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Synthesis of poly-yne polymers containing transition metals, disilane, disiloxane and phosphine groups in the main chain

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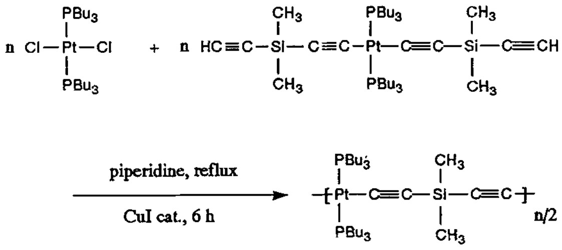
The synthesis and characterization of metal poly-yne polymers containing disilane, disiloxane and phosphine groups in the main chain are described. The platinum and palladium poly-yne polymers were synthesized by polycondensation reactions between a metal chloride and an α, ω-bisethynyl complex in amines in the presence of cuprous iodide as a catalyst. The nickel poly-yne polymers were synthesized by an alkynyl ligand exchange reaction between a nickel acetylide and an α, ω-bisethynyl complex in diethylamine in the presence of cuprous iodide as a catalyst. The reaction of the platinum poly-yne polymer, containing disiloxane groups in the main chain, with copper (I) salts afforded adducts of η^2-bonded σ-acetylide polymer complexes. The reactions of the palladium poly-yne polymer, containing phosphine groups in the main chain, with transition-metal carbonyl complexes afforded polymer complexes which have phosphorus in the main chain–transition-metal bonds. A concentrated solution of the platinum poly-yne polymer containing disiloxane groups in the main chain forms a lyotropic liquid crystal in dichloromethane or 1, 2-dichloroethane.

Keywords: Metal poly-yne polymer, disilane, disiloxane, ligand exchange reaction, cuprous iodide catalyst, lyotropic liquid crystal

INTRODUCTION

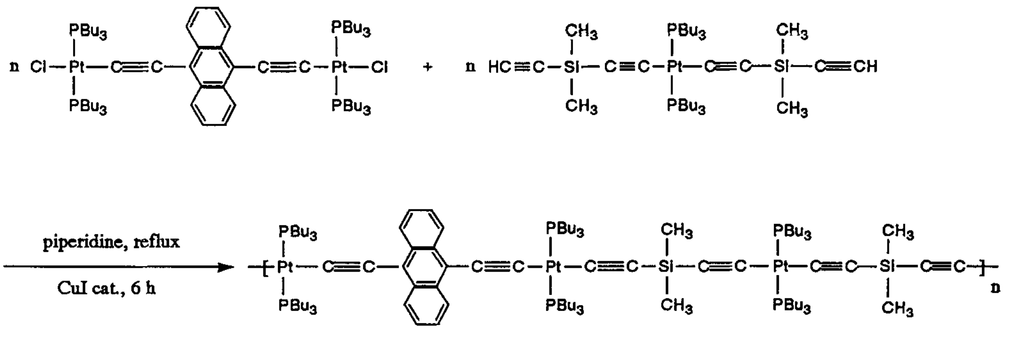
We recently reported a synthesis of platinum poly-yne polymers containing a monosilane and 9,10-anthracenediyl groups in the main chain (Eqns [1], [2]).[1] The platinum poly-yne polymers are of interest in terms of their characteristic properties based on *d*π(metal)-*p*π(acetylenic carbon)–empty *d*(silicon) orbital conjugation and regular arrangement of platinum atom in the polymer chain.



$$n\,\mathrm{Cl{-}Pt(PBu_3)_2{-}Cl} + n\,\mathrm{HC{\equiv}C{-}Si(CH_3)_2{-}C{\equiv}C{-}Pt(PBu_3)_2{-}C{\equiv}C{-}Si(CH_3)_2{-}C{\equiv}CH} \xrightarrow[\text{CuI cat., 6 h}]{\text{piperidine, reflux}} \left[\mathrm{Pt(PBu_3)_2{-}C{\equiv}C{-}Si(CH_3)_2{-}C{\equiv}C}\right]_{n/2}$$

[1]

Aryl- and alkynyl-substituted organodisilanes are photoactive under ultraviolet irradiation, and their photochemical behavior has been extensively studied.[2] Furthermore, when the films of poly[(disilanylene)ethynylenes] were treated with



[2]

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antimony(V)fluoride (SbF_5) vapor, highly conducting films were obtained.[3] Poly(organosiloxanes) have the inherent flexibility of the siloxane chain and the hydrophobicity and thermo-oxidative stability associated with the presence of alkyl or aryl groups linked to silicon atoms.[4]

The most important feature of polymers containing phosphine groups, such as poly(organophosphazenes), is the ease with which different organic or organometallic side groups can be attached to the backbone. This is a consequence of the substitutive mode of assembly used for these polymers.[5-12]

In this paper we report on the synthesis and characterization of metal poly-yne polymers containing disilane, disiloxane, and phosphine groups in the main chain and also on the reactions of these polymers with transition-metal carbonyl complexes and on studies of their concentrated solution properties.

EXPERIMENTAL

Apparatus

Infrared (IR) spectra were taken on KBr tablets with a JEOL IRA-2 spectrometer. Electronic spectra were recorded in cyclohexane solution with a Hitachi 200-10 spectrometer. ^1H NMR spectra were run on a JEOL GX 400 spectrometer in deuterobenzene (C_6D_6) solution, referred to tetramethylsilane as an internal standard. ^{31}P NMR spectra were run on a JEOL FX 100 spectrometer in dichloromethane (CH_2Cl_2) solution referred to (D_3)phosphoric acid (D_3PO_4) as an external standard. Molecular weights of polymers were determined by a TOSOH-HLC-801A as related to a polystyrene standard. Intrinsic Viscosities were measured using an Ubberlohde-type viscometer in benzene solution at 30°C.

Materials

Diethylamine, piperidine and acetonitrile were purchased from Wako Pure Chemical Co. and used without further purification. Tetrahydrofuran was distilled from sodium/benzophenone ketyl. 1,3-Diethynyl-1,1,3,3-tetramethyldisiloxane was purchased from Shin-etu Chemical Co. Ltd. 1,2-Diethynyl-1,1,2,2-tetramethyldisilane was a gift from Professor M. Ishikawa, Hiroshima University. The following compounds were prepared according to literature methods: *trans*-$[M(PBu_3)_2Cl_2]$ ($M = Pt$[13] and Pd[14]), *trans*-$[Ni(PBu_3)_2(C{\equiv}CH)_2]$,[15] $[Mo(CO)_3(CH_3CN)_3]$,[16] and $[Cr(CO)_3(CH_3CN)_3]$.[16]

Polymerization procedure

Platinum poly-yne polymer (2)

A catalytic amount of cuprous iodide was added to a deoxygenated solution of 1,2-diethynyl-1,1,2,2-tetramethyldisilane (0.5 g, 3.0 mmol) and *trans*-$[Pt(PBu_3)_2Cl_2]$ (2.0 g, 3.0 mmol) in piperidine (30 cm^3) under an argon atmosphere. After stirring at room temperature for 1 h the reaction mixture was heated to reflux for 6 h and then evaporated to dryness under reduced pressure. In order to remove the cuprous compounds, the residue was dissolved in hexane and the resulting solution was filtered through an alumina column (30 mm × 50 mm). After evaporation of the filtrate, a pale yellow product was collected and purified by reprecipitation from benzene into methanol. Finally, a benzene solution (20 cm^3) of the product was freeze-dried under reduced pressure to afford a pale yellow polymer **2** in 70% yield.

Anaysis: Calcd for $C_{32}H_{66}P_2Si_2Pt$: C, 50.30; H, 8.70. Found: C, 49.87; H, 8.97%.

Platinum poly-yne polymer (3)

Compound **3** was similarly prepared by a polycondensation reaction between *trans*-$[Pt(PBu_3)_2Cl_2]$ (2.0 g, 3.0 mmol) and 1,3-diethynyl-1,1,3,3-tetramethyldisiloxane (0.55 g, 3.0 mmol). A similar procedure gave a pale yellow polymer **3** in 70% yield.

Analysis: Calcd for $C_{32}H_{66}P_2Si_2OPt$: C, 49.27; H, 8.53; P, 9.94. Found: C, 49.00; H, 8.35; P, 7.80%.

Palladium poly-yne polymer (4)

Compound **4** was similarly prepared by a polycondensation reaction between *trans*-$[Pd(PBu_3)_2Cl_2]$ (0.45 g, 0.79 mmol) and 1,3-diethynyl-1,1,3,3-tetramethyldisiloxane (0.14 g, 0.79 mmol) at room temperature in diethylamine for 6 h. A similar procedure gave a pale yellow polymer **4** in 60% yield.

Analysis: Calcd for $C_{32}H_{66}P_2Si_2OPd$: C, 55.59, H, 9.62. Found: C, 54.91; H, 9.10%.

Palladium poly-yne polymer (5)

Compound **5** was similarly prepared by the polymerization reaction between *trans*-[Pd(PBu$_3$)$_2$Cl$_2$] (0.45 g, 0.79 mmol) and diethynylphenylphosphine (124 mg, 0.79 mmol) at room temperature in diethylamine for 6 h. A similar procedure gave a pale yellow polymer **5** in 60% yield.

Analysis: Calcd for $C_{34}H_{59}P_3Pd$: C, 61.21; H, 8.91; P, 13.9. Found: C, 61.72; H, 8.27; P, 12.41%.

Nickel poly-yne polymer (6)

Compound **6** was similarly prepared using CuI catalyst by alkynyl ligand exchange between *trans*-[Ni(PBu$_3$)$_2$(C≡CH)$_2$] (0.13 g, 0.26 mmol) and 1,2-diethynyl-1,1,2,2-tetramethyldisilane (40 mg, 0.26 mmol) under reflux of diethylamine for 7 h. A similar procedure gave a yellow polymer **6** in 45% yield.

Analysis: Calcd for $C_{32}H_{66}P_2Si_2Ni$: C, 61.23; H, 10.60. Found: C, 61.41; H, 9.99%.

Nickel poly-yne polymer (7)

Compund **7** was similarly prepared from alkynyl ligand exchange between *trans*-[Ni(PBu$_3$)$_2$(C≡CH)$_2$] (0.13 g, 0.26 mmol) and 1,3-diethynyl-1,1,3,3-tetramethyldisiloxane (47 mg, 0.26 mmol) under reflux of diethylamine for 7 h. A similar procedure gave a yellow polymer **7** in 45% yield.

Analysis: Calcd for $C_{32}H_{66}P_2Si_2ONi$: C, 59.7; H, 10.3. Found: C, 58.79; H, 9.75%.

Reactions of metal poly-yne polymers with cuprous iodide and transition-metal carbonyl complexes

Reaction of platinum poly-yne polymer 3 with cuprous iodide

A mixed solution of platinum poly-yne polymer **3** (0.24 g, 0.30 mmol) and cuprous iodide (60 mg, 0.30 mmol) in diethylamine (30 cm^3) was stirred under an argon atmosphere for 1 h and then evaporated to dryness under reduced pressure. The residue was dissolved in benzene and the solution was washed thrice with water. The organic layer was separated and removed under reduced pressure to give a yellow solid in 90% yield.

Reaction of palladium-poly-yne polymer 5 with [Mo(CO)$_3$(CH$_3$CN)$_3$]

A solution of palladium poly-yne polymer **5** (103 mg, 0.155 nmmol) in THF was added to a solution of [Mo(CO)$_3$(CH$_3$CN)$_3$] (19.1 mg, 0.051 mmol) in acetonitrile (5 cm^3) to precipitate a yellow solid. The reaction mixture was filtered to give a polymer complex in 60% yield. IR: ν_{CO} 1900, 1910, 1950 cm^{-1}.

Reaction of palladium poly-yne polymer 5 with [Cr(CO)$_3$(CH$_3$CN)$_3$]

The similar reaction of palladium poly-yne polymer **5** (103 mg, 0.155 nmmol) with [Cr(CO)$_3$(CH$_3$CN)$_3$] (13.2 mg, 0.051 mmol) afforded a yellow polymer complex in 60% yield. IR: ν_{CO}1850, 1890, 1900, 1930, 1990 cm^{-1}.

RESULTS AND DISCUSSION

Synthesis of metal poly-yne polymers

Previously we reported conventional methods for the preparation of transition-metal acetylide complexes by dehydrohalogenation between a metal halide and a terminal acetylene, and by alkynyl ligand exchange between a nickel acetylide and a terminal acetylene using cuprous iodide (CuI) catalyst in amines. These methods have been successively applied to the synthesis of the metal poly-yne polmers.[15,17]

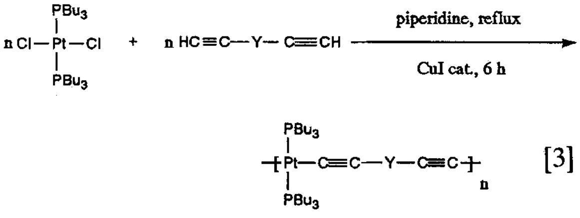
Poly[*trans*-bis(tri-*n*-butylphosphine)platinum 3,3-dimethyl-3-sila-penta-1,4-diyne-diyl] (**1**)[1] was synthesized by a convenient two-step condensation reaction in amine with a CuI catalyst, although poly[*trans*-(tri-*n*-butylphosphine)platinum 3,3,4,4-tetramethyl-3,4-disilahexa-1,5-diynediyl] (**2**) and poly[*trans*-(tri-*n*-butylphosphine)platinum 3,3,5,5-tetramethyl-3,5-disila-4-oxohepta-1,6-diynediyl] (**3**) were synthesized by one-step polycondensation reactions of a 1:1 mixture of *trans*-bis(tri-*n*-butylphosphine)dichloroplatinum(II) with 1,2-diethynyl-1,1,2,2-tetramethyldisilane and 1,3-

Table 1 Time dependence of molecular weight (M_n) and degree (DP) of polymerization[a]

Time (h)	Mn[b]	DP[c]
1	6,400	8
6	17,000	22
10	11,000	14

[a] Conditions: *trans*-$[(PBu_3)_2PtCl_2]$ and 1,3-diethynyl-1,1,3,3-tetramethyldisiloxane, 3.0 mmol; CuI, 1.0 mol%; piperidine (solvent), 30 cm^3; under reflux. [b] Estimated by GPC. [c] Calculated using DP = M_n/780.6.

diethynyl-1,1,3,3-tetramethyldisiloxane in the presence of cuprous iodide as a catalyst under reflux in piperidine for 6 h (Eqn [3]).



$$n\,\mathrm{Cl{-}\overset{PBu_3}{\underset{PBu_3}{Pt}}{-}Cl} + n\,\mathrm{HC{\equiv}C{-}Y{-}C{\equiv}CH} \xrightarrow[\text{CuI cat., 6 h}]{\text{piperidine, reflux}} \left[\mathrm{\overset{PBu_3}{\underset{PBu_3}{Pt}}{-}C{\equiv}C{-}Y{-}C{\equiv}C}\right]_n \qquad [3]$$

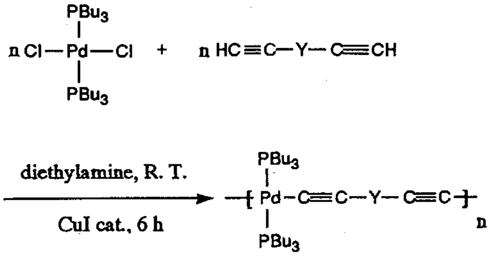
Y = $SiMe_2SiMe_2$: **2**

Y = $SiMe_2OSiMe_2$: **3**

For example, the time dependence of the degree of polymerization traced by gel-permeation chromatography of the platinum poly-yne polymer **3** is shown in Table 1. The polymerization of **3** carried out under optimum conditions, i.e. in the presence of a CuI catalyst in piperidine under reflux for 6 h gave a high-molecular-weight (m_n) polymer: $M_n = 17000$ ($n = 22$).

Platinum poly-yne polymers **2** and **3**, which were purified by alumina column chromatography with a hexane eluent and reprecipitation from benzene into methanol, have a refractive index of $[\eta]^{30\,^{\circ}\mathrm{C}} = 0.17$ and 0.18 respectively (in benzene), $M_n = 15000$ and 17000 (Table 2).

Palladium poly-yne polymers, poly[*trans*-bis(tri-*n*-butylphosphine)palladium 3,3,5,5-tetramethyl-3,5-disila-4-oxohepta-1,6-diynediyl] (**4**) and poly[*trans*-bis(tri-*n*-butylphosphine)palladium 3-phenyl-3-phosphapenta-1,4-diynediyl] (**5**), were synthesized by polycondensation reactions of *trans*-bis(tri-*n*-butylphosphine)dicloropalladium(II) with 1,3-diethynyl-1,1,3,3-tetramethyldisiloxane and diethynylphenylphosphine with a CuI catalyst in diethylamine at room temperature for 6 h (Eqn [4]).



$$n\,\mathrm{Cl{-}\overset{PBu_3}{\underset{PBu_3}{Pd}}{-}Cl} + n\,\mathrm{HC{\equiv}C{-}Y{-}C{\equiv}CH} \xrightarrow[\text{CuI cat., 6 h}]{\text{diethylamine, R. T.}} \left[\mathrm{\overset{PBu_3}{\underset{PBu_3}{Pd}}{-}C{\equiv}C{-}Y{-}C{\equiv}C}\right]_n \qquad [4]$$

Y = $SiMe_2OSiMe_2$: **4**

Y = PPh: **5**

The polymerizations carried out under optimum conditions, i.e. in the presence of CuI catalyst in diethylamine at room temperature for 6 h gave high-molecular weight polymers **4**, $M_n = 14000$, and **5**, $M_n = 12000$ (Table 2). Palladium poly-yne polymer **4** was purified by alumina column chromatography with a hexane eluent and reprecipitation from benzene into methanol; however, **5** was only purified by reprecipitation from benzene into methanol because it was oxidized over alumina.

Nickel poly-yne polymers, poly[*trans*-bis(tri-*n*-butylphosphine)nickel 3,3,4,4-tetramethyl-3,4-disilahexa-1,5-diynediyl] (**6**) and poly[*trans*-bis(tri-*n*-butylphosphine)nickel 3,3,5,5-tetramethyl-3,5-disila-4-oxohepata-1,6-diynediyl] (**7**), were synthesized by alkynyl ligand exchange between *trans*-bis(tri-*n*-butylphosphine)diethynylnickel(II) and 1,2-diethynyl-1,1,2,2-tetramethyldisilane or 1,3-diethynyl-1,1,3,3-tetramethyldisiloxane with a CuI catalyst in diethylamine under reflux for 7 h (Eqn [5]).

Table 2 Molecular weight and physical data of metal poly-yne polymers

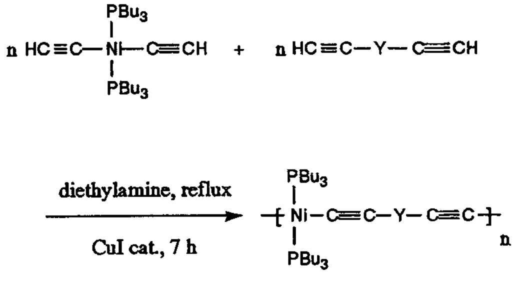
Polymer	M_n[a]	$[\eta]$[b]	Dec. pt[c]
2	15000; $n = 20$	0.17	235
3	17000; $n = 22$	0.18	335
4	14000; $n = 20$	0.14	227
5	12000; $n = 18$	0.14	170[d]
6	16000; $n = 25$	0.17	125[d]
7	16000; $n = 25$	0.13	150[d]

[a] Estimated by GPC. [b] Refractive index $[\eta]$ in benzene at 30 °C. [c] TG in vacuum. [d] In air.

Table 3 Spectral data of metal poly-yne polymers

	IR (cm^{-1})^{a}		^{1}H NMR (ppm)^{b}				^{31}P NMR (ppm)^{c}	
Polymer	$\nu_{C\equiv C}$	$\delta_{Si\text{-}Me}$	P-*Bu*		Si-*Me*	P-*Ph*	Bu-*P*($J_{Pt\text{-}P}$, Hz)	Ph-*P*
2	2070	1250	0.97 1.6	1.5 2.2	0.66	—	6.5 (2394)	—
3	2070	1250	0.99 1.5	1.6 2.0	0.61	—	2.4 (2374)	—
4	2070	1260	0.99 1.6	1.5 2.0	0.66	—	9.5	—
5	2050		1.0 1.6	1.5 2.0	—	7.3 8.1 8.3	10.2	−50.8
6	2050	1250	1.0 1.6	1.5 2.0	0.59		21.6	—
7	2050	1260	1.0 1.7	1.5 2.0	0.55		11.8	—

^{a} KBr tablet. ^{b} In C_6D_6 at room temperature; chemical shifts are in ppm referred to tetramethylsilane as an intrernal standard. ^{c} In dichloromethane at room temperature; chemical shifts are in ppm referred to D_3PO_4 as an external standard; positive shifts to low field.



[5]

Y = SiMe$_2$SiMe$_2$: **6**

Y = SiMe$_2$OSiMe$_2$: **7**

The polymerizations carried out under optimum conditions, i.e. in the presence of a CuI catalyst diethylamine under reflux for 7 h gave high-molecular-weight polymers **6**, $M_n = 16000$, and **7**, $M_n = 16000$ (Table 2). Nickel poly-yne polymers **6** and **7** were purified by alumina column chromatography with a hexane eluent and reprecipitation from benzene into methanol, and have $[\eta] = 0.17$ and 0.13 (Table 2).

The structures of the metal poly-yne polymers **2–7** were identified from ^{1}H NMR and ^{31}P NMR, IR and elemental analysis.

Characterization of metal poly-yne polymers

Platinum poly-yne polymers **2** and **3** were obtained as pale yellow solids and were very stable in air. Palladium poly-yne polymer **4** was obtained as a pale yellow solid and was somewhat unstable in air—on standing in sunlight it decomposed slowly with a color change from pale yellow to black. However, **5** was obtained as a pale yellow viscous oil and was very stable in air. Nickel poly-yne polymers **6** and **7** were obtained as yellow solids and were somewhat unstable, similarly to the palladium poly-yne polymer **4**.

The IR spectra of metal poly-yne polymers containing disilane, disiloxane and phosphine groups exhibit intense bands in the region attributed to stretching frequencies (2050–2070 cm^{-1}) of acetylenic bonds and to bending frequencies (1250–1260 cm^{-1}) of silyl–methyl bonds, with no trace of bands due to acetylenic hydrogen bonds (Table 3).

^{31}P NMR spectral analysis provides information about the oxidation state, gross geometry and the substituents on the metal, as well as the regularity of the polymer structure. The ^{31}P NMR spectral data of metal poly-yne polymers **2–7** in Table 3 are consistent with M(II) oxidation states (M = Pt, Pd, Ni) and all-*trans* configurations.[17–19] Furthermore, the sharp absorptions suggest a regular alternate arrangement of a transition metal and disilane, disiloxane or phosphine groups in the main chain. The ^{31}P NMR spectra of platinum poly-yne polymers **2** and **3** have attendant satellites due to coupling ($J_{Pt\text{-}P} = 2394$ and 2374 Hz) with ^{195}Pt. For example, the ^{31}P NMR spectrum of **3** is shown in Fig. 1. The ^{31}P NMR spectrum of palladium poly-yne polymer **5** was reported to be

10.2 ppm assigned to side-chain phosphine (*n*-Bu-*P*) and −50.8 ppm assigned to main-chain phosphine (Ph-P) (Fig. 2).

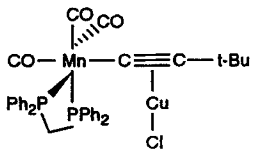
^{1}H NMR spectral data of metal poly-yne polymers **2–7** are shown in Table 5. For example, the ^{1}H NMR chemical shifts of platinum poly-yne polymer **2** were reported to be 0.66 (singlet, Si–*Me*) and 0.97–2.2 ppm (multiplets, P–*n*–*Bu*) of integrated intensity ratio 12:54 from high to low field, respectively (Fig. 3).

Electronic spectral data of metal poly-yne polymers **2–7** are shown in Table 4. In Fig. 4, the electronic spectrum of platinum poly-yne polymer **2** is compared with those of platinum poly-yne polymers **1** and **3**. The lowest energy bands of **1–3** are assigned to metal-to-ligand charge-transfer transitions (MLCT bands) which have λ_{max} values of 313, 321 and 308 nm, respectively. A small bathochromic shift (308 nm < 313 nm < 321 nm) in the electronic spectra of platinum poly-yne polymers **1–3** should be observed for the σ, π-conjugation of silicon–silicon σ-bonds with the acetylenic π-system.[20] Figure 5 shows that the MLCT transitions move to lower energy in the series Pd < Pt < Ni reflecting the increasing MLCT interaction.

Reactivity of metal poly-yne polymers containing disiloxane and phosphine groups in the main chain

In the past decade, there has been considerable interest in the chemical and physical properties of one-dimensional metal cluster complexes. There are many possible bonding modes of acetylene ligands in organometallic compounds,[21] because acetylene can act as a ligand bridging a pair of metal atoms. The purpose of this work was to investigate the possibility of preparation of a new type of one-dimensional metal cluster, in which the polymer chain is used as a supporting axis within the clusters.

For example, Riera and co-workers[21] reported syntheses of complexes of a Group IB metal such as copper with η^2-bonded σ-alkynyl compounds of manganese(I) (**8**) in 1986. Furthermore, $[\eta^2\text{-}(CH_3)_3Si{-}C{\equiv}C{-}Si(CH_3)_3]_2Cu_2Cl_2$ (**9**), a η^2-bonded alkynyl complex, was synthesized by the reaction between copper(I) chloride and bis(trimethylsilyl)acetylene by Macomber and Rausch in 1983.[22]



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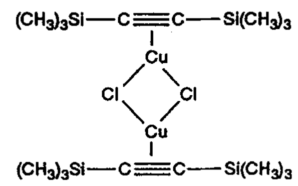

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The reaction of the platinum poly-yne polymer **3** with cuprous iodide in diethylamine gave adducts of η^2-bonded σ-acetylide polyer complexes, the stoichiometry of which was dependent on the initial ratio of CuI and **3**. The adducts are soluble in organic solvents such as benzene, and IR spectra of the platinum poly-yne polymer **3** and the adducts of CuI and **3** are shown in Fig. 6. The acetylide stretching band in the IR spectrum of adducts of CuI and platinum poly-yne polymer

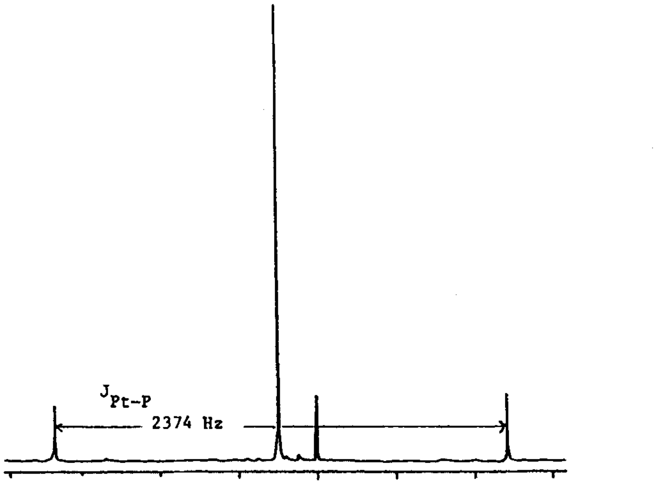


Figure 1 $^{31}P\{^1H\}$ NMR spectrum of platinum poly-yne polymer **3** in CH_2Cl_2 (reference D_3PO_4).

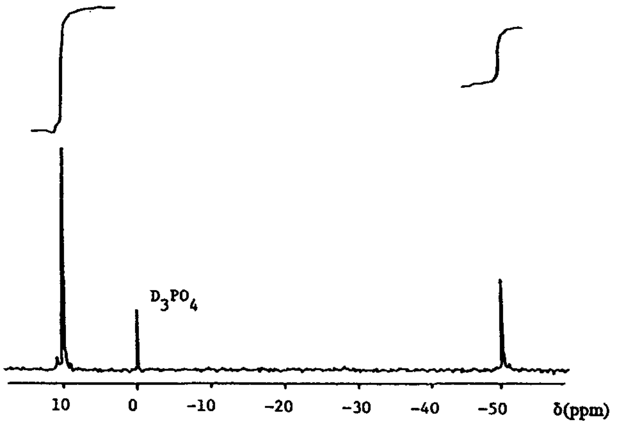


Figure 2 $^{31}P\{^{1}H\}$ NMR spectrum of palladium poly-yne polymer **5** in CH_2Cl_2 (reference D_3PO_4).

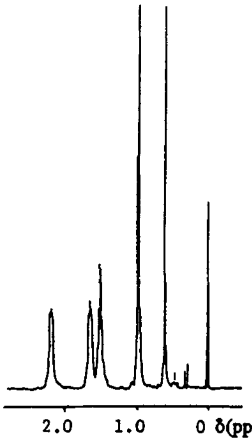


Figure 3 ^{1}H NMR spectrum of platinum poly-yne polymer **3** in C_6D_6 (reference $SiMe_4$).

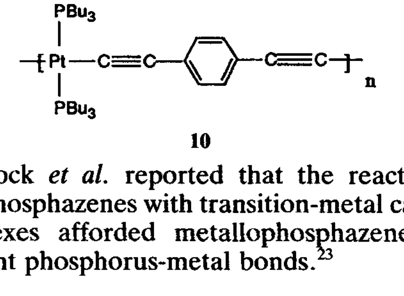
3 shifts to 1930 from 2050 cm^{-1} by the coordination of cuprous iodide, but the free acetylide stretching band which does not coordinate to cuprous iodide at (2050 cm^{-1}) remained. The adducts of CuI and platinum poly-yne polymer **1** have a similar tendency.

The reaction of the platinum poly-yne polymer (**10**), having a rod-like structure with cuprous iodide, did not give a product as a η^2-bonded polymer complex, since the acetylide stretching band in the IR spectrum of the product is similar to that of platinum poly-yne polymer **10**. π-Coodination to acetylides of platinum poly-yne polymers **1** and **3**, which have a tetrahedral structure at the silicon center, with cuprous iodide is preferred to that of platinum poly-yne polymer **10** which has a backbone of a rod-like structure.

Table 4 UV data of metal poly-yne polymers

Polymer	UV (nm) ($\varepsilon \times 10^{-4}$)[a]			
2	208 (4.4)	259 (1.3)	281 (1.6)	321 (2.7)
3	205 (3.8)	265 (0.77)	273 (1.0)	308 (1.2)
4	208 (3.3)	237 (2.5)	250 (1.8)	
5	207 (4.0)	249 (3.6)	270 (1.9)	
6	215 (3.8)	263 (1.9)	334 (1.6)	
7	207 (2.6)	268 (1.3)	326 (0.83)	

[a] In cyclohexane.



10

Allcock *et al.* reported that the reactions of cyclophosphazenes with transition-metal carbonyl complexes afforded metallophosphazenes with covalent phosphorus-metal bonds.[23]

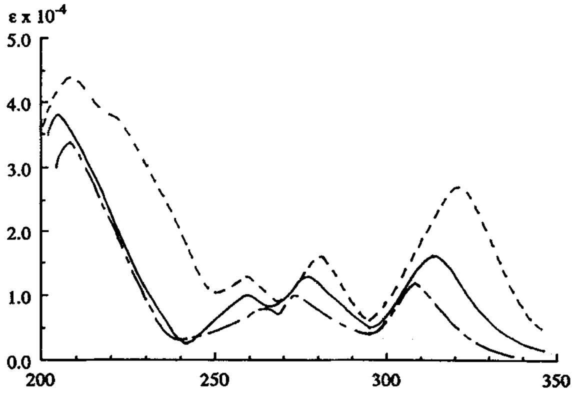


Figure 4 Electronic spectra of platinum poly-yne polymers in cyclohexane: ———, **1**; - - -, **2**; —·—, **3**.

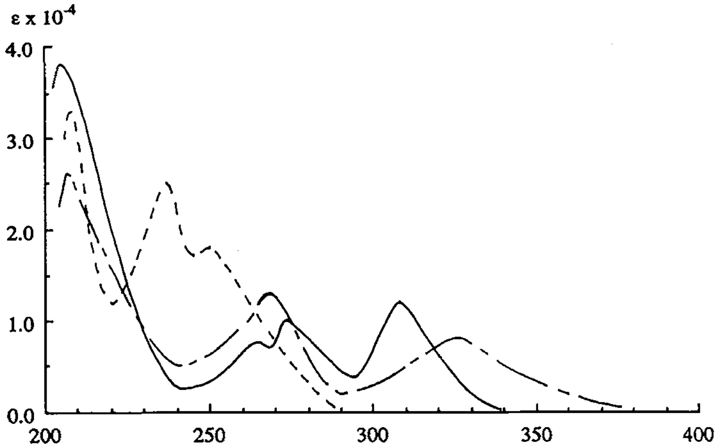


Figure 5 Electronic spectra of metal poly-yne polymers containing disiloxane groups in the main chain: ———, **3**; – – –, **4**; —·—, **7**.

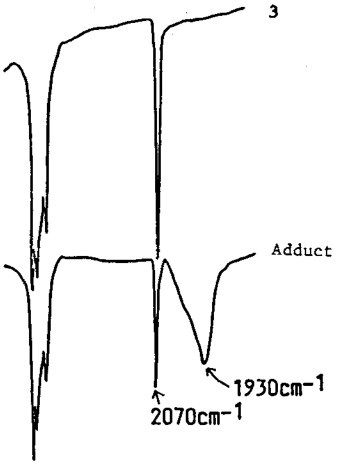


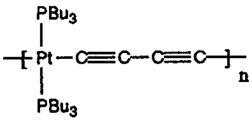
Figure 6 IR spectra of **3** and 1:1 adduct of **3** and CuI.

We also studied the reactions of palladium poly-yne polymer **5** containing a phosphine group in the main chain with transition-metal carbonyl complexes. For example, the reactions of palladium poly-yne polymer **5** with $[Mo(CO)_3(CH_3CN)_3]$ and $[Cr(CO)_3(CH_3CN)_3]$ gave cross-linked polymer complexes which were insoluble in organic solvents. The IR spectra of these polymer complexes exhibited intense bands in the region attributed to stretching frequencies (1850–1990 cm^{-1}) of carbonyl bonds.

Concentrated solution properties

One of the characteristic properties of rod-like polymers is that their concentrated solutions form lyotropic liquid crystal.[24] Such examples among synthetic polymers are polyamides[25-28] and polyisocyanates[29] which form cholesteric or nematic liquid crystals in selected solvents.

The poly-yne polymer poly[bis(tri-*n*-butylphosphine)platinum 1,3-butadiynediyl] (**11**), containing a transition metal and having a rod-like structure, has been shown to be in a new class of polymers exhibiting lyotropic liquid crystalline behavior.[30]



$$\left[\overset{PBu_3}{\underset{PBu_3}{Pt}} - C \equiv C - C \equiv C \right]_n$$

11

A concentrated solution of platinum poly-yne polymer **3**, the tetrahydral silyl-containing metal poly-yne polymers **1**, **2**, **3**, **4**, **6** and **7** above, forms a lyotropic liquid crystal in dichloromethane or 1,2-dichloroethane. The onset of birefrigence observed under a polarizing microscope is shown in droplets of the liquid crystals with a clear Maltese cross and indicates a regular orientation of the polymer molecule in the spherical liquid crystal. It has been suggested, by using a gypsum wedge, that the liquid crystals are positive and therefore the *c* axes, i.e. molecular direction, of the polymer molecules lie consistently parallel to the radius of the spherical liquid-crystalline phase.

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