were collected on a Bruker AM200 spectrometer operating at a frequency of 81 MHz, and were recorded with a $\approx 20°$ pulse length of 2 μs and a recycle time of 3–5 s. No proton decoupling was used, and so the relative intensities of the signals are quantitative. Spectra were referenced to phosphoric acid as the standard ($\delta = 0$). The data were processed with the PC version of WINNMR (Bruker).

Received: March 12, 1998 [Z11580IE]
German version: *Angew. Chem.* **1998**, *110*, 1773–1776

Keywords: liquid crystals · metathesis · nickel · polymers · thiophosphates

---

[1] P. Davidson, J.-C. Gabriel, A.-M. Levelut, P. Batail, *Europhys. Lett.* **1993**, *21*, 317–322.

[2] H. Zocher, *Z. Anorg. Allg. Chem.* **1925**, *147*, 91–114.

[3] a) P. Davidson, A. Garreau, J. Livage, *Liq. Cryst.* **1994**, *16*, 905–910; b) X. Commeinhes, P. Davidson, C. Bourgaux, J. Livage, *Adv. Mater.* **1997**, *9*, 900–903.

[4] J.-C. P. Gabriel, C. Sanchez, P. Davidson, *J. Phys. Chem.* **1996**, *100*, 11139–11143.

[5] P. Davidson, J.-C. Gabriel, A.-M. Levelut, P. Batail, *Adv. Mater.* **1993**, *5*, 665–668.

[6] Review: P. Davidson, P. Batail, J.-C. P. Gabriel, J. Livage, C. Sanchez, C. Bourgaux, *Prog. Polym. Sci.* **1997**, *22*, 913–936.

[7] A. Meerschaut, J. Rouxel in *Crystal Chemistry and Properties of Materials with Quasi-One-Dimensional Structures* (Ed.: J. Rouxel), Reidel, Hingham, MA, **1986**, pp. 205–279.

[8] W. Bronger, P. Müller, *J. Less-Common Met.* **1984**, *100*, 241–247.

[9] Y.-J. Lu, J. A. Ibers, *Comments Inorg. Chem.* **1993**, *14*, 229–243.

[10] a) S. H. Elder, A. van der Lee, R. Brec, E. Canadell, *J. Solid State Chem.* **1995**, *116*, 107–112; b) S. H. Elder, A. van der Lee, R. Brec, E. Canadell, *J. Solid State Chem.* **1995**, *117*, 432; c) K. Chondroudis, M. G. Kanatzidis, J. Sayettat, S. Jobic, R. Brec, *Inorg. Chem.* **1997**, *36*, 5859–5868.

[11] KMPS$_4$ compounds are soluble in DMF at all concentrations. Highly viscous gels (resembling modelling clay) have been obtained at concentrations as high as 2.2 mol L^{-1} (KMPS$_4 \cdot$6DMF).

[12] The difference between the crystal and the solution can be readily determined by uncrossing the polarizers, which reveals a crystal surrounded by a particle-free phase that flows when compressed; this confirms its fluid nature.

[13] Relaxation times are on the order of about 1 s at 10^{-2} mol L^{-1} and about 15 min at 1.2 mol L^{-1} (KMPS$_4 \cdot$11DMF).

[14] a) G. Champetier, L. Monnerie, *Introduction à la chimie macromoléculaire*, Masson, Paris, **1969**, pp. 351–365; b) S. Chandrasekhar, *Liquid Crystals*, Cambridge University Press, Cambridge, **1992**, pp. 69–71.

[15] Electron micrographs were obtained with a CM30T Philips microscope (LaB$_6$ cathode) operating at 300 kV. The spherical aberration was 2 mm, and the point resolution was 2.3 Å.

[16] Crystal data for (PPh$_4$)$_3$[Ni$_3$P$_3$S$_{12}$]: monoclinic, space group $P2_1/c$, $a = 15.828(2)$, $b = 10.099(1)$, $c = 47.112(6)$ Å, $\beta = 91.11(1)°$, 6862 independent reflections with $I \geq 3\sigma(I)$, $RF = 0.0624$, $R_wF = 0.0848$, min./max. residual electron density: $-0.61/0.76$ e Å^{-3}, $S = 1.88$. The data were collected on a Siemens CCD single diffractometer with an automated three-axis goniometer; Mo$_{K\text{-}L2,3}$ radiation was used. The data collected at room temperature were reduced to net intensities, and estimated standard deviations were calculated on the basis of counting statistics; Lorentz polarization corrections were applied, and equivalent reflections were averaged. The structures were solved by direct methods with SHELXTL (G. M. Sheldrick, SHELXTL version 5, Siemens Analytical X-Ray Instruments, Inc. Madison, WI) and refined with JANA98 (V. Petøièek, M. Dušek, JANA98 Crystallographic Computing System, Institute of Physics, Academy of Sciences of the Czeck Republic, Prague, **1998**). Final refinements were performed on F_0 with anisotropic atomic displacement parameters for Ni, P, and S atoms and isotropic parameters for C atoms. The positions of the H atoms were introduced in the structure factors calculations with the same isotropic atomic displacement as the C atoms on which they ride. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101227. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[17] As only one peak is observed for the chain, we assume that either there is no difference in the chemical shifts of phosphorus atoms in the middle and at the ends of a chain, or that the chains are so long that the intensities of the signals for phosphorus atoms at the ends are negligible with respect to those phosphorous atoms in the central part. The latter is more probable based on the observation from electron microscopy. No other peaks, apart from those from the chain and the cyclic structure, are observed during the in situ NMR study. If we assume that the chemical shift is different for the atoms at the ends and the middle of a chain, then the breaking of the chains must be the rate-limiting step for the cyclization, and hence the concentration of the chain fragments in solution is never high enough to be observed.

[18] S. C. Lee, R. H. Holm, *Angew. Chem.* **1990**, *102*, 868–884; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 840–856.

Organometallic Triskelia: Novel Tris(vinylideneruthenium(II)), Tris(alkynylruthenium(II)), and Triruthenium–Triferrocenyl Complexes**

Mitsunari Uno* and Pierre H. Dixneuf*

Dedicated to Professor Warren Roper
on the occasion of his 60th birthday

Multitopic carbon-rich metal complexes, with rigid conjugated branches are potentially useful for building carbon-rich networks,[1] supramolecular polymetallic assemblies,[2] and nanoarchitectures for material science.[3] They have found application as the core of metal-containing dendrimers[4, 5] and polymers,[6] and as the basis of liquid crystals.[7] Polymetallic complexes containing multiple identical redox systems are of special interest for electron storage[5, 8] and as modified electrodes[9] due to their ability to provide several electrons at the same potential.

We now report the novel polymetallic complexes containing reversible redox systems, and displaying a C_3-symmetric triskelion shape,[10] formed by activation of the tritopic polyyne $1,3,5\text{-}(HC{\equiv}CC_6H_4C{\equiv}C)_3C_6H_3$ (**1**) namely the first examples of tris(vinylideneruthenium(II)) complexes (**2**),

---

[*] Prof. Dr M. Uno,[+] Prof. Dr P. H. Dixneuf
UMR 6509 CNRS-Université de Rennes
"Organométalliques et Catalyse"
Campus de Beaulieu, F-35042 Rennes (France)
Fax: (+33)2-99-28-69-39
E-mail: dixneuf@univ-rennes1.fr

[+] Permanent address:
Institute of Scientific and Industrial Research
Osaka University, 8-1, Mihogaoka, Ibaraki, Osaka 567 (Japan)
Fax: (+81)68-53-5823
E-mail: uno@sanken.osaka-u.ac.jp

[**] This work was supported by Osaka University and CNRS especially through an associate researcher position to Dr. M. Uno.

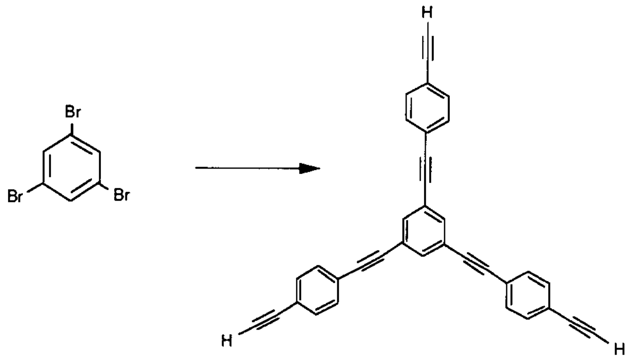
tris(alkynylruthenium) derivatives (**3** and **4**), and mixed triruthenium–triferrocenyl systems (**5**).

Tris(alkynylmetal) derivatives with identical Pt^{II}[4] or Fe^{II}[11] moieties and an apparently redox-passive bridge were synthesized from 1,3,5-triethynylbenzene. The bridge legs were too short to allow the incorporation of three bulky ruthenium(II) redox systems by direct activation of the terminal C≡CH bonds. We therefore synthesized the rigid, long-legged tripodal polyyne **1** from 1,3,5-tribromobenzene by successive catalytic reactions adapted from the preparation of unidimensional polyynes,[12] as indicated in Scheme 1.

The activation of **1** containing three terminal C≡CH functionalities was attempted with the bulky 16-electron species [RuCl(dppe)$_2$]PF$_6$, generated in situ from [RuCl$_2$(dppe)$_2$] in the presence of KPF$_6$ at room temperature. This reaction led to the isolation of the novel tris(vinylideneruthenium(II)) complex **2** [70%; $\tilde{\nu}$(Ru=C=C) = 1627 cm^{-1} (KBr)]. The ^{13}C NMR spectrum of complex **2** shows the three vinylidene (Ru=C) carbon nuclei as a multiplet at very low field ($\delta = 356.6$). The high symmetry of complex **2** is reflected by the singlets in the ^{13}C NMR spectrum for the two C≡C ($\delta = 88.23$ and 90.70) and Ru=C=*C* ($\delta = 109.47$) carbon nuclei, and in the ^{31}P NMR spectrum at $\delta = 37.55$ for the twelve Ph$_2$P phosphorus nuclei. The latter signal is consistent with a *trans* arrangement of the chloro and vinylidene ligands in the complex (Scheme 2).

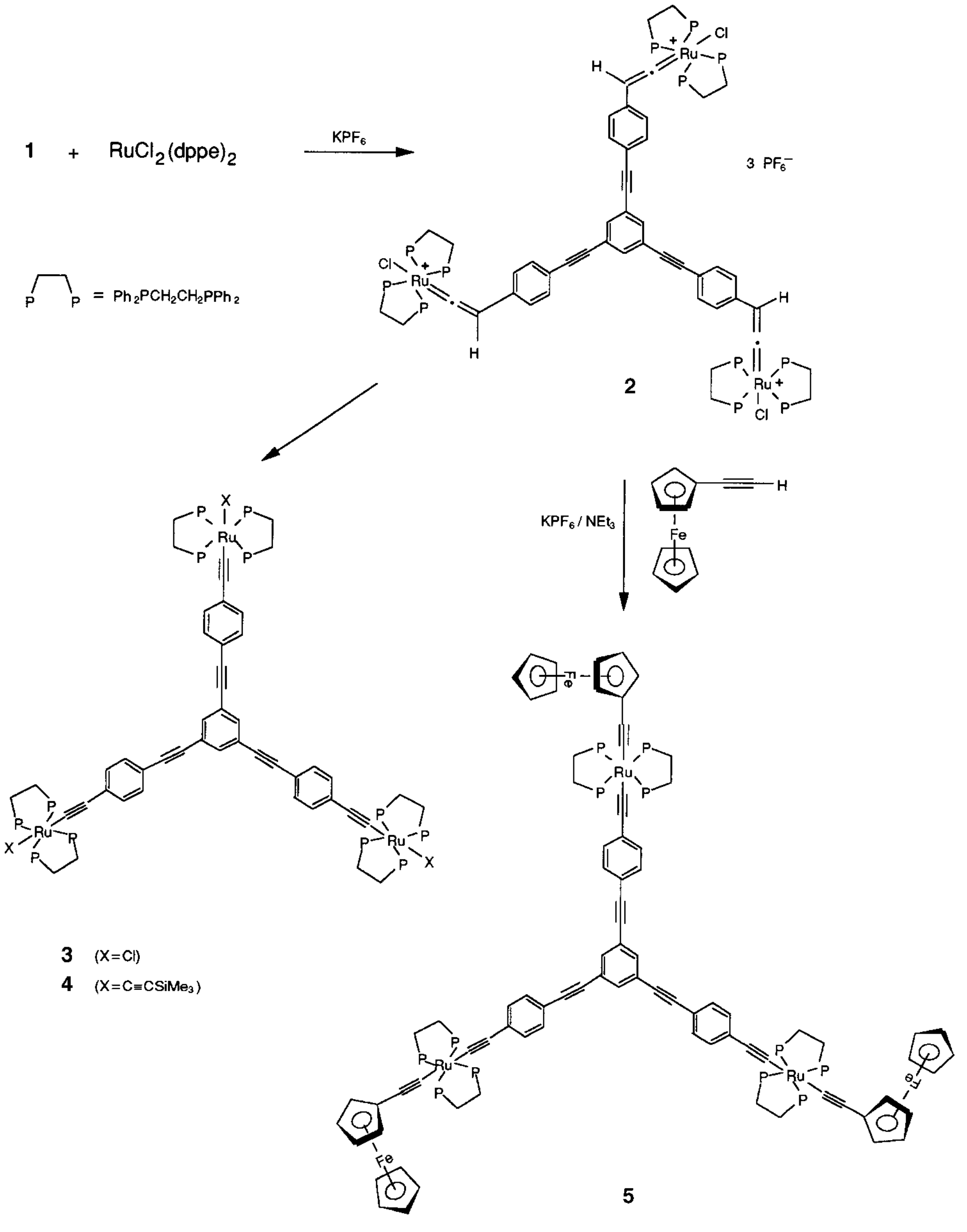
The tris(vinylidene) complex **2**, like most vinylideneruthenium(II) complexes,[13] is acidic and easily deprotonated on treatment with NEt$_3$ to afford the new yellow tris(alkynylruthenium) complex **3** [93% $\tilde{\nu}$(C≡C) = 2056 cm^{-1}; ^{31}P NMR $\delta = 49.93$ (s, 12 PPh$_2$)].

The complexes **2** and **3** show different behavior in their coupling to an additional functionalized alkynyl group. The remaining three halogen atoms of complex **3** can be substituted on reaction with trimethylsilylacetylene by the cooperative action of KPF$_6$ and NEt$_3$ for Ru–Cl bond dissociation and alkyne deprotonation. Complex **4** was isolated in 42% yield [$\tilde{\nu}$(cm^{-1}) = 2199 (CC≡CC), 2059 (CC≡CRu), 1992 (RuC≡CSi)] and displays mixed alkynyl ligands in a *trans* arrangement as indicated by the observation of only one singlet in its ^{31}P NMR spectrum [$\delta = 54.28$] (Scheme 2).



1

Scheme 1. Catalytic synthesis of the tripodal polyyne **1**. a) HC≡CSiMe$_3$, NEt$_3$, Pd/Cu catalyst; b) NaOH (aq); c) IC$_6$H$_4$C≡CSiMe$_3$, NEt$_3$, Pd/Cu catalyst; d) NaOH(aq).



Scheme 2. Synthesis of the triskelion-shaped, carbon-rich ruthenium complexes.

By contrast it was not possible to incorporate the ferrocenylacetylene unit directly into **3**, but the reaction of the tris(vinylidene) complex **2** with $FcC\equiv CH$, KPF_6, and NEt_3 led to the slow, but selective, formation of the novel mixed hexanuclear triruthenium–triferrocenyl complex **5** (92%) containing a linear arrangement of the alkynyl fragments [$\delta = 53.95$ (s, 12 PPh_2)] (Scheme 2).

The isolation of the tris(vinylidene) complex **2** is a keystep in the formation of **5**, as in the absence of NEt_3, the vinylidene ligand inhibits the introduction of an additional alkynyl group in the *trans* position and thus avoids the formation of oligomers from **1**.

A cyclic voltammetric study of complexes **2**–**4** showed that each produces a single quasi-reversible redox wave for the three ruthenium systems, but the peak separation is larger for the cationic tris(vinylidene) derivative **2** [$E_{1/2}$ versus Cp_2Fe^+/Cp_2Fe: +0.72 V ($\Delta E_p = 135$ mV) for **2**; +0.02 ($\Delta E_p = 100$ mV) for **3**; +0.03 ($\Delta E_p = 115$ mV) for **4**].[14] This unique oxidation wave shows that **3** and **4**, in particular, are able to provide three electrons at the same potential, and that their long-legged carbon-rich C_{3v} bridge *does not* allow significant communication between the three ruthenium(II) centres.

Of special interest is the behavior of **5**, which provides two reversible oxidation waves at $E_{1/2} = -0.28$ V ($\Delta E_p = 75$ mV) and at $E_{1/2} = +0.30$ V ($\Delta E_p = 75$ mV). These data show that both the sets of three ruthenium and three ferrocenyl units are able to provide three electrons at a specific potential. The redox potentials of **5** can be assigned on the basis of the redox potentials of **3** ($E_{1/2} = +0.02$ V), **4** ($E_{1/2} = +0.03$ V), ferrocenylacetylene ($E_{1/2} = +0.16$ V), and *trans*-[$Ru(C\equiv CPh)_2(dppe)_2$] ($E_{1/2} = +0.40$ V). Further evidence for the assignments is the observation that the linear mixed-metal derivative *trans*-[$FcC\equiv CRu(dppe)_2C\equiv CFc$] (**I**)[15] provides three reversible waves at $E_{1/2} = -0.36$, -0.16 and $+0.53$ V in its cyclic voltammogram. The wave of **5** at low potential ($E = -0.28$ V) is thus attributed to the three equivalent ferrocenyl groups and that at higher potential ($E = +0.30$ V) to the three (Ru^{II}/Ru^{III}) redox processes in the $Ru(dppe)_2$ subunits. The linkage of the alkynyl–$Ru(dppe)_2$ unit to the $C\equiv CFc$ groups, therefore, increases the ease of oxidation of the ferrocenyl groups. Surprisingly, the tripodal tris(alkynylruthenium(II)) moieties are electron-releasing toward the ferrocenyl groups. This is likely a result of the unique capability of a $RuC\equiv CCFc$ moiety to rearrange by oxidation into the stable allenylidene intermediate ($Ru^+=C=C=C(Fc)$.

The hexametallic species **5** contrasts with the linear trimetallic $FcC\equiv CRuC\equiv CFc$ derivative **I**: While **I** contains an organometallic redox-active communicating bridge between the two ferrocenyl groups, the tripodal triruthenium carbon-rich bridge in **5** behaves as an apparent redox-passive noncommunicating bridge between the ethynylferrocene units.

Experimental Section

2: Ligand **1** (0.135 g, 0.300 mmol), *cis*-[$RuCl_2(dppe)_2$] (0.872 g, 0.900 mmol), KPF_6 (0.331 g, 1.80 mmol), and CH_2Cl_2 (50 mL) were stirred at room temperature for 72 h. After evaporation of the solvent, a brown solid was obtained and purified by recrystallization from mixture of CH_2Cl_2 (100 mL) and pentane (200 mL). The pure tris(rutheniumvinylidene) complex **2** was isolated as a brown solid (0.771 g, yield 70%). ^1H NMR (300.133 MHz, $CDCl_3$): $\delta = 7.51$ (s, 3H, C_6H_3), 6.75 (AB, $J = 8.0$ Hz, 6H, 3 × 2H of C_6H_4), 5.59 (AB, $J = 8.0$ Hz, 6H, 3 × 2H of C_6H_4), 3.75 (br. s, 3H, 3 × $Ru=C=CH$); ^{13}C NMR (75.469 MHz, $CDCl_3$): $\delta = 356.6$ (m, $Ru=C$), 109.48 (br, $Ru=C=CH-$) 90.72, 88.23 ($C\equiv C$); ^{31}P NMR (121.496 MHz, $CDCl_3$): $\delta = 37.55$ (s, $RuPPh_2$), -143.40 (sept $J_{P,F} = 713$ Hz, PF_6); IR (KBr, cm^{-1},): $\tilde{\nu} = 2199$ ($C\equiv C$), 1627 ($C=C$); elemental analysis calcd for $C_{192}H_{162}Cl_3F_{18}P_{15}Ru_3$: C 62.57, H 4.43; found: C 62.43, H 4.62.

3: Complex **2** (0.869 g, 0.236 mmol) was suspended in THF (50 mL) and then triethylamine (1 mL) added. After stirring at room temperature for 1 h, the solvent was evaporated. The yellowish brown residue was dissolved in CH_2Cl_2 (40 mL) and washed with water. A yellow-orange powder was obtained and characterized as **3** (0.713 g, yield 93%). ^1H NMR: $\delta = 7.55$ (s, 3H, C_6H_3), 6.56 (AB, $J = 8.5$ Hz, 6H, 3 × 2H of C_6H_4); ^{13}C NMR: $\delta = 132.95$ (quint, $J_{P,C} = 15$ Hz, $RuC\equiv C$), 131.22 (C_{ipso} of C_6H_3), 130.40 (CH of C_6H_3), 114.39 ($RuC\equiv C$), 91.67, 88.39 ($C\equiv C$); ^{31}P NMR: $\delta = 49.90$ (s, $RuPCH_2$); IR (KBr, cm^{-1}): $\tilde{\nu} = 2199$, 2056 ($C\equiv C$); elemental analysis calcd for $C_{192}H_{159}Cl_3P_{12}Ru_3$: C 71.01, H 4.93; found: C 70.81, H 5.00.

4: To a solution of **3** (0.330 g, 0.1 mmol) and KPF_6 (0.130 g, 0.7 mmol) in CH_2Cl_2, (20 mL) was added trimethylsilylacetylene (0.2 mL 1.4 mmol) and NEt_3 (0.5 mL). After stirring for 72 h, the reaction mixture was filtered through celite and the filtrate evaporated. The yellow solid was dissolved in CH_2Cl_2 (40 mL) and washed with water. After drying in vacuo, **4** was obtained as a yellow powder and recrystallized from a mixture of CH_2Cl_2 and pentane (0.148 g, yield 42%). ^1H NMR: $\delta = 7.61$ (s, 3H, C_6H_3), -0.02 (s, 27H, 3 × $SiMe_3$); ^{13}C NMR: $\delta = 153.36$ (quint, $J_{C,P} = 14$ Hz, $RuC\equiv C$), 140.98 (quint, $J_{C,P} = 14$ Hz, $RuC\equiv C$), 131.06 (C_{ipso} of C_6H_3), 133.23 (CH of C_6H_3), 116.15, 115.61, 91.74, 88.29 ($C\equiv C$ carbon), 1.09 ($SiMe_3$); ^{31}P NMR: $\delta = 54.64$ (s, $RuPPh_2$); IR (KBr, cm^{-1}): $\tilde{\nu} = 2199$, 2058, 1992 ($C\equiv C$); elemental analysis calcd for $C_{207}H_{186}P_{12}Ru_3Si_3$: C 72.42, H 5.46; found: C 72.18, H 5.51.

5: Complex **2** (0.120 g, 0.032 mmol), ferrocenylethyne (0.050g, 0.23 mmol), and KPF_6 (0.055 g, 0.3 mmol) were dissolved in CH_2Cl_2 (15 mL) and then NEt_3 (0.2 mL) was added. After stirring for 5 days the reaction mixture was evaporated under reduced pressure to give a yellow solid. Recrystallization from CH_2Cl_2 and pentane gave **5** as small orange crystals (0.112 g, yield 92%). ^1H NMR: $\delta = 7.62$ (s, 3H, C_6H_3), 7.32 (AB, $J = 8.7$ Hz, 6H, 3 × 2H of C_6H_4), 6.59 (AB, $J = 8.7$ Hz, 6H, 3 × 2H of C_6H_4), 4.05 (m, 27H, $3C_5H_5 + 3C_5H_4$); ^{13}C NMR $\delta = 133.66$ (CH of C_6H_3), 125.14, 116.78 ($RuC\equiv C$), 122.80, 118.21 (m, $Ru\text{-}C\equiv C$), 92.18, 88.63 ($C_6H_3C\equiv CC_6H_4$), 69.306, 69.150, 68.45, 67.27 (C_5H_5, C_5H_4); ^{31}P NMR: $\delta = 53.95$ (br. s, PCH_2); IR (KBr, cm^{-1}): $\tilde{\nu} = 2199$, 2053 ($C\equiv C$); elemental analysis calcd for $C_{228}H_{186}P_{12}Fe_3Ru_3$: C 72.67, H 4.98; found: C 72.18, H 5.03.

Received: Janurary 5, 1998 [Z11324IE]
German version: *Angew. Chem.* **1998**, *110*, 1822–1824

Keywords: dendrimers · ferrocene · redox chemistry · ruthenium · vinylidene complexes

---

[1] a) F. Diederich, *Nature* **1994**, *369*, 149–207; b) F. Diederich in *Modern Acetylene Chemistry* (Eds.: P. J. Stang, F. Diederich), VCH, Weinheim, **1995**, 443; U. H. F. Bunz, *Synlett* **1997**, 1117–1127; R. Faust, F. Diederich, V. Gramlich, P. Seiler, *Chem. Eur. J.* **1995**, *1*, 111–117.

[2] a) D. Venkataraman, S. Lee, J. S. Moore, P. Zhang, K. A. Hirsch, G. B. Gardner, A. C. Covey, C. L. Prentice, *Chem. Mater.* **1996**, *8*, 2030–2040; b) M. J. Irwin, L. Manojlovic-Muir, K. W. Muir, R. J. Puddephatt, D. S. Yufit, *Chem. Commun.* **1997**, 219–220.

[3] a) J. S. Schumm, D. L. Pearson, J. M. Tour, *Angew. Chem.* **1994**, *106*, 1455–1547; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1360–1362; b) J. Zhang, J. S. Moore, Z. Xu, R. A. Aguirre, *J. Am. Chem. Soc.* **1992**, *114*, 2273–2274; c) S. Campagna, G. Denti, S. Serroni, A. Juris, M. Venturi, V. Riceunto, V. Balzani, *Chem. Eur. J.* **1995**, *1*, 211–221; d) M. A. Keegstra, S. De Feyter, F. C. De Schryver, K. Müllen, *Angew. Chem.* **1996**, *108*, 830–833; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 774–776.

[4] a) N. Ohshiro, F. Takei, K. Onitsuka, S. Takahashi, *Chem. Lett.* **1996**, 871–872; b) M. S. Khan, D. J. Schwartz, N. A. Pasha, A. K. Kakkar, B. Lin, R. Raithby, J. Lewis, *Z. Anorg. Allg. Chem.* **1992**, *616*, 121–124.

[5] P. Jutzi, C. Batz, B. Neumann, H.-G. Stammler, *Angew. Chem.* **1996**, *108*, 2272–2274; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2118–2121.

[6] I. Manners, *Angew. Chem.* **1996**, *108*, 1712–1731; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1603–1620.

[7] a) S. Takahashi, Y. Takai, H. Morimoto, K. Sonogashira, *J. Chem. Soc., Chem. Commun.* **1984**, 3–5; b) A. Altmann, V. Enkelmann, G. Lieser, U. H. F. Bunz, *Adv. Mater.* **1995**, *7*, 726.

[8] a) A. J. Bard, *Nature* **1995**, *374*, 13; b) D. Astruc, *New J. Chem.* **1992**, *16*, 305.

[9] B. Alonso, M. Morain, C. M. Casado, F. Lobete, J. Losada, I. Cuadrado, *Chem. Mater* **1995**, *7*, 1440–1442.

[10] A triskelion is a typical celtic symbol. Its stucture consists of three identical curved branches meeting in the center. [triskelia (plural), greek *triskeles* = three-legged].

[11] a) T. Weyland, C. Lapinte, G. Frapper, M. J. Calhorda, J.-F. Halet, L. Toupet, *Organometallics* **1997**, *16*, 2024–2031; b) H. Fink, N. J. Long, A. J. Martin, G. Opromolla, A. J. P. White, D. J. Williams, P. Zanello, *Organometallics* **1997**, *16*, 2646–2650.

[12] O. Lavastre, L. Ollivier, P. H. Dixneuf, S. Sinbandhit, *Tetrahedron* **1996**, *52*, 5495–5504.

[13] D. Touchard, P. Haquette, S. Guesmi, L. Le Pichon, A. Daridor, L. Toupet, P. H. Dixneuf, *Organometallics*, **1997**, *16*, 3640–3648.

[14] Cyclic voltammograms were obtained in CH_2Cl_2 solutions $[0.5-1.10^{-3}\,\mathrm{M}]$ with NBu_4PF_6 (0.1M) as electrolyte, 100 $\mathrm{mV\,s^{-1}}$ scan rate, Pt working electrode and counter-electrode (1 mm diameter), standard calomel electrode (SCE) reference electrode. Potentials are given with respect to $E(Cp_2Fe^+/Cp_2Fe) = 0.45$ V vs. SCE.

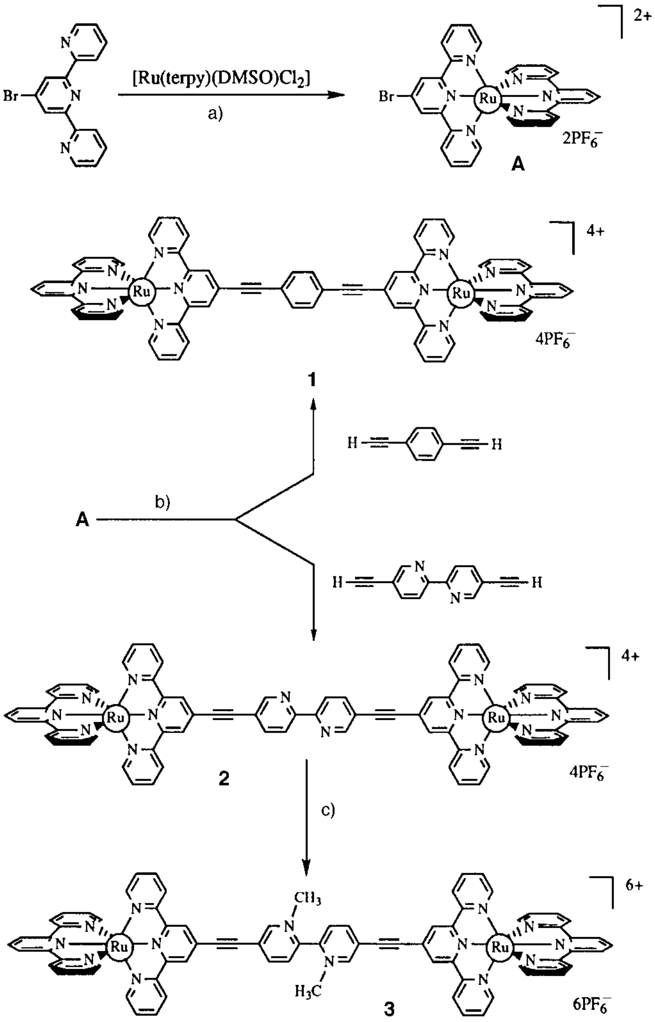
[15] C. Lebreton, D. Touchard, L. Le Pichon, A. Daridor, L. Toupet, P. H. Dixneuf, *Inorg. Chim. Acta* **1998**, *272*, 188–196.

Fine-Tuning the Electronic Properties of Binuclear Bis(terpyridyl)ruthenium(II) Complexes[**]

Muriel Hissler, Abdelkrim El-ghayoury, Anthony Harriman,[*] and Raymond Ziessel[*]

Bis(2,2′:6′,2″-terpyridine)ruthenium(II) is essentially nonemissive in fluid solution, and in deoxygenated acetonitrile at 20 °C the lifetime of the excited triplet state is about 550 ps.[1] Such photophysical properties compare unfavorably with tris(2,2′-bipyridine) ruthenium(II) and have restricted the utilization of $[Ru(terpy)_2]^{2+}$ as a building block for preparation of photoactive supramolecular assemblies. Recently, however, it was shown that attaching an acetylenic function at the 4′-position caused a dramatic prolongation of the triplet lifetime,[1, 2] especially in those cases where the acetylene group was the bridge for a ditopic ligand capped with "Ru(terpy)" metallo-fragments. This upgrade to the photophysical properties provides new opportunities to construct elaborate molecular assemblies around the photoactive Ru(terpy) unit.[3] The protracted triplet lifetime can be explained within the framework of the energy-gap law in terms of residence of the promoted electron in an extended π* orbital that encompasses much of the bridging ligand.[4] Enlargement of the LUMO lowers the triplet energy, and thereby curtails mixing with higher-energy, metal-centered excited states.[5] In attempting to exploit this effect further we have found that the acetylene residue must be attached directly to the coordinated terpyridine ligand while the polyacetylenic bridge cannot comprise more than four ethynylene groups. Longer carbon chains act as a low-energy sink for photons absorbed by the terminal chromophores.[6] We now describe an alternative strategy for extending the length of the acetylenic bridge that involves the use of a central aromatic core.

Thus, two new Ru(terpy)-based binuclear complexes were synthesized in which the butadiynylene bridge is interspersed with either a 1,4-phenylene (**1**) or a 5,5′-(2,2′-bipyridylene) (**2**) spacer. Preparation of these complexes was accomplished with an original strategy by using a metallo-synthon bearing a bromide group in conjunction with 1,4-diethynylbenzene or 5,5′-diethynyl-2,2′-bipyridine in Sonogashira-type cross-coupling reactions (Scheme 1). These coupling reactions proceed



Scheme 1. Synthetic method used to prepare the binuclear Ru^{II} terpy-based complexes **1** and **2**: a) Ag^+ dehalogenation in methanol (6 h) followed by reaction with terpy-Br in methanol at 80 °C (19 h); b) $[Pd^{II}(PPh_3)_2Cl_2]$ 6 mol%, CH_3CN/C_6H_6, $(iPr_2)NH$, 25 °C (6 days); c) CH_3I (excess) in CH_3CN, 80 °C (5 days), anion exchange.

---

[*] Prof. A. Harriman, Dr. R. Ziessel, M. Hissler, A. El-ghayoury
Laboratoire de Chimie
d'Electronique et Photonique Moléculaires
Ecole Européenne de Chimie, Polymères et Matériaux (ECPM)
Université Louis Pasteur
1, rue Blaise Pascal, F-67008 Strasbourg Cedex (France)
Fax: (+33) 388-41-68-25
E-mail: harriman@chimie.u-strasbg.fr

[**] This work was supported by the ECPM, the CNRS, and the Royal Society of London.