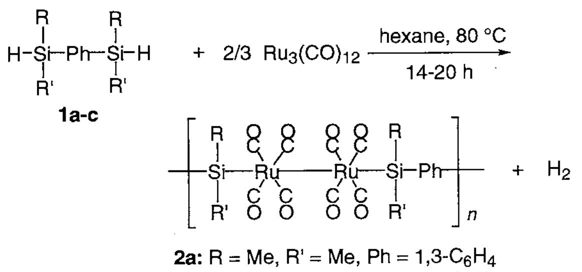
Synthesis and Spectral Properties of Novel Si-Ru-Ru-Si-C_6H_4 Polymers

Paul Nombel, Yasuo Hatanaka,* Shigeru Shimada, and Masato Tanaka*
National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305-8565

(Received November 10, 1998; CL-980852)

Dehydrogenative coupling reactions of bis(hydrosilyl)benzenes with $[Ru_3(CO)_{12}]$ afford moderate yields of the polymers $[\text{-SiRR'-Ru(CO)}_4\text{-Ru(CO)}_4\text{-SiRR'-C}_6\text{H}_4\text{-}]_n$ which exhibit large solvent-dependent change of the UV-VIS spectra. The absorption maximum of the polymer is markedly red-shifted, compared with monomeric complex $[PhMe_2SiRu(CO)_4Ru(CO)_4SiMe_2Ph]$.

Organometallic polymers in which metal fragments are linked with conjugated organic groups have attracted considerable attention due to the unique electronic properties attributed to the electron delocalization along the polymer backbone.[1] We report herein the synthesis and the spectral properties of organometallic polymers containing tetranuclear Si-Ru-Ru-Si units bridged by phenylene groups and their remarkable solvent-dependent change of the UV-VIS spectra in polar and nonpolar solvents.



2a: R = Me, R' = Me, Ph = 1,3-C_6H_4
2b: R = Me, R' = Ph, Ph = 1,4-C_6H_4
2c: R = Me, R' = Me, Ph = 1,4-C_6H_4

Our synthetic strategy to prepare these polymers involves dehydrogenative coupling of bis(hydrosilyl)benzenes **1** and $[Ru_3(CO)_{12}]$.[2] Treatment of $[Ru_3(CO)_{12}]$ (137 mg, 0.21 mmol) with 1,3-bis(dimethylsilyl)benzene (**1a**) (125 mg, 0.63 mmol) in hexane (5 ml) at 80 °C for 14 h under nitrogen produced a clear yellow solution with evolution of hydrogen.[3] After evaporation of the solvent under vacuum, acetone (6ml) was added to a yellow oily residue to precipitate the polymer, which was washed with the same solvent (6 ml x 7) to yield 47 mg (24% yield) of $[\text{-SiMe}_2\text{-Ru(CO)}_4\text{-Ru(CO)}_4\text{-SiMe}_2\text{-1,3-C}_6\text{H}_4\text{-}]_n$ (**2a**) as an air-stable yellow solid.[4] Analysis of **2a** by GPC using polystyrene standards and tetrahydrofuran (THF) as eluent revealed that M_W was 15000 and polydispersity (M_W/M_N) was 2.5. Polymer **2a** was soluble in THF and chloroform, and moderately soluble in acetonitrile and cyclohexane. The ^{29}Si NMR spectrum of **2a** in $CDCl_3$ exhibited a single peak at 5.43 ppm. A broad intense CO stretching band at 2004 cm^{-1} in the IR spectrum of **2a** (in KBr) was indicative of $Ru(CO)_4$-$Ru(CO)_4$ units in the polymer chain. These spectral data are nearly identical with those of model complex $[PhMe_2SiRu(CO)_4Ru(CO)_4SiMe_2Ph]$ (**3**) ($\delta^{29}Si$ = 5.28; ν(CO) = 2000 cm^{-1}) which is regarded as a segment of the polymer main chain.[5] The linear geometry of the metal units in **2a** as depicted in the above scheme was unequivocally confirmed by the X-ray structure of **3** (Figure 1).[6] Although each Ru atom in **3** is coordinated by four CO ligands, disorder effect in the region of CO ligands provides eight equidistant CO positions.[7]

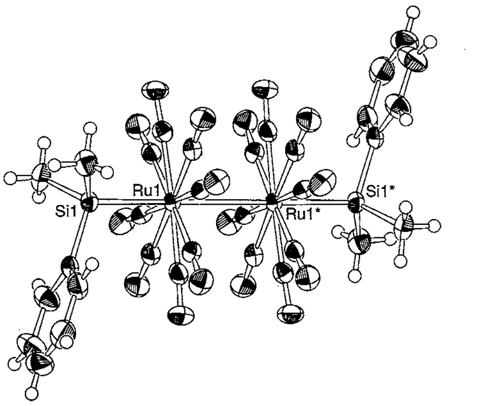


Figure 1. ORTEP view of $[Me_2PhSiRu(CO)_4Ru(CO)_4SiPhMe_2]$ (**3**) (50 % probability).

Similar reaction of 1,4-bis(methylphenylsilyl)benzene (**1b**) (0.27 mmol) with $[Ru_3(CO)_{12}]$ (0.18 mmol) afforded the desired polymer $[\text{-SiMePh-Ru(CO)}_4\text{-Ru(CO)}_4\text{-SiMePh-1,4-C}_6\text{H}_4\text{-}]_n$ (**2b**) (M_W = 11000, M_W/M_N = 2.6) in 36% yield as a yellow solid after reprecipitation from THF (1.5 ml) and ethanol (50 ml).[4] Polymer **2b** showed higher solubility than **2a** in organic solvents like THF, cyclohexane and acetonitrile; however, an attempt to prepare $[\text{-SiMe}_2\text{-Ru(CO)}_4\text{-Ru(CO)}_4\text{-SiMe}_2\text{-1,4-C}_6\text{H}_4\text{-}]_n$ (**2c**) by the reaction of 1,4-bis(dimethylsilyl)benzene (**1c**) with $[Ru_3(CO)_{12}]$ gave polymeric materials insoluble in common organic solvents.

The UV-VIS spectra of the obtained polymers are shown in Figure 2, in which the spectra of the complex **3** (dotted line) are also given for comparison. Polymer **2a** exhibited an intense absorption maximum at 385 nm in cyclohexane ((*a*), *e* = 2.5 x 10^4 $M^{-1}cm^{-1}$ per repeat unit) which is assignable to the $\sigma \rightarrow \sigma^*$ transition of the Ru-Ru bond.[8] Compared with the spectrum of complex **3** ((*c*), λ_{max} = 362 nm, *e* = 2.1 x 10^4 $M^{-1}cm^{-1}$), the position of the λ_{max} of **2a** was found to be markedly red-shifted by 23 nm. The observed shift can be ascribed to an electronic perturbation of the Ru-Ru bond caused by the elongation of the polymer chain, demonstrating a decreased $\sigma \rightarrow \sigma^*$ excitation energy of the Ru-Ru bonds in the polymer. In contrast, polymer **2b** exhibited slight red-shift of the λ_{max} relative to **3** in cyclohexane ((*b*), λ_{max} = 367 nm, *e* = 1.6 x 10^4 $M^{-1}cm^{-1}$ per repeat unit), presumably due to the presence of the bulky phenyl group on the silicon atom which can interrupt the effective interaction between the Si-Ru bond and the phenylene moiety.

These polymers exhibited a reversible spectral change with variation in solvent (solvatochromism). As shown in the UV-

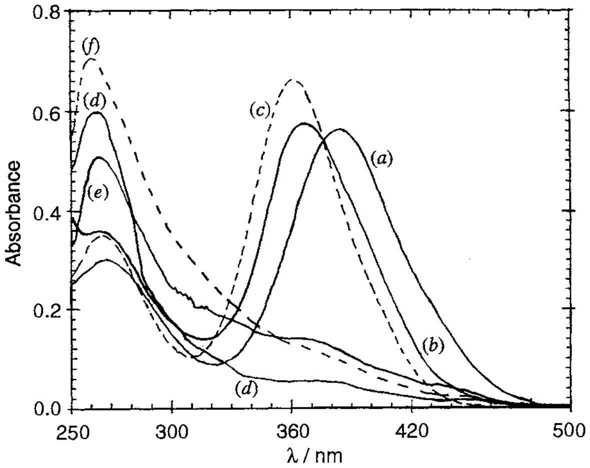


Figure 2. UV-VIS spectra of **2a** (*a*), **2b** (*b*) and complex **3** (*c*) in cyclohexane solution. UV-VIS spectra of **2a** (*d*), **2b** (*e*) and complex **3** (*f*) in acetonitrile solution.

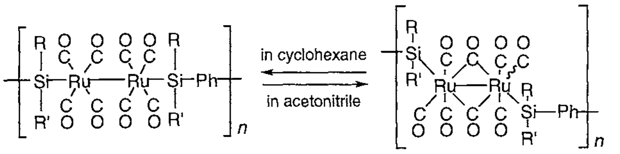
VIS spectrum of **2a** in acetonitrile solution (*d*), an intense band grew at 262 nm ($e = 1.3 \times 10^4$ $M^{-1}cm^{-1}$ per repeat unit) at the expense of a longer wave length absorption at 385 nm when the solvent was changed to acetonitrile from cyclohexane. After evaporation of the acetonitrile solution, the absorption at 385 nm reappeared on addition of cyclohexane to the residue.

Complex **3** displayed similar solvatochromic change of the absorption spectra in cyclohexane and acetonitrile ((*c*) and (*f*)); however, the change of the λ_{max} (λ_{max} = 261 nm in acetonitrile, $\Delta\lambda_{max}$ = 101 nm) was smaller than that of **2a** ($\Delta\lambda_{max}$ = 123 nm).

A reversible spectral change was also observed for **2b** ((*b*) and (*e*)), which showed an intense band at 367 nm in cyclohexane, but this band was completely replaced by a shorter wave length band at 264 nm ($e = 8.4 \times 10^3$ $M^{-1}cm^{-1}$ per repeat unit) in acetonitrile.

Unlike the solvatochromic shift of the λ_{max} observed for conjugated organic polymers such as polyacetylene[9] and polysilanes,[10] where the spectral shift is in the range 20-70 nm, the spectral change exhibited by **2a** and **2b** are very large ($\Delta\lambda_{max}$ = 103-123 nm). These results revealed that the optical properties of the present polymers are extremely sensitive to a change of physical environment, suggesting their potential applications as optoelectronic materials.[11]

The solvatochromic behavior of these polymers is best explained by assuming a solvent-dependent equilibrium between bridged and non-bridged forms of the Si-Ru-Ru-Si units. These polymers prefer the non-bridged form in cyclohexane, but are exclusively bridged in acetonitrile as indicated by the absorptions in the range 250-270 nm, characteristic of dinuclear bridging carbonyl complexes.[8,12] The IR spectra of **2a** and **2b** in acetonitrile also support this assumption, showing CO stretching at 1865 cm^{-1} for **2a** and 1870 cm^{-1} for **2b**, which are assignable to bridging carbonyls.[13] In solid state, however, **2a** and **2b** seem to exist in the non-bridged form as proved by the X-ray structure of **3**.



In summary, we have shown that the σ→σ* excitation energy of the organometallic polymers consisting of main group elements and transition metals was markedly reduced relative to the monomeric complex. The remarkable solvatochromism displayed by these polymers would be ascribed to the solvent-sensitive structural change of the Si-Ru-Ru-Si unit.

We are grateful to the Japan Science and Technology Corporation (JST) for financial support through the CREST (Core Research for Evolution Science and Technology) program and for a postdoctoral fellowship to P. N.

References and Notes

1 For reviews, see: a) "Inorganic and Organometallic Polymers II," ACS Symposium Series 572, ed by P. W. Neilson, H. R. Allcock, and K. J. Wynne, American Chemical Society, Washington, D.C. (1994). b) I. Manners, *Angew. Chem., Int. Ed. Engl.*, **35**, 1602 (1996).

2 S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. (A)*, **1969**, 2559.

3 Use of excess amount of **1a** (2 eq.) was essential for the formation of high molecular weight **2a**. The reaction using one equivalent of **1a** gave oligomeric product.

4 **2a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (s, 12 H, $SiCH_3$), 7.33-7.78 (m, 4 H, arom); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 5.99 ($SiCH_3$), 127.32, 131.91(arom), 136.01 (arom), 145.45 (arom), 206.47 (CO); ^{29}Si NMR (59.6 MHz, $CDCl_3$) δ 5.43; IR(KBr) 2004, 1408, 1361, 1249, 1102, 1065, 835, 806, 777, 758, 704, 683, 648, 588 cm^{-1}. **2b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15 (s, 6 H, $SiCH_3$), 7.36-7.66 (m, 14 H, arom); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 5.38 ($SiCH_3$), 127.89 (arom), 128.47 (arom), 133.13 (arom), 133.87 (arom), 142.81 (arom), 143.39 (arom), 205.63 (CO); ^{29}Si NMR (59.6 MHz, $CDCl_3$) δ 4.76; IR (KBr) 2005, 1429, 1253, 1123, 1100, 1080, 779, 737, 4700, 669, 590 cm^{-1}.

5 Complex **3** was prepared by the reaction of $Ru_3(CO)_{12}$ (0.33 mmol) and $PhMe_2SiH$ (0.99 mmol) in hexane at 80 °C for 12 h. NMR analysis of the reaction mixture revealed quantitative formation of **3**. Purification by florisil column chromatography (dichloromethane : pentane = 1 : 9) to give complex **3** as a yellow solid (65-70 % yield). **3**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (s, 12 H, $SiCH_3$), 7.26-7.61 (m, 10 H, arom); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 6.12 ($SiCH_3$), 127.89 (arom), 128.15(arom), 132.17(arom), 146.10(arom), 206.40 (CO); ^{29}Si NMR (59.6 MHz, $CDCl_3$) δ 5.28; IR (KBr) 2000, 1427, 1408, 249, 1108, 839, 810, 764, 741, 702, 688, 650, 623, 584 m^{-1}. Anal. Found: C, 41.10; H, 3.04%. Calcd for $C_{24}H_{22}O_8Si_2Ru_2$: C, 41.37; H, 3.18%.

6 Crystal data for **3**: MF = $C_{24}H_{22}O_8Ru_2Si_2$, MW = 696.74, *monoclinic*, a = 6.89(6) Å, b = 29.73(6) Å, c = 7.63(9) Å, β = 115.4(7)°, V = 1412(22) $Å^3$, space group $P2_1/c$, Z = 2, D_{calcd} = 1.638 g/cm^3. R (R_W) = 0.019 (0.026).

7 P. Braunstein, J. R. Galsworthy, and W. Massa, *J. Chem. Soc., Dalton Trans.*, **1997**, 4677.

8 H. B. Abrahamson, M. C. Palazzotto, C. L. Reichel, and M. S. Wrighton, *J. Am. Chem. Soc.*, **101**, 4123 (1979).

9 W. H. Kim, N. B. Kodali, J. Kumar, and S. K. Tripathy, *Macromolecules*, **27**, 1819 (1994).

10 K. Oka, N. Fujiue, T. Dohmaru, C.-H. Yuan, and R. West, *J. Am. Chem. Soc.*, **119**, 4074 (1997).

11 "Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics and Molecular Electronics," ed by J. L. Bredas and R. R. Chance, Kluwer, New York (1990).

12 T. J. Meyer and J. V. Caspar, *Chem. Rev.*, **85**, 187 (1985).

13 a) A. Bonny, *Coord. Chem. Rev.*, **25**, 229 (1978). b) G. Bor and K. Noack, *J. Organomet. Chem.*, **64**, 367 (1974).