**), 1,3-$[\{Ru_2(ap)_4(C{\equiv}C)\}_2]C_6H_3{-}5{-}C{\equiv}CH$ (**5**) and 1-$[Ru_2(ap)_4(C{\equiv}C)]C_6H_3{-}3,5{-}(C{\equiv}CH)_2$ (**6**), where *ap* is 2-anilinopyridinate. The spectroscopic and electrochemical properties of the new complexes have been assessed. Complexes **3**, **4** and **6** display two-electron oxidation and reductions, implying the absence of any significant electronic interaction between the two $Ru_2(ap)_4$ units in these complexes. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Diruthenium; Acetylide; Electrochemistry; Paramagnetism; 2-Anilinopyridinate

1. Introduction

Transition metal-containing complexes linked via π-delocalized framework have attracted much recent interest as models for potential molecular devices [1]. Although systems based on mononuclear complex have been heavily investigated, significantly less work has been undertaken on similarly linked systems based on dinuclear complexes. One and two-dimensional structures have been constructed using bimetallic subunits, but these have for the most part been linked through dicarboxylate ligands [2]. An alternate methodology has been based on utilizing cyano-compounds to link bimetallic tetracarboxylate complexes through the axial sites [3]. Since the first synthesis of $Ru_2(ap)_4(C{\equiv}CPh)$ by Cotton and coworker [4], $Ru_2(ap)_4Cl$ has proven highly amenable to selective alkynylation [5,6]. The use of the $Ru_2(ap)_4$ unit in molecular design is appealing not only because of the large number of accessible redox states [7], but also because an additional acetylide ligand may be selectively attached to the parent complex at the second axial site [8]. Further exemplifying the depth and breadth of this field, Ru_2 and Rh_2 compounds bearing alkynyl ligands were also reported recently by the laboratories of Kühn [9] and Bear [10].

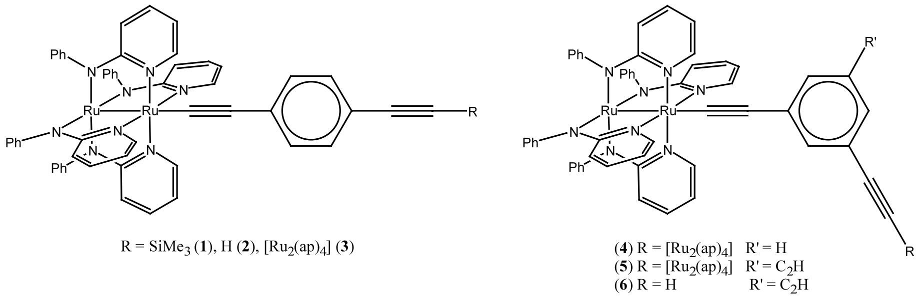
Dimeric metal complexes linked by μ-*C*,*C′*-polyynediyls have been investigated by Gladyz [11], Lapinte [12], Bruce [13], and Berke [14]; however, incorporation of such a linear architecture into multi-dimensional networks is difficult to achieve due to the extensive use of $CpML_3$ motifs in these studies. Alternatively, branched structures and even two-dimensional grids of metallaynes can be achieved through the π-bonding of η^2-C≡C [15] or alkynyl-substituted cyclo-butadienes [16]. It was therefore of interest to us to investigate linkage of $[Ru_2(ap)_4]$ through the axial site with aryl acetylide bridges. The parent aryl acetylenes are readily available and can provide not only structural diversity but may facilitate electronic communication between the metal centers. Such complexes might serve not only as electron reservoirs, but may be useful as synthons in supramolecular systems such as dendrimers. We report herein the syntheses and characterization of the *mono* and *di*-substituted acetylide complexes **1**–**6** (see Scheme 1), where, by considering the $Ru_2(ap)_4$ unit as a *substituent*, complexes **1**, **2** and **6** are *mono*-substituted and **3**, **4** and **5** are *di*-substituted.

---

* Corresponding author. Tel.: +1-305-2846617; fax: +1-305-2841880

E-mail address: tren@miami.edu (T. Ren).

0022-328X/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0022-328X(02)01809-0



R = SiMe$_3$ (**1**), H (**2**), [Ru$_2$(ap)$_4$] (**3**)

(**4**) R = [Ru$_2$(ap)$_4$] R' = H
(**5**) R = [Ru$_2$(ap)$_4$] R' = C$_2$H
(**6**) R = H R' = C$_2$H

Scheme 1. *Mono*- and *di*-substituted alkynyl adducts of Ru$_2$(*ap*)$_4$.

2. Results and discussion

2.1. Synthesis and characterization of σ-acetylide complexes

The synthetic methodologies employed for the preparation of the new complexes are adaptations of those successfully utilized for the preparation of the mono-ethynyl complexes [6]. Complexes **1**, **3**–**6** were resulted by treating Ru$_2$(*ap*)$_4$Cl with lithiated acetylenes prepared from the parent acetylene and *n*-BuLi in situ. Complex **2** was readily obtained by treating **1** with NaOH in THF, while the use of *n*-Bu$_4$NF resulted in formation of side products. Attempts to synthesize the ethynyl complexes via a base-promoted vinylidene intermediate were unsuccessful. Despite the use of large excesses of Ru$_2$(*ap*)$_4$Cl, attempts to form the tris-substituted complex 1,3,5-[Ru$_2$(*ap*)$_4$C≡C]$_3$C$_6$H$_3$ were unsuccessful. This may be due to steric hindrance, as Humphrey and co-workers have previously demonstrated that this factor prevents tris-substitution around 1,3,5-C$_6$H$_3$(C≡CH)$_3$ in the cases of Ni(PPh$_3$)(η^5-C$_5$H$_5$) [17] and *trans*-RuCl(dppe)$_2$ [18]. The preparation of **6** was complicated by the co-synthesis of **5**. We were unable to synthesize **6** without **5** even when less than a stoichiometric amount of Ru$_2$(*ap*)$_4$Cl was utilized. Nonetheless, the separation of **5** and **6** can be effected with column chromatography. It is possible that despite stoichiometric addition of *n*-BuLi, some 1,3-(LiC≡C)$_2$C$_6$H$_3$–5-C≡CH was formed in the lithiation step. Complex **3** was significantly less soluble than the other complexes and thus necessitated an alternate work-up. The reduction in solubility can presumably be attributed to the *para*-substitution around the phenyl bridge.

The new complexes were characterized by FAB mass spectrometry, microanalyses, UV–vis and IR spectroscopy. The IR spectra for the new ruthenium acetylide complexes display characteristic ν(C≡C) bands around 2048 cm^{-1}, accompanied in the case of **1** by a ν(C≡C) band at 2152 cm^{-1} corresponding to the trimethylsilyl-protected acetylene. The visible absorption spectra for these alkynylmetal complexes contain two intense absorption bands in the ranges of 753–757 and 477–480 nm and are analogous to those reported for [Ru$_2$(*ap*)$_4$(C≡CPh)] (735 and 480 nm). These peaks have been previously [4] attributed to π(Ru–N)→π*/σ*(Ru$_2$) and π(CCR)→π*/σ*(Ru$_2$) transitions for the low and high-energy bands, respectively. All the complexes reported here are paramagnetic, which preclude the collection of NMR data. Effective magnetic moments of **1**, **2** and **6** at room temperature are 3.92, 4.25 and 4.18 Bohr magneton (B.M.), respectively, which are consistent with a $S = 3/2$ ground state as previously noted [6]. Those of complexes **3**, **4** and **5** are, respectively 5.51, 5.29 and 5.83 B.M., which are consistent with a molecule containing two non-interacting $S = 3/2$ centers (expected spin-only value is 5.48 B.M.).

2.2. Electrochemical studies

The results of cyclic voltammetry (CV) measurements of the new ruthenium acetylide complexes are summarized in Table 1 together with previously reported data for related complexes. Previous work with diruthenium metallaynes demonstrated their redox flexibility, and the current examples are no exception. All the complexes studied here exhibit three redox couples: an oxidation (**A**), and two reductions (**B** and **C**), as shown by the cyclic voltammograms in Fig. 1. Couples **A** and **B** are quasi-reversible, as reflected by both the ΔE values and

Table 1
Cyclic voltammetric data for **1**–**6** and related complexes

Complex	$E_{1/2}$/V (**A**)	$E_{1/2}$/V (**B**)	E_{pc}/V (**C**)[a]
[Ru$_2$(*ap*)$_4$(C≡C–4-C$_6$H$_4$C≡CSiMe$_3$)] (**1**)	0.45	−0.83	−1.98
[Ru$_2$(*ap*)$_4$(C≡C–4-C$_6$H$_4$C≡CH)] (**2**)	0.45	−0.83	−1.98
[Ru$_2$(*ap*)$_4$(C≡CPh)] [b]	0.44	−0.88	–
1,4-[Ru$_2$(*ap*)$_4$(C≡C)]$_2$C$_6$H$_4$ (**3**)	0.43	−0.88	−2.05
1,3-[Ru$_2$(*ap*)$_4$(C≡C)]$_2$C$_6$H$_4$ (**4**)	0.44	−0.87	−2.04
1,3-[{Ru$_2$(*ap*)$_4$(C≡C)}$_2$]C$_6$H$_3$–5-C≡CH (**5**)	0.45	−0.85	−2.03
1-[Ru$_2$(*ap*)$_4$(C≡C)]C$_6$H$_3$–3,5-(C≡CH)$_2$ (**6**)	0.46	−0.81	−1.94

[a] Irreversible process.

[b] Originally measured in CH$_2$Cl$_2$ [4], re-measured in THF for comparison purposes.

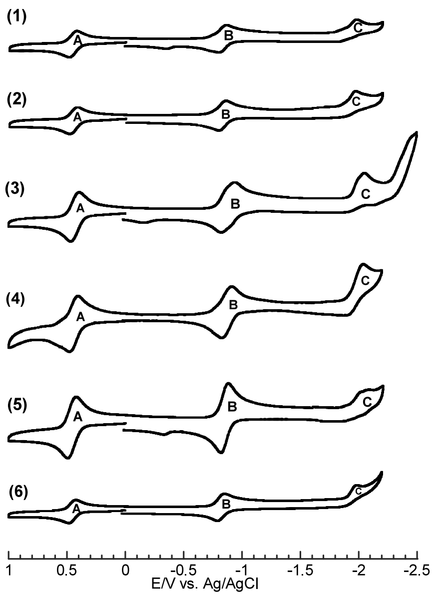


Fig. 1. Cyclic voltammograms of complexes **1**–**6** recorded in 0.20 M THF solution of $Bu_4^nNPF_6$ at a scan rate of 0.10 V s^{-1}.

near unity $i_{backward}/i_{forward}$ ratio. The $E_{1/2}$ value of the oxidation (**A**) is relatively invariant to the nature of the substituent with a separation of only 0.03 V between all complexes. Comparison of the $E_{1/2}$ values for the quasi-reversible reduction (**B**) reveals several trends. The presence of an alkyne substituent leads to an anodically shifted couple, the only complex with two terminal acetylene substituents (**6**) has the most positive value (−0.81 V) while the complexes with no free acetylene substituents (**3** and **4**) have values of −0.88 and −0.87 V, respectively, similar to that of $Ru_2(ap)_4(C{\equiv}CPh)$. The $E_{1/2}$ (**B**) does not significantly change upon altering the phenyl substituent pattern, either in conjugation with the metal (**4**) or out of conjugation (**3**). Neither is there an effect upon replacement of the trimethylsilyl group (**1**) with a terminal acetylene group (**2**). Although a larger variance (0.11 V) among E_{pc} (**C**)s was observed, structure-potential correlation was not made due to the irreversible nature of **C**.

Instead of exhibiting the pair-wise redox waves similar to those recorded for $[Ru_2(ap)_4]_2(\mu\text{-}C_{2m})$ ($m = 1$ and 2) [7], the di-substituted complexes simply display two-electron redox couples at the potentials corresponding to those of one-electron couples observed for mono-substituted species (note that the concentration of all complexes was normalized to 1.0 mM). This may be interpreted as the absence of strong electronic coupling between the $Ru_2(ap)_4$ units bridged by aryl acetylides. Clearly, the aryl portion of the bridging unit provides an inefficient conduit for electronic communication between $Ru_2(ap)_4$ units. This is in contrast to other systems where strong interaction takes places between metal centers separated by a $C{\equiv}C\text{-}4\text{-}C_6H_4C{\equiv}C$ bridge [19,20]. Following the Robin and Day classification [21], complexes **3**, **4** and **5** are Class 1 systems in which the metal centers are non-interacting.

3. Conclusions

The present studies have afforded *mono*- and *di*-substituted aryl acetylide complexes with the axially coordinated $Ru_2(ap)_4$ unit as the substituents. Although the complexes do not exhibit electronic coupling between the metal centers, the complexes are still of interest in the context of supramolecular chemistry. The presence of terminal $C{\equiv}CH$ groups in complexes **2**, **5** and **6** may provide a starting point for more sophisticated structures formed by Hay or Eglington coupling. Additionally, a vacant axial bonding site is available at the $Ru_2(ap)_4$ core, which presents opportunity for the synthesis of *trans*-alkynyl adducts. Such possibilities are currently being investigated.

4. Experimental

4.1. General conditions, reagents and instruments

n-BuLi was purchased from Aldrich, and silica gel from Merck. $Ru_2(ap)_4Cl$ [6], $1,3\text{-}C_6H_4(C{\equiv}CSiMe_3)_2$ [22], $1,4\text{-}C_6H_4(C{\equiv}CSiMe_3)_2$ [23] and $1,3,5\text{-}C_6H_3(C{\equiv}CH)_3$ [24] were prepared as previously described. THF and hexanes were distilled over Na/benzophenone under an N_2 atmosphere prior to use. Infrared spectra were recorded on a Perkin–Elmer 2000 FT-IR spectrometer using KBr disks. Absorption spectra were obtained with a Perkin–Elmer Lambda-900 UV–vis–NIR spectrophotometer. Cyclic voltammograms were recorded in 0.2 M $(n\text{-}Bu)_4NPF_6$ solution (THF, N_2-degassed) on a CHI620A voltammetric analyzer with a glassy carbon working electrode (diameter = 2 mm), a Pt-wire auxiliary electrode and a Ag/AgCl reference electrode. The concentration of diruthenium species was always 1.0 mM. The ferrocenium/ferrocene couple was observed at 0.575 V (vs. Ag/AgCl) at the experimental conditions.

4.2. Preparation of $[Ru_2(ap)_4(C{\equiv}C\text{-}4\text{-}C_6H_4C{\equiv}CSiMe_3)]$ (*1*)

$Ru_2(ap)_4Cl$ (190 mg, 0.21 mmol) was dissolved in 20 ml THF, to which was added $Me_3SiC{\equiv}C\text{-}4\text{-}C_6H_4C{\equiv}CLi$ (0.21 mmol) prepared in situ from $1,4\text{-}C_6H_4(C{\equiv}CSiMe_3)_2$ and *n*-BuLi. The solution changed from dark green to dark brown immediately upon the addition of the lithiated acetylene. After stirring for 1 h under argon, the solvent was removed under reduced pressure. The residue was loaded onto a silica gel column deactivated by 10% Et_3N in hexanes and eluted with EtOAc–hexanes–Et_3N (15/80/5, v/v), yielding pure

1 as a brown material which was recrystallized from $CHCl_3$–hexanes. Yield: (165 mg, 74% based on Ru). Data for **1**, R_f, 0.82 (EtOAc–hexanes–Et_3N, 20/70/10, v/v, the same combination is also used for the determination of other R_f's). Anal. Found(Calc.) for $C_{64}H_{64}Cl_3N_8Ru_2Si$ (**1**$\cdot C_6H_{14}\cdot CHCl_3$): C, 60.43(59.97); H, 5.31(5.03); N, 8.70%(8.74). MS-FAB (*m/e*, based on ^{101}Ru): 1078 [M^+ +H]; UV–vis, λ_{max} (nm, ε (M^{-1} cm^{-1})): 755(6400), 480(9000); IR, $\nu(C\equiv C)/cm^{-1}$: 2152(m), 2048(w); Electrochemical, $E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$: (A) 0.45, 0.069, 0.99; (B) −0.83, 0.073, 0.92; Magnetic (293 K): χ_{mol}(corr): 5.96×10^{-3} esu mol^{-1}. μ_{eff}: 3.92 μ_B.

4.3. Preparation of [$Ru_2(ap)_4(C\equiv C$–4-$C_6H_4C\equiv CH)$] (2)

[Ru_2(*ap*)$_4$($C\equiv C$–4-$C_6H_4C\equiv CSiMe_3$)] (**1**) (108 mg, 0.10 mmol) was dissolved in 20 ml THF to which was added NaOH (3.0 g). After stirring for 1 h under Ar the solution was filtered, extracted against water (2×50 ml), dried with Na_2SO_4 and the solvent removed under reduced pressure. The residue was placed on a sintered funnel and washed with MeOH and then hexanes, yielding pure **2** as a sticky brown material. Although the material was thoroughly dried under vacuum, we were unable to obtain a suitable sample for microanalysis. Yield: 78 mg (78% based on Ru). Data for **2**, R_f, 0.66. MS-FAB (*m/e*, based on ^{101}Ru): 1006 [M^+ +H]; MS-MALDI (*m/e*, based on ^{101}Ru): 1004 [M^+ −H]; UV–vis, λ_{max} (nm, ε (M^{-1} cm^{-1})): 754 (5100), 480 (7100); IR, $\varepsilon(\equiv CH)/cm^{-1}$, 3298(m), $\nu(C\equiv C)/cm^{-1}$, 2111(w), 2047(w); Electrochemical, $E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$: (A) 0.45, 0.070, 0.96; (B) −0.83, 0.066, 0.90; magnetic (293 K): χ_{mol}(corr): 6.98×10^{-3} esu mol^{-1}. μ_{eff}: 4.25 μ_B.

4.4. Preparation of 1,4-[$Ru_2(ap)_4(C\equiv C)]_2C_6H_4$ (3)

Ru_2(*ap*)$_4$Cl (201 mg, 0.219 mmol) was dissolved in 40 ml THF, to which was added 1,4-$C_6H_4(C\equiv CLi)_2$ (0.10 mmol) prepared in situ from 1,4-$C_6H_4(C\equiv CH)_2$ and *n*-BuLi. The solution changed from dark green to brown immediately upon the addition of the lithiated acetylene. After stirring for 1 h under argon, the solution was filtered and then the solvent was removed under reduced pressure. The residue was placed on a sintered funnel and washed with EtOAc–hexanes (20/80, v/v), yielding pure **3** as a brown crystalline material. Yield: 136 mg (72% based on 1,4-$C_6H_4(C\equiv CH)_2$). Data for **3**, R_f, 0.52. Anal. Found(Calc.) for $C_{98}H_{76}N_{16}Ru_4$: C, 61.96(62.54); H, 4.16(4.07); N, 11.71%(11.91). MS-FAB (*m/e*, based on ^{101}Ru): 1882 [M^+]; UV–vis, λ_{max} (nm, ε (M^{-1} cm^{-1})): 754(8900), 479(12 300); IR, $\nu(C\equiv C)/cm^{-1}$, 2046(w); Electrochemical, $E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$: *(A) 0.43, 0.070, 0.94; (B) −0.88, 0.117, 0.93. Magnetic (293 K):* χ_{mol}(corr): 12.76×10^{-3} esu mol^{-1}. μ_{eff}: 5.51 μ_B.

4.5. Preparation of 1,3-[$Ru_2(ap)_4(C\equiv C)]_2C_6H_4$ (4)

Ru_2(*ap*)$_4$Cl (235 mg, 0.257 mmol) was dissolved in 40 ml THF, to which was added 1,3-$C_6H_4(C\equiv CLi)_2$ (0.082 mmol) prepared in situ from 1,3-$C_6H_4(C\equiv CSiMe_3)_2$ and *n*-BuLi. The solution changed from dark green to brown immediately upon the addition of the lithiated acetylene. After stirring for 1 h under argon, the solvent was removed under reduced pressure. The residue was loaded onto a silica gel column deactivated by 10% Et_3N in hexanes and eluted with EtOAc–hexanes–Et_3N (40/60/5, v/v), yielding pure **4** as a brown crystalline material which were recrystallized from CH_2Cl_2–hexanes. Yield: 86 mg (56% based on 1,3-$C_6H_4(C\equiv CSiMe_3)_2$). Data for **4**, R_f, 0.52. Anal. Found(Calc.) for $C_{111}H_{106}Cl_2N_{16}Ru_4$ (**4**$\cdot 2C_6H_{14}\cdot CH_2Cl_2$): C, 62.91(62.32); H, 5.24(4.99); N, 10.46%(10.48). MS-FAB (*m/e*, based on ^{101}Ru): 1882 [M^+]; UV–vis, λ_{max} (nm, ε (M^{-1} cm^{-1})): 754(8900), 479(12300); IR, $\nu(C\equiv C)/cm^{-1}$, 2047(w); Electrochemical, $E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$: (A) 0.44, 0.066, 0.90; (B) −0.87, 0.087, 0.96. Magnetic (293 K): χ_{mol}(corr): 11.72×10^{-3} esu mol^{-1}. μ_{eff}: 5.29 μ_B.

4.6. Preparation of 1,3-[$\{Ru_2(ap)_4(C\equiv C)\}_2]C_6H_3$–5-$C\equiv CH$ (5)

Ru_2(*ap*)$_4$Cl (186 mg, 0.203 mmol) was dissolved in 30 ml THF, to which was added 1,3,5-$C_6H_3(C\equiv CLi)_3$ (0.069 mmol) prepared in situ from 1,3,5-$C_6H_3(C\equiv CH)_3$ and *n*-BuLi. The solution changed from dark green to dark brown immediately upon the addition of the lithiated acetylene. After stirring for 1 h under argon, the solvent was removed under reduced pressure. The residue was loaded onto a silica gel column deactivated by 10% Et_3N in hexanes and eluted with EtOAc–hexanes–Et_3N (40/60/5, v/v), yielding pure **5** as a brown material which was recrystallized from CH_2Cl_2–hexanes. Yield: 89 mg (67% based on triethynyl benzene). Data for **5**, R_f, 0.42; Anal. Found(Calc.) for $C_{113}H_{106}Cl_2N_{16}Ru_4$ (**5**$\cdot 2C_6H_{14}\cdot CH_2Cl_2$): C, 63.32(62.74); H, 5.12(4.94); N, 10.18%(10.36). MS-FAB (*m/e*, based on ^{101}Ru): 1906 [M^+]; UV–vis, λ_{max} (nm, ε (M^{-1} cm^{-1})): 759 (9200), 476 (13 100); IR, $\nu(\equiv CH)/cm^{-1}$, 3290(m), $\nu(C\equiv C)/cm^{-1}$, 2113(m), 2046(w); Electrochemical, $E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$: (A) 0.45, 0.082, 0.95; (B) −0.85, 0.060, 0.87. Magnetic (293 K): χ_{mol}(corr): 13.1×10^{-3} esu mol^{-1}. μ_{eff}: 5.83 μ_B.

4.7. Preparation of 1-[$Ru_2(ap)_4(C{\equiv}C)$]C_6H_3-3,5-($C{\equiv}CH)_2$ (**6**)

$Ru_2(ap)_4Cl$ (183 mg, 0.200 mmol) was dissolved in 20 ml THF, to which was added lithiated acetylene (0.064 mmol) prepared in situ from 1,3,5-$C_6H_3(C{\equiv}CH)_3$ and *n*-BuLi. The solution changed from dark green to dark brown immediately upon the addition of the lithiated acetylene. TLC analysis indicated the presence of both **5** and **6**. After stirring for 1 h under argon, the solvent was removed under reduced pressure. The residue was loaded onto a silica gel column deactivated by 10% Et_3N in hexanes and eluted with EtOAc–hexanes–Et_3N (linear gradient 15/85/5–40/60/5, v/v), yielding **5** and **6** as brown materials which were recrystallized from CH_2Cl_2–hexanes. Yields from workup: **5**, 29 mg (24% based on triethynyl benzene); **6**, 30 mg (46% based on triethynyl benzene). Data for **6**, R_f, 0.56. Anal. Found(Calc.) for $C_{59}H_{53}N_8O_3Ru_2$ ($\mathbf{6}\cdot C_6H_{14}\cdot CH_2Cl_2$): C, 62.77(63.10); H, 4.47(4.79); N, 9.75%(9.34). MS-FAB (*m*/*e*, based on ^{101}Ru): 1029 [M^+]; UV–vis, λ_{max} (nm, ε (M^{-1} cm^{-1})): 752 (7500), 477 (10400); IR, $\nu(\equiv CH)/cm^{-1}$, 3296(m), $\nu(C{\equiv}C)/cm^{-1}$, 2108(w), 2048(w); Electrochemical, $E_{1/2}$/V, ΔE_p/V, $i_{backward}/i_{forward}$: (A) 0.46, 0.061, 0.92; (B) −0.81, 0.067, 0.86; Magnetic (293 K): χ_{mol}(corr): 7.42×10^{-3} esu mol^{-1}. μ_{eff}: 4.18 μ_B.

Acknowledgements

We thank both the University of Miami and Petroleum Research Fund/ACS (36595-AC3) for the financial support, and Dr G. Zou for earlier exploratory work on the synthesis of compound **3**.

References

[1] (a) F. Paul, C. Lapinte, Coord. Chem. Rev. 180 (1998) 431;
(b) J.M. Tour, Acc. Chem. Res. 33 (2000) 791.

[2] (a) F.A. Cotton, C. Lin, C.A. Murillo, Acc. Chem. Res. 34 (2001) 759;
(b) F.A. Cotton, C. Lin, C.A. Murillo, Proc. Natl. Acad. Sci. USA 99 (2002) 4810;
(c) M. Eddaoudi, D.B. Moler, H.L. Li, B.L. Chen, T.M. Reineke, M. O'Keeffe, O.M. Yaghi, Acc. Chem. Res. 34 (2001) 319.

[3] (a) H. Miyasaka, C.S. Campos-Fernandez, R. Clerac, K.R. Dunbar, Angew Chem. Int. Ed. Engl. 39 (2000) 3831;
(b) H. Miyasaka, C.S. Campos-Fernandez, J.R. Galan-Mascaros, K.R. Dunbar, Inorg. Chem. 39 (2000) 5870.

[4] A.R. Chakravarty, F.A. Cotton, Inorg. Chim. Acta 113 (1986) 19.

[5] F.A. Cotton, S.E. Stiriba, A. Yokochi, J. Organomet. Chem. 595 (2000) 300.

[6] G. Zou, J.C. Alvarez, T. Ren, J. Organomet. Chem. 596 (2000) 152.

[7] T. Ren, G. Zou, J.C. Alvarez, Chem. Comm. (2000) 1197.

[8] (a) G. Xu, T. Ren, Organometallics 20 (2001) 2400;
(b) T. Ren, Organometallics 21 (2002) 732;
(c) G. Xu, T. Ren, J. Organomet. Chem. 655 (2002) 239.

[9] (a) J.-L. Zuo, E. Herdtweck, F.F.d. Biani, A.M. Santos, F.E. Kühn, New J. Chem. 26 (2002) 889;
(b) J.-L. Zuo, E. Herdtweck, F.E. Kühn, J. Chem. Soc. Dalton Trans. (2002) 1244.

[10] J.L. Bear, B. Han, Z. Wu, E.V. Caemelbecke, K.M. Kadish, Inorg. Chem. 40 (2001) 2275.

[11] (a) R. Dembinski, T. Bartik, B. Bartik, M. Jaeger, J.A. Gladysz, J. Am. Chem. Soc. 122 (2000) 810;
(b) J. Stahl, J.C. Bohling, E.B. Bauer, T.B. Peters, W. Mohr, J.M. Martín-Alvarez, F. Hampel, J.A. Gladysz, Angew Chem. Int. Ed. Engl. 41 (2002) 1871.

[12] (a) S. Le Stang, F. Paul, C. Lapinte, Organometallics 19 (2000) 1035;
(b) F. Paul, W.E. Meyer, L. Toupet, H. Jiao, J.A. Gladysz, C. Lapinte, J. Am. Chem. Soc. 122 (2000) 9405;
(c) F. Coat, P. Thominot, C. Lapinte, J. Organomet. Chem. 629 (2001) 39.

[13] M.I. Bruce, P.J. Low, K. Costuas, J.-F. Halet, S.P. Best, G.A. Heath, J. Am. Chem. Soc. 122 (2000) 1949.

[14] (a) S. Kheradmandan, K. Heinze, H.W. Schmalle, H. Berke, Angew Chem. Int. Ed. Engl. 38 (1999) 2270;
(b) F.J. Fernández, O. Blacque, M. Alfonso, H. Berke, Chem. Commun. (2001) 1266.

[15] (a) R.D. Adams, B. Qu, M.D. Smith, T.A. Albright, Organometallics 21 (2002) 2970;
(b) R.D. Adams, B. Qu, Organometallics 19 (2000) 2411.

[16] (a) U.H.F. Bunz, Y. Rubin, Y. Tobe, Chem. Soc. Rev. 28 (1999) 107;
(b) U.H.F. Bunz, in: A. De Meijere (Ed.), Carbon Rich Compounds II, Springer-Verlag, Berlin, 1999, p. 131;
(c) M. Laskoski, J.G.M. Morton, M.D. Smith, U.H.F. Bunz, Chem. Commun. (2001) 2590;
(d) M. Laskoski, W. Steffen, J.G.M. Morton, M.D. Smith, U.H.F. Bunz, Angew Chem. Int. Ed. Engl. 41 (2002) 2378.

[17] I.R. Whittall, M.P. Cifuentes, M.G. Humphrey, B. Luther-Davies, M. Samoc, S. Houbrechts, A. Persoons, S. Heath, A. Persoons, Organometallics 16 (1997) 2631.

[18] S.K. Hurst, M.P. Cifuentes, M.G. Humphrey, Organometallics 21 (2002) 2353.

[19] M.C.B. Colbert, J. Lewis, N.J. Long, P.R. Raithby, M. Younus, A.J.P. White, D.J. Williams, N.N. Payne, L. Yellowlees, D. Beljonne, N. Chawdhury, R.H. Friend, Organometallics 17 (1998) 3034.

[20] S.K. Hurst, M.P. Cifuentes, A.M. McDonagh, M.G. Humphrey, M. Samoc, B. Luther-Davies, I. Asselberghs, A. Persoons, J. Organomet. Chem. 642 (2002) 259.

[21] (a) C. Creutz, Prog. Inorg. Chem. 30 (1983) 1;
(b) R.J. Crutchley, Adv. Inorg. Chem. 41 (1994) 273.

[22] T.X. Neenan, G.M. Whiteside, J. Org. Chem. 53 (1988) 2489.

[23] S. Takahashi, Y. Kuriyama, K. Sonogashira, N. Hagihara, Synthesis (1980) 627.

[24] M. Osawa, H. Sonoki, M. Hoshino, Y. Wakatsuki, Chem. Lett. (1998) 1081.