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Synthesis of poly-yne polymer containing platinum and silicon atoms in the main chain by oxidative coupling and its reactions with transition-metal carbonyl complexes

Toshihiro Matsumoto, Sonae Kotani, Kyo Shiina and Kenkichi Sonogashira*
Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558, Japan

The platinum poly-yne polymer, $[-C\equiv C-SiMe_2-C\equiv C-Pt(PBu_3)_2-C\equiv C-SiMe_2-C\equiv C-]_n$ (2), was synthesized by the oxidative coupling of a silicon–platinum monomer, *trans*-$[(PBu_3)_2Pt(C\equiv C-SiMe_2-C\equiv CH)_2$ (1). The reaction of platinum poly-yne polymer 2 with dicobaltoctacarbonyl gave μ-coordinated complexes, $\{[-C\equiv C-SiMe_2-C\equiv C-Pt(PBu_3)_2-C\equiv C-SiMe_2-C\equiv C-][Co_2(CO)_6]_2\}_n$ (4). the electric conductivity of iodine adducts of the polymer complexes 4 was 3.0×10^{-5} S cm^{-1}. As an aid to spectroscopic characterization of the polymer complex 4, a model complex, $\{$*trans*-$[(PBu_3)_2Pt-(C\equiv C-SiMe_2-C\equiv CH)_2]\}$ $\{[Co_2(CO)_6]_2\}$ (3), was also prepared by the reaction of 1 with dicobaltocatacarbonyl. Selective coordination of $Co_2(CO)_6$ groups to $-SiMe_2-C\equiv CC\equiv C-Si(Me)_2-$ moieties and coordinative inertness of the $Pt-C\equiv C-$ moieties were confirmed by comparison of the NMR spectra of 3 with those of 4. All new compounds have been characterized by analytical and spectral analysis (IR, ^{1}H NMR).

Keywords: Metal poly-yne polymer, oxidative coupling, μ-coordinated complex, dicobaltoctacarbonyl, iodine doping, electric conductivity.

INTRODUCTION

There is a continuing interest[1-6] in the synthesis and properties of transition-metal acetylide polymers of the type $[-M(PBu_3)_2-C\equiv C-Y-C\equiv C-]_n$ (M = Pt, Pd or Ni), because of their liquid-crystal and non-linear optical properties.[7,8] We previously synthesized poly-yne polymers containing silicon and transition-metal atoms in the main chain by polycondensation between a transition-metal halide and a silylacetylene derivative using a cuprous halide as a catalyst in amines.[9,10] One of the purposes of introducing silicon atoms into the polymer main chain is to use their flexibility in chelation of the acetylenic polymer chains to transition metals. We report here an application of the oxidative coupling of *trans*-$[(PBu_3)_2Pt-(C\equiv C-SiMe_2-C\equiv CH)_2]$ (1) to the synthesis of high-molecular-weight polymers, and the reactions of these polymers with tansition-metal carbonyl complexes to give a new class of organometallic polymers.

EXPERIMENTAL

Apparatus

Infrared (IR) spectra and electronic spectra were recorded on a JEOL IRA-2 spectrometer and a Hitachi 200-12 spectrometer, respectively. $^{31}P\{^1H\}$ NMR spectra were measured on a JEOL FX 100 spectrometer at 40.25 MHz in dichloromethane solution referred to PPh_3 as an external standard. ^{1}H NMR spectra were measured at 400 MHz on a JEOL GX 400 spectrometer in a C_6D_6 solution referred to tetramethylsilane as an internal standard.

Molecular weights of polymers were determined by a TOHSO HLC-801A column using TSK-gel [G 2000 HG, 7.5 mm (i.d.) × 600 mm, +G 4000 HG, 7.5 mm (i.d.) × 600 mm] at 40 °C with tetrahydrofuran (THF) at 0.1 cm^3 min^{-1}). Calibration was carried out by using polystyrene standards. Intrinsic viscosity was measured using an Ubbelohde-type viscometer in a benzene solution at 30 °C. The electric conductivity of the polymers as compacted samples was measured by the conventional two-probe technique.[11]

Thin films of platinum poly-yne polymer 2 could be prepared from the benzene solution.

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* Author to whom correspondence should be addressed.

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Materials

N,*N*,*N*′,*N*′-Tetramethylethylenediamine (TMEDA) and diethylamine were distilled under nitrogen from calcium hydride. Dichloromethane and the other solvents were purchased from Wako Pure Chemical Co. and used without further purification. Dicobaltoctacarbonyl was purchased from Aldrich. The following compounds were prepared according to literature methods: *trans*-$[Pt(PBu_3)_2Cl_2]$,[12] diethynyldimethylsilane[13] and *trans*-$[Pt(PBu_3)_2(C{\equiv}C{-}SiMe_2{-}C{\equiv}CH)_2]$.[9]

PREPARATIONS

Platinum poly-yne polymer (2)

Oxygen ($7\ dm^3$) was passed into a mixture of cuprous chloride (500 mg, 5.0 mmol) and TMEDA ($2\ cm^3$) in $5\ cm^3$ of dichloromethane with vigorous stirring at room temperature. To the resulting green oxidant, silicon–platinum monomer **1**, *trans*-$[Pt(PBu_3)_2(C{\equiv}C{-}SiMe_2{-}C{\equiv}CH)_2]$ (400 mg, 0.49 mmol) and molecular sieve 3A (2.5 g) were added under an argon atmosphere. After being stirred for 3 h, the reaction mixture was evaporated under reduced pressure. In order to remove the cupric compounds formed, the residue was dissolved in benzene and the solution was filtered through a short alumina column (27 mm × 15 mm) using hexane as eluent. After evaporation of the filtrate, the white product was purified by precipitation from hexane into methanol. Finally, a benzene solution of the product was frozen and then freeze-dried under reduced pressure to give a white polymer **2** with $[\eta]=0.49$ (in benzene at 30 °C) and $\bar{M}_n=77\,000$ (estimated by GPC), yield 306 mg (76%).

Analysis: Calcd for $C_{36}H_{66}P_2PtSi_2$: C, 53.24; H, 8.19; P, 7.63. Found: C, 53.28; H, 8.30, P, 7.33%.

Reaction of silicon–platinum monomer 1 with $Co_2(CO)_8$

Addition to a stirred solution of silicon–plantinum monomer **1** (163 mg, 0.20 mmol) in cyclohexane ($10\ cm^3$) under an argon atmosphere of $Co_2(CO)_8$ (208 mg, 0.60 mmol) was accompanied by the evolution of gas. After the stirring had been continued for 6 h at room temperature, the solvent was evaporated under reduced pressure. A hexane solution of the crude product was chromatographed over silica gel (30 mm × 50 mm) using hexane as eluent. Recrystallization from ether at −70 °C gave dark red crystals of **3** in 90% yield, m.p. 66–67 °C.

Analysis: Calcd for $C_{48}H_{68}Co_4O_{12}P_2PtSi_2$: C, 41.60; H, 4.95; P, 4.70. Found: C, 41.42; H, 4.81; P, 4.80%.

Reaction of platinum poly-yne polymer 2 with $Co_2(CO)_8$

(a) Polymer 2/$Co_2(CO)_8$ = 1:1 reaction

To a solution of platinum poly-yne-polymer **2** (121 mg, 0.15 mmol equiv. for the polymer unit) in cyclohexane ($6\ cm^3$) was added $Co_2(CO)_8$ (52 mg, 0.15 mmol) under an argon atmosphere. After being stirred for 6 h at room temperature, the solution was concentrated to one-fifth of its original volume and chromatographed over silica gel (30 mm × 30 mm) using hexane/benzene (1:1) as eluent to give a dark red film (**4′**) (63 mg, 38% yield).

(b) Polymer 2/$Co_2(CO)_8$ = 1:3 reaction

To a solution of platinum poly-yne polymer **2** (89 mg, 0.11 mmol) in cyclohexane ($10\ cm^3$) was added $Co_2(CO)_8$ (104 mg, 0.30 mmol) under an argon atmosphere. A procedure similar to that described above gave a green polymer (**4**) in 45% yield.

Analysis: Calcd for $C_{48}H_{66}Co_4O_{12}P_2PtSi_2$: C, 41.65; H, 4.80. Found: C, 41.86, H, 4.86%.

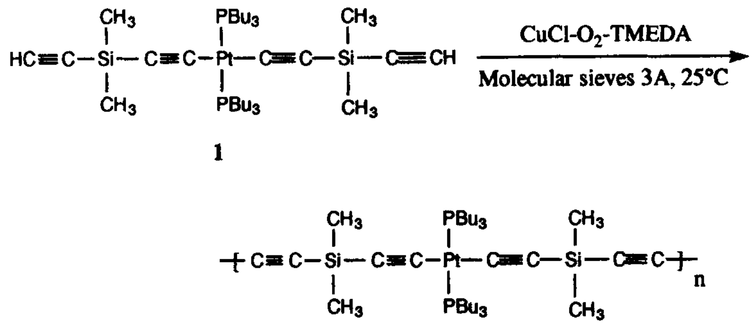
Doping with iodine

Poly-yne polymer **2** could easily be doped with iodine, simply by exposing it to the vapor in a Schlenk's tube. The iodine-doped polymer was relatively stable; dopant was lost very slowly. The dopant concentration was varied by adjusting the doping time. The amount of iodine absorbed was determined by measuring the weight increase of the polymer.

RESULTS AND DISCUSSION

Synthesis of platinum poly-yne polymer by oxidative coupling

The oxidative coupling of acetylenes is frequently a high-yield reaction and thus can be used as a polymerization system.[14] Furthermore, oxidative



$$HC\equiv C-\overset{CH_3}{\underset{CH_3}{Si}}-C\equiv C-\overset{PBu_3}{\underset{PBu_3}{Pt}}-C\equiv C-\overset{CH_3}{\underset{CH_3}{Si}}-C\equiv CH \xrightarrow[\text{Molecular sieves 3A, 25°C}]{CuCl\text{-}O_2\text{-}TMEDA} \left[C\equiv C-\overset{CH_3}{\underset{CH_3}{Si}}-C\equiv C-\overset{PBu_3}{\underset{PBu_3}{Pt}}-C\equiv C-\overset{CH_3}{\underset{CH_3}{Si}}-C\equiv C \right]_n \qquad [1]$$

1 **2**

coupling is extremely attractive for attaining a high degree of polymerization because there is no stoichiometric restriction for reactants having identical functional groups, while in a polycondensation between two reactants their ratio essentially affects the molecular weight of the product. A variety of α, ω-diethnyl compounds undergo oxidative coupling to form polymers in a system composed of an amine complex of a copper (I) salt and oxygen.[15, 16]

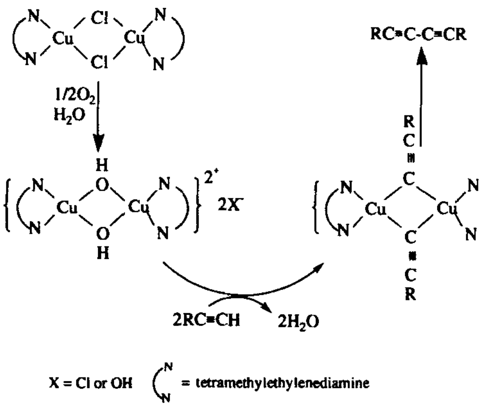
The Hay modification can be applied to 1,3-bis(dimethylethynyl)disiloxane.[15] However, diethynyldimethylsilane did not give the polymer, as the silicon–ethynyl bond was cleaved under the conditions of oxidative coupling. We have examined several systems involving various amines and copper salts such as pyridine and copper(I) acetate[17] in order to obtain a high-molecular-weight polymer from *trans*-$[(PBu_3)_2Pt(C\equiv C—SiMe_2—C\equiv CH)_2]$ **1**, and found that the oxidative polymerization of **1** is accomplished using the oxidant prepared from cuprous chloride and oxygen with TMEDA as a ligand (Eqn [1]). A mechanism for the oxidative coupling using a $CuCl–O_2–TMEDA$ reagent is shown in Scheme 1.

In this polymerization reaction, the choice of solvents is very important, because the precipitation of polymeric products during the polymerization reaction essentially prevents further reaction yielding high-molecular-weight products. The coupling reaction of **1** in acetone or pyridine, which are good solvents for the oxidant, proceeded smoothly to give a oligomer which was precipitated during the oxidative polymerization reaction. Dichloromethane is preferred in the present case since it is a good solvent for both the oxidant and the polymer formed (Table 1).

Since the silicon–acetylenic carbon bond, Si—C≡, may be cleaved by a free cupric ion, a large excess of TMEDA must be added to catch free cupric ions and this may retard the formation of the oxygen complex. Therefore, a large excess of oxygen and a longer reaction time are required for the formation of the oxygen complex.

Although the coupling reaction could be carried out in the presence of a catalytic amount of the oxidant with continuous bubbling of oxygen, we employed an excess of the oxidant and the reaction was carried out in an argon atmosphere or in a sealed system in order to prevent further oxidation of the polymer by oxygen.

Havinga and co-workers[18] recently reported that the oxidative polymerization of 1,8-nonadiyne was carried out smoothly by adding some molecualr sieves to the reaction mixture, thus removing the water[19] generated during the reaction (Scheme 1). The oxidative polymerization of **1** was carried out in both the presence and the absence of molecular sieves. Clearly, the presence of molecular sieves greatly favoured the formation of higher-molecular-weight **2** (Table 1, runs 2–4). Next, the time dependence of the degree of polymerization was traced by gel-permeation chromatography (runs 3–6).



Scheme 1 Mechanism for the oxidative coupling of acetylenes

Table 1 Oxidative coupling polymerization of silicon–platinum monomer **1** at 25 °C, in different conditions

Run	Conditions[a]	Reaction time (h)	Solvent	$\bar{M}_n$[b]	DP[c]
1	A	4	Acetone	Oligomer	—
2	A	4	CH_2Cl_2	20 000	25
3	B	1	CH_2Cl_2	28 000	35
4	B	3	CH_2Cl_2	77 000	95
5	B	6	CH_2Cl_2	76 000	94
6	B	11	CH_2Cl_2	71 000	88

[a] Conditions A: CuCl, 0.17 mmol; TMEDA, 0.3 cm³; *trans*-[$(PBu_3)_2Pt(C{\equiv}C{-}SiMe_2{-}C({\equiv}CH)_2$], 0.1 mmol; solvent, 0.7 cm³. Conditions B: as in A, but in the presence of molecular sieves 3A, 2.5 g.

[b] Estimated by GPC.

[c] Calculated using DP = $\bar{M}_n$/811.3.

Polymerization in dichloromethane proceeded smoothly at room temperature and after 3 h the degree of polymerization reached the maximum value of 95 ($\bar{M}_n$ = 77 000). Longer polymerization times resulted in gradually decreasing molecular weights. Thus, the oxidative polymerization of **1** carried out under the optimum conditions, i.e. adding some molecular sieves with an excess of the oxidant ($CuCl{-}O_2{-}TMEDA$) as a catalyst in dichloromethane at room temperature for 3 h, almost quantiatively gave high-molecular-weight platinum poly-yne polymer **2**, $[C{\equiv}C{-}SiMe_2{-}C{\equiv}C{-}Pt(PBu_3)_2-C{\equiv}C{-}SiMe_2{-}C{\equiv}C]_n$, in an almost quantitative yield (Eqn [1]). The structure of platinum poly-yne polymer **2** was identified from ^1H and ^{31}P NMR spectra and elemental analysis.

Characterization of platinum poly-yne polymer 2

Platinum poly-yne polymer **2** was obtained as a white film and was very stable in air. Physical and spectral data of polymer **2** and silicon–platinum monomer **1** are summarized in Table 2. The IR spectrum of platinum poly-yne polymer **2** exhibits intense bands in the region attributed to stretching frequencies (2050, 2070 cm^{-1}) of the acetylenic bonds and to bending frequencies (1250 cm^{-1}) of silicon–methyl bonds, and no trace due to acetylenic hydrogen bonds.

The electronic spectrum of platinum poly-yne polymer **2** is shown in Fig. 1 and spectroscopic data for **1** and **2** appear in Table 2. The lowest energy band of **2** assigned to the metal-to-ligand charge-transfer transitions (MLCT band) is observed at a λ_{max} value of 308 nm. The absorption band assigned to π-π^* transitions of diacetylenes in platinum poly-yne polymer **2** is observed at 230 nm as a shoulder. As indicated in Table 2, the electronic spectrum of the monomer complex **1** is essentially identical to that of **2** except for the peak of 230 nm observed in polymer **2**.

The ^{31}P NMR spectral analysis provides information about the gross geometry of a metal as the regularity of the polymer structure.[1, 10] The ^{31}P NMR spectrum of platinum poly-yne polymer **2** shows a resonance at 2.2 ppm with attendant satellites due to coupling (J = 2342 Hz) with ^{195}Pt

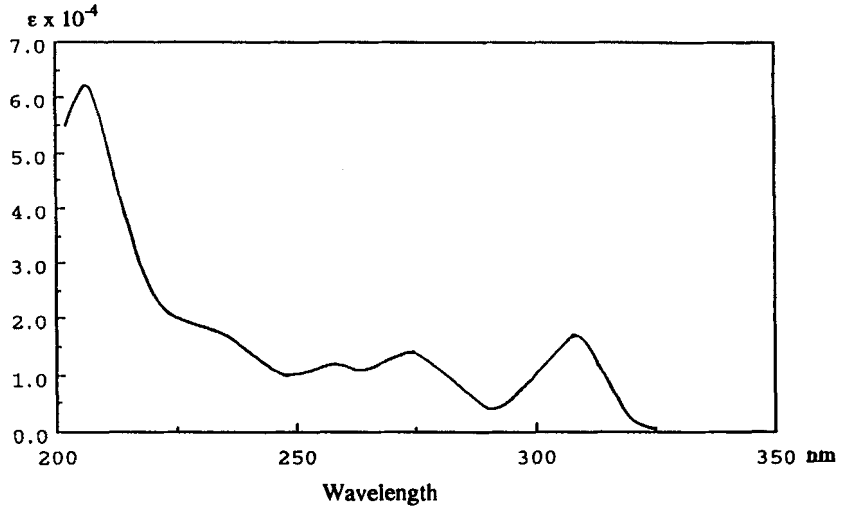


Figure 1 Electronic spectrum of platinum poly-yne poymer **2**.

Table 2 Spectral data of platinum poly-yne compounds **1–4**, and **4′**

					^{31}P NMR^{c}		UV^{d}	
Compound	IR (cm^{-1})^{a}		^{a}H NMR (ppm)^{b}		δ (ppm)	^{J}Pt–P (Hz)	λ (nm)	ε
1	δ_{Si-Me}	1250	Si—*Me*	0.48	2.3	2392	206	54 000
	$\nu_{C\equiv C}$	2050	P—*Bu*	0.95			258	11 000
	$\nu_{C\equiv CH}$	3280		1.45			274	12 000
				1.61			308	13 000
			C≡CH	2.13				
2	δ_{Si-Me}	1250	Si—*Me*	0.44	2.2	2342	206	62 000
	$\nu_{C\equiv C}$	2050	P—*Bu*	1.00			230	shoulder
		2070		1.50			258	12 000
				1.63			274	14 000
				2.11			308	17 000
3	δ_{Si-Me}	1250	Si—*Me*	0.55	1.9	2362	206	130 000
	$\nu_{\equiv CH}$	3110	P—*Bu*	0.97			258	48 000
	ν_{CO}	2050		1.47			274	48 000
		2080		1.54			310	36 000
		2120		2.09			350	13 000
			C≡CH	6.14			413	1700
4	δ_{Si-Me}	1250	Si—*Me*	0.8	1.54	2359	206	150 000
	ν_{CO}	2030	P—*Bu*	1.02			258	46 000
		2070		1.57	—		274	46 000
		2090		2.21	—		309	41 000
							450	1300
							590	750
4′	δ_{Si-Me}	1250	Si—*Me*	0.44	0.98		212	49 000
	ν_{CO}	2030		0.54	1.32		258	29 000
		2070		0.68	1.54	2359	274	29 000
		2090		0.84			308	24 000
		2100	P—*Bu*	1.02			430	920
				1.53			530	500
				1.64				
				2.18				

^{a} KBr tablets. ^{b} In C_6D_6; chemical shifts are referred to tetramethylsilane as an internal standard. ^{c} In CH_2Cl_2; chemical shifts are referred to D_3PO_4 as an external standard. ^{d} In cyclohexane.

(Fig. 2). These data for polymer **2** are consistent with the Pt(II) oxidative state and all-*trans* configurations. Furthermore, the sharp absorption suggests a fairly good regular alternate arrangement of *trans*-diethynylplatinum complex and 1,6-disila-1,1,6,6-tetramethyl-2,4-hexadiynediyl moieties, *trans*-$(PBu_3)_2Pt(—C{\equiv}C—)_2$ and $—SiMe_2—C{\equiv}C—C{\equiv}C—SiMe_2—$, in the main chain. The ^{1}H NMR spectrum of platinum poly-yne polymer **2** shows a single resonance at 0.44 ppm assigned to trimethylsilyl protons and multiplet peaks at 1.00–2.11 ppm assigned to tri-n-butylphosphine protons of integrated intensity ratio 12:54 from high to low field (Fig. 3). The observation of only one peak of dimethylsilyl protons suggests a fairly regular alternate arrangement in the polymer chain.

These data reveal that the oxidative polymerization proceeds according to Eqn (1) without any side reactions.

Reactions of silicon–platinum monomer 1 and platinum poly-yne polymer 2 with dicobaltoctacarbonyl

It is well known that $Co_2(CO)_8$ reacts easily with a large variety of alkynes to produce the μ-alkyne complexes, $[Co_2(CO)_6(RC{\equiv}CR')]$ (R, R′ = alkyl).[20–23] For example, the rections of bis(trimethylsilyl)acetylene and bis(trimethylsilyl)butadiyne with $Co_2(CO)_8$ afford μ-alkyne complexes, $[Co_2(CO)_6(Me_3Si—C{\equiv}C—SiMe_3)]$ as red crystals, and $\{[Co_2(CO)_6]_2(Me_3Si—C{\equiv}C—C{\equiv}C—SiMe_3)\}$ as green crystals, respectivley.[24] The

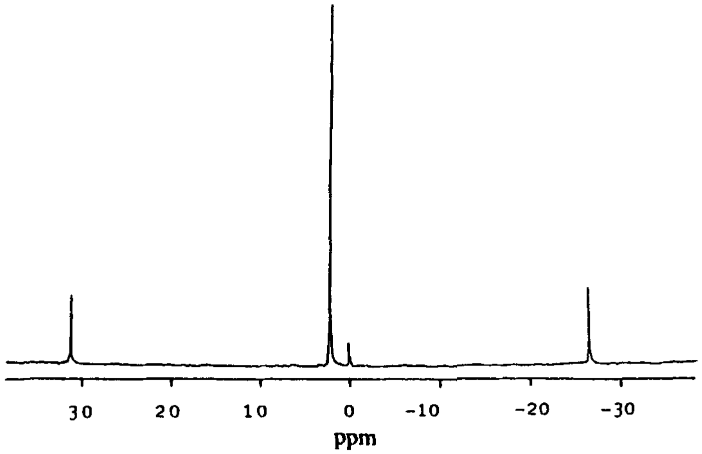


Figure 2 $^{31}P\{^{1}H\}$ NMR spectrum of platinum poly-yne polymer **2** in CH_2Cl_2.

above silylacetylenes also react with $[(\eta^5-C_5H_5)Ni(CO)]_2$ to give the μ-alkyne complexes.[25] We recently reported formation of μ-silylacetylene complexes such as $[\mathrm{HMe_2Si{-}C{\equiv}C{-}SiMe_2H}]Co_2(CO)_6$ by the reaction of bis(dimethylsilyl)acetylene with $Co_2(CO)_8$.[26]

Therefore, we examined the preparation of polymer 4 by the reaction of platinum poly-yne polymer **2** which contains acetylide and silylacetylene groups, $\mathrm{Pt{-}C{\equiv}C}$ and $\mathrm{Si{-}C{\equiv}C{-}C{\equiv}C{-}Si}$, with excess of $Co_2(CO)_8$. In order to prepare model complexes for the spectroscopic characterization of the polymer **4**, the reaction of monomer **1** with excess of $Co_2(CO)_8$ and equimolar reaction of polymer **2** with $Co_2(CO)_8$ were also studied. The reaction of silicon–platinum monomer **1** and platinum poly-yne polymer **2** with an excess of $Co_2(CO)_8$ in cyclohexane gave dark red crystals **3** (Eqn [2]) and a green polymer **4** (Eqn [3]) in a good yield, respectively. The equimolar reaction of **2** with $Co_2(CO)_8$ gave a red film (**4′**).

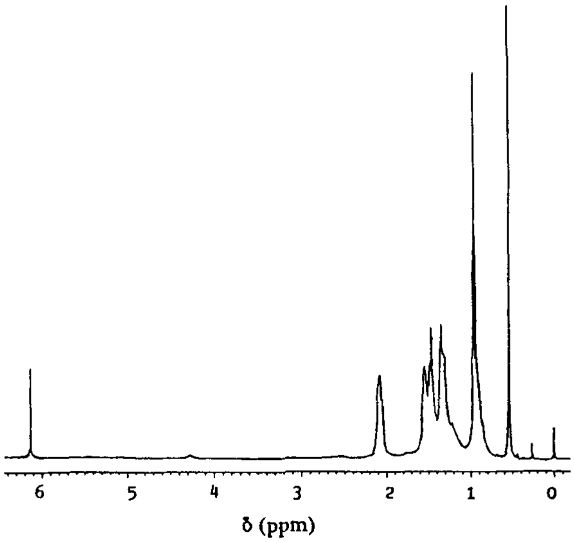
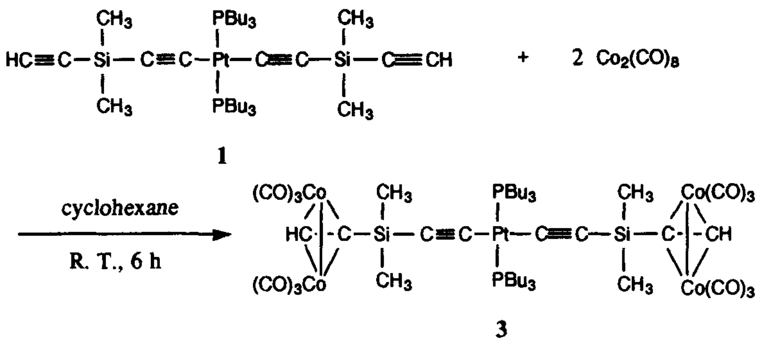


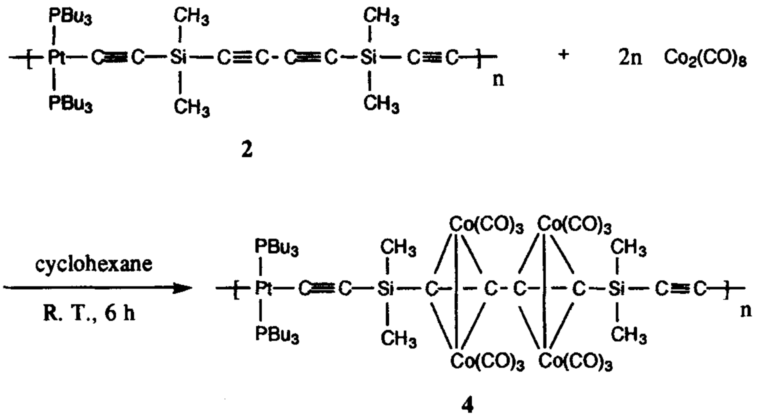
Figure 3 ^{1}H NMR spectrum of platinum poly-yne polymer **2** in C_6D_6.

Spectral data of **3**, **4** and **4′** are summarized in Table 2. The IR spectrum of **3** in the CO stretching region is very simlar to those of μ-alkyne complexes.[27,28] Furthermore, the stretching band of the terminal acetylenes, $\mathrm{C{\equiv}C{-}H}$, shifts to 3110 cm^{-1} from 3280 cm^{-1} by coordination of the $Co_2(CO)_6$ groups. In the ^{1}H NMR spectrum of **3**, resonances at 2.13 and 0.48 ppm attributed to terminal acetylene and dimethylsilyl protons for **1** shift to 6.14 and 0.55 ppm by the coordination of the $Co_2(CO)_6$ groups. The ^{31}P NMR spectrum of **3** is similar to that of silicon–platinum monomer **1**. The coupling constant (2362 Hz) of the plantinum–phosphine bond of **3** is of the order of that (2392 Hz) of **1**. Therefore, it is suggested that the $Co_2(CO)_6$ groups in the μ-alkyne complex **3** coordinate only terminal acetylenes of **1**, because the coordination of $Co_2(CO)_6$ groups to the acetylide $\mathrm{Pt{-}C{\equiv}C}$ is hindered by the steric hindrance of tri-n-butylphosphine ligands. Electronic spectra of **1** and **3** are shown in Fig. 4. In the electronic spectrum of **3**, the absorption band assigned to *d*–*d* transitions of metal–metal bonds was detected at 413 nm. the other MLCT transitions of **3** are similar to that of **1**, but their absorption intensity rises four- and five-fold. These data suggest weak interaction between cobalt and platinum atoms.

As shown in Table 2, spectroscopic data of **4**



[2]



[3]

are similar to those of the model complex 3. In the ^1H NMR spectrum of 4′, a resonance at 0.44 ppm attributed to dimethylsilyl protons in platinum poly-yne polymer 2 shifts stepwise to 0.54, 0.68 and 0.84 ppm by step coordination of the $Co_2(CO)_6$ groups. It is concluded from comparison of the ^1H and ^{31}P NMR data of 3, 4′ and 4 that all of the diacetylene groups of polymer 4 are coordinated by $Co_2(CO)_6$ groups. In the electronic spectrum of 4, the absorption band assigned to *d–d* transitions moves to lower energy compared with that of 3. This suggests that there is some

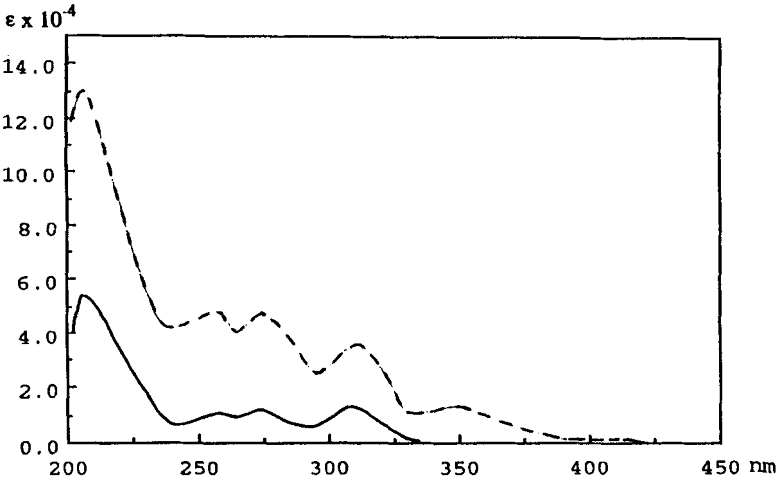
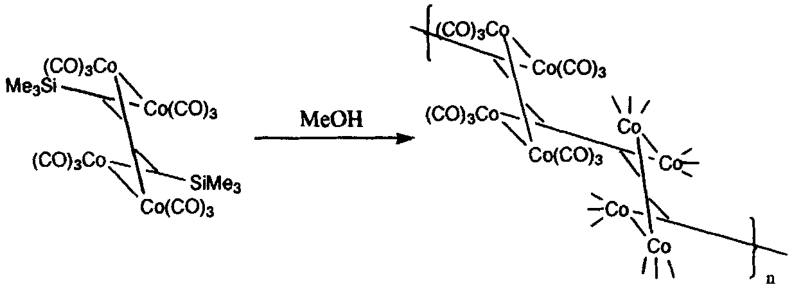


Figure 4 Electronic spectra of silicon–platinum monomer *1* (——) and its $Co_2(CO)_6$ derivative 3 (---) in cyclohexane.



[4]

Table 3 Electrical conductivity data for polymer complexes **2** and **4**

	σ_{RT}[a]	
Polymer	Undoped	Doped[b]
2	3.7×10^{-11}	1.2×10^{-9}
4	5.0×10^{-9}	3.0×10^{-5}

[a] RT = 300 K. [b] Doped with iodine by exposing the sample to the vapour in a desiccator. The dopant concentration, determined by measuring the weight increase of the sample, was adjusted to 20%.

interaction between cobalt atoms through diacetylene moities of the main chain in polymer complex **4**.

Recently Magnus and Becker[29] reported that a cobalt cluster complex, which was prepared from the reaction of bis(trimethylsilyl)butadiyne cobalt complex with methanol (Eqn [4]), exhibited electrical conductivity. This prompted us to examine the electric properties of the polymers. Polymer complexes **2** and **4** were insulators having electric conductivity (σ) of 3.7×10^{-11} and 5.0×10^{-9} cm^{-1}, respectively. When polymer **4** was doped with iodine, it turned deep black and showed an electric conductivity σ of 3.0×10^{-5} S cm^{-1} (Table 3). The electric conductivities of iodine and ferric chloride adducts (20% weight) of polymer complex **4** were about 10^{-5} and 10^{-6} S cm^{-1}, respectively. Polymer **4** was easily soluble in benzene and moderately stable in air. Dark green films were obtained from the solution. The iodine-doped film was obtained by exposing the film to iodine vapour in vacuum. The conductivity was found to increase linearly with iodine content up to 20 wt%.

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