ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 611 (2000) 570–576

Journal of Organometallic Chemistry

Reaction of organocobalt polymers with isocyanide. Synthesis of novel poly[(η^5-cyclopentadienyl)(η^5-amino-cyclopentadienyl)-cobalticinium-diyl-*alt*-biphenyl-4,4′-diyl)]s

Ikuyoshi Tomita* [a,1], Jong-Chan Lee [b], Takeshi Endo* [b,2]

[a] *Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan*

[b] *Research Laboratories of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*

Received 3 March 2000; accepted 26 March 2000

Abstract

On the basis of the fact that the reaction of a cobaltacyclopentadiene derivative with *t*-butyl isocyanide quite effectively provides a (η^5-cyclopentadienyl)(η^4-iminocyclopentadiene)cobalt derivative which reveals a unique solvatochromic behavior, the polymers having cobaltacyclopentadiene-diyl and biphenyl-4,4′-diyl repeating units **1** were subjected to the reaction with *t*-butyl isocyanide to give those having (η^5-cyclopentadienyl)(η^4-iminocyclopentadiene)cobalt moieties in the main chain **2**. By the subsequent reaction with iodomethane, the polymers **2** were converted quantitatively into cobalticinium-containing polymers **3** (i.e. poly[(η^5-cyclopentadienyl)(η^5-amino-cyclopentadienyl)cobalticinium-diyl-*alt*-biphenyl-4,4′-diyl)]s). The results of the spectroscopic, the electrochemical, and thermal analyses of the polymers (**2** and **3**) are also described. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Organometallic polymer; Reactive polymer; Polymer reaction; Cobaltacyclopentadiene; Cobalticinium; Isocyanide; Solvatochromism

---

1. Introduction

Polymers having organometallic repeating units are potentially of importance as reactive and functional materials with advanced features. On the basis of the reports of Yamazaki et al. that cobaltacyclopentadiene derivatives are useful intermediates leading to many useful organic molecules with versatile functional groups [1], we have reported the synthesis and reactions of organocobalt polymers having cobaltacyclopentadiene moieties in the main chain **1**. That is, the reaction of (η^5-cyclopentadienyl)bis(triphenylphosphine)cobalt complex and diyne monomers provides the organocobalt polymers **1** [2] and their reactions with isocyanates, nitriles, sulfur, etc., give rise to polymers possessing various main chain structures [3]. These examples demonstrate that the organocobalt polymers **1** are quite powerful intermediates leading to the functional polymers possessing various main chain structures. Namely, they can be regarded as a new type of main chain reactive polymers.

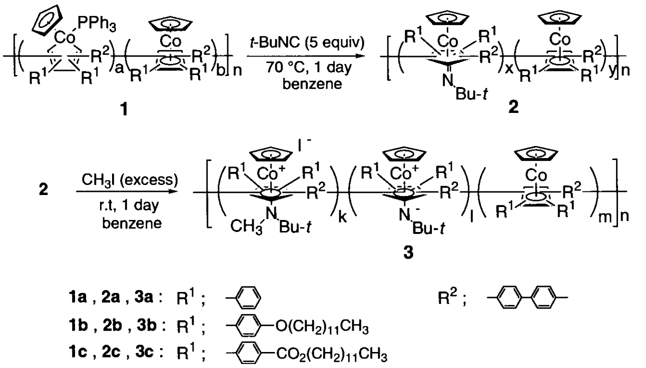
Besides the applications of **1** as a precursor for organic polymers, they are also potentially of importance as a precursor of organometallic polymers with different organometallic centers. For example, the organocobalt polymers **1** could be converted to cyclobutadienecobalt-containing polymers by the rearrangement reaction [4]. By using (or developing) the reactions of the cobaltacyclopentadiene derivatives providing novel organometallic complexes, a new type of organometallic polymers revealing unique functions might be produced from the organocobalt polymers **1** [5]. According to Yamazaki et al., the cobaltacyclopentadiene derivatives are reported to be converted to (η^5 - cyclopentadienyl)(η^4 - iminocyclopentadiene)cobalt complexes by the reaction with isocyanides and the resulting complexes undertake an alkylation to give

---

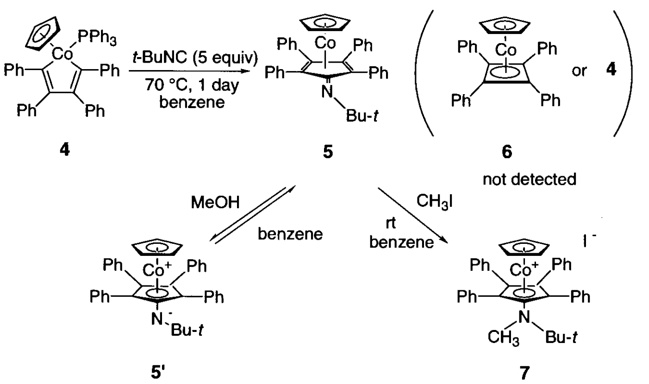
[1] *Corresponding author. Fax: + 81-45-9245489; e-mail: tomita@echem.titeh.ac.jp.

[2] *Corresponding author.

PII: S0022-328X(00)00393-4



Scheme 1.



Scheme 2.

(η^5-cyclopentadienyl)(η^5-aminocyclopentadienyl)cobalticinium derivatives [6a]. Therefore, the reaction of the cobaltacyclopentadiene moieties in the organocobalt polymer **1** with isocyanides may provide the organometallic polymers bearing (η^5-cyclopentadienyl)(η^4-iminocyclopentadiene)cobalt moieties as a repeating unit **2** and the subsequent treatment of **2** with alkyl halides is expected to give polymers bearing (η^5-cyclopentadienyl)(η^5-aminocyclopentadienyl)cobalticinium moieties **3** (Scheme 1). The polymers (**2** and **3**) might serve as a new type of poly(metallocene)s that might reveal interesting properties.

We describe herein the results on the reaction of the organocobalt polymers **1** with an isocyanide followed by the alkylation, and the electrochemical and the thermal properties of the resulting polymers are also discussed.

2. Results and discussion

*2.1. Synthesis and physical properties of the model compounds **5** and **7***

In order to clarify the efficiency of the reaction of the cobaltacyclopentadienes with isocyanides reported by Yamazaki et al. [6a], the reaction of a (η^5-cyclopentadienyl)(triphenylphosphine)cobaltacyclopentadiene derivative **4** with *t*-butyl isocyanide was re-investigated to confirm the quite effective nature of the reaction. That is, an iminocyclopentadiene-cobalt complex **5** was obtained in 88% yield as black crystals by recrystallization from *n*-hexane–benzene. The reaction did not provide any side products such as a cyclobutadiene-cobalt **6** via the rearrangement of **4**. In benzene, **5** was converted quantitatively to a derivative of cobalticinium iodide **7** by the reaction with iodomethane, while the alkylation did not take place in a MeOH solution (Scheme 2).

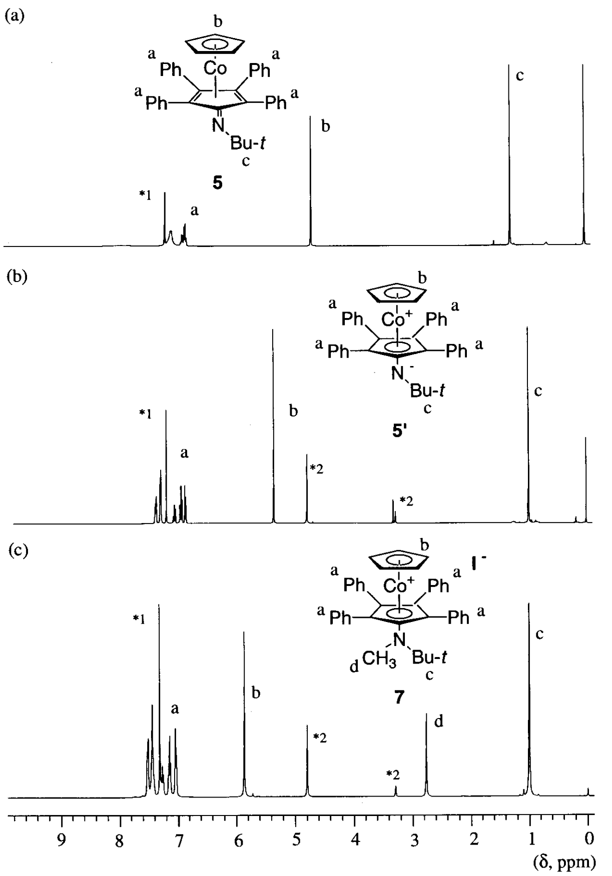


Fig. 1. ^{1}H-NMR spectra of **5** in C_6D_6 (a), **5′** in $C_6D_6 + CD_3OD$ (b), and **7** in $C_6D_6 + CD_3OD$ (c) (*1: C_6D_6, *2: CD_3OD).

The complex **5** revealed unique solvatochromism. That is, **5** dissolves in benzene to form a purple-colored solution which turns to red in (or by the addition of) MeOH. This color change is a reversible process and can be observed not only in MeOH but also in aprotic polar solvents such as tetrahydrofuran and *N*,*N*-dimethylformamide. In the ^{1}H-NMR spectrum of **5** in C_6D_6 (Fig. 1(a)), a singlet peak at δ 4.68 and that at 1.28 ppm attributable to the cyclopentadienyl (Cp) and to the *t*-butylimino groups, respectively, were observed.

In the ^{1}H-NMR spectrum of **5** in a mixed solvent of C_6D_6 and CD_3OD (Fig. 1(b)), the peak of the Cp shifted to the lower field by 0.73 ppm and the peak of *t*-butylimino group shifted to the higher field by 0.28 ppm [7]. The difference was also observable in the ^{13}C-NMR spectra. In the mixed solvent of C_6D_6 and CD_3OD, the peaks of the Cp and of the *t*-butylimino groups were found at 87.31 and 30.09 ppm, respectively, which were lower by 3.0 and higher by 2.1 ppm, respectively, than those taken in C_6D_6. Judging from these results, **5** was supposed to have a zwitterionic character (**5′**) in polar solvents. This behavior might originate from the equilibrium between **5** and **5′** whose distribution depends upon the character of the solvents. The hypothesis of the zwitterionic structure of **5** was also supported by IR spectra. The peak attributable to the C=N stretching was observed at 1584 cm^{-1} in the solid state (KBr disk) which disappeared when measured in a MeOH solution.

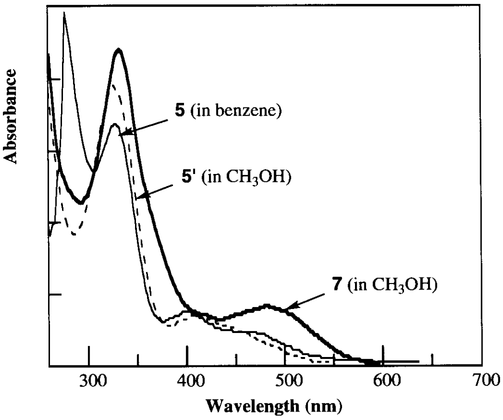


Fig. 2. UV–vis absorption spectra of **5** (5×10^{-5} M benzene solution), **5′** (5×10^{-5} M methanol solution), and **7** (5×10^{-5} M methanol solution).

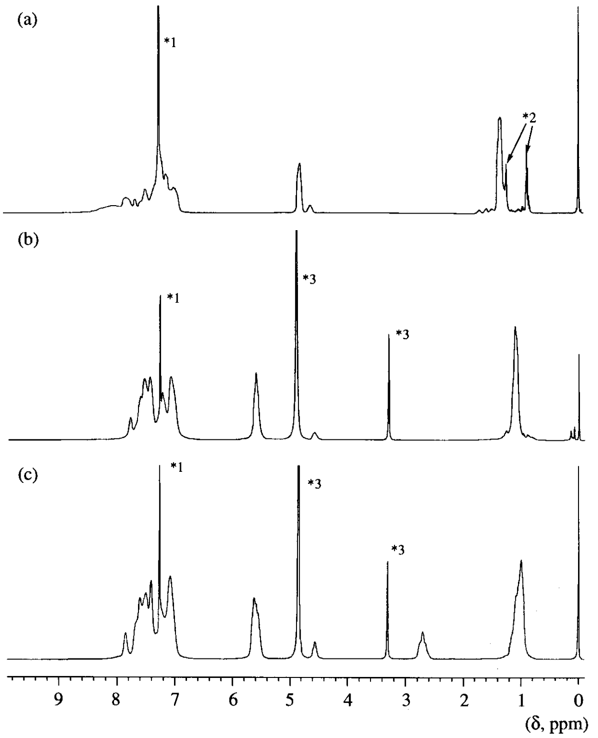


Fig. 3. ^{1}H-NMR spectra of **2a** in C_6D_6 (a), **2a′** in $C_6D_6 + CD_3OD$ (b), and **3a** in $C_6D_6 + CD_3OD$ (c) (*1: C_6D_6, *2: *n*-hexane, and *3: CD_3OD).

UV–vis spectra of **5** (both in benzene and MeOH) and **7** (in MeOH) are shown in Fig. 2. Compared to the case of **5** in benzene ($\lambda_{max} = 400$ nm), λ_{max} of **5′** in MeOH shifted to the longer wavelength by 10 nm, probably because of the more ionic character of the complex in MeOH. In the case of **7**, the corresponding λ_{max} was observed at 484 nm.

2.2. Polymer reactions

The organocobalt polymer **1a** [8] was subjected to the reaction with *t*-butyl isocyanide under the same conditions to the model experiments. The reaction proceeded homogeneously and a powdery polymer **2a** was obtained in 90% yield by the precipitation with *n*-hexane under nitrogen. Similar to the case of the model compound **5**, **2a** also revealed solvatochromism depending upon the solvents. The polymer **2a** was relatively unstable under air to be converted to an insoluble material [9]. When the alkylation of **2a** was carried out in situ (i.e. **2a** obtained from **1a** was subjected to the reaction with an excess of iodomethane without isolation), an air-stable polymer having cobalticinium units **3a** was obtained.

The structure of the obtained polymers (**2a** and **3a**) was confirmed by ^{1}H-, ^{13}C-NMR, and IR spectra. In the ^{1}H-NMR spectrum of the polymer **2a** (Fig. 3(a)), two peaks attributable to the Cp originated from those of the iminocyclopentadienecobalt and the cyclobutadienecobalt units were observed at 4.65–4.85 and 4.50–4.60 ppm, respectively. The peak of the *t*-butyl group also appeared at 1.20–1.50 ppm. From the integral ratio of the Cps, the polymer **2a** was found to contain ca. 85% of the iminocyclopentadiene cobalt units. In the case of a mixed solvent of C_6D_6 and CD_3OD (Fig. 3(b)), peaks of the Cps were observed at 5.50–5.70 and at 4.50–4.60 ppm (those of the iminocyclopentadienylcobalt and of the cyclobutadienecobalt units, respectively), in which the former peak shifted to lower field by ca. 0.85 ppm. Besides, the peak of the *t*-butyl group shifted to higher field by ca. 0.3 ppm in accordance with the proposed zwitterionic structure of the iminocyclopentadienecobalt units **2a′**. In the ^{1}H-NMR spectrum of **3a** (Fig. 3(c)), a new peak attributable to the methyl group was observed at 2.60–2.80 ppm and the integral ratio of the Cps and the methyl group made it possible to determine the unit ratio of aminocyclo-

Table 1
Synthesis of cobalticinium-containing polymers (**3**) [a]

1			**3**		
Reactant	a:b [b]	M_n (M_w/M_n) [c]	Product	Yield (%)	*k*:*l*:*m* [b]
1a	85:15	6800 (1.5)	**3a**	96 [d]	70:15:15
1b	80:20	22 600 (1.6)	**3b**	81 [e]	65:20:15
1c [f]	80:20	9100 (1.3)	**3c**	96 [e]	55:25:20

[a] The reaction of **1** with *t*-butyl isocyanide was carried out in benzene at 70°C for 1 day under N_2. Without isolation of the resulting iminocyclopentadienecobalt-containing polymers, the reaction with iodomethane was carried out at r.t. for 1 day under N_2.

[b] Determined by ^{1}H-NMR.

[c] Estimated by GPC (THF, PSt standard).

[d] Isolated yield by the precipitation with benzene.

[e] Isolated yield by the precipitation with MeOH.

[f] **1c** was reacted with t-butyl isocyanide for 3 days and then the reaction with iodomethane was also carried out for 3 days.

pentadienyl cobalticinium:iminocyclopentadienecobalt: cyclobutadienecobalt units in **3a** to be ca. 70:15:15.

The organocobalt polymer bearing electron-donating groups **1b** and that bearing electron-withdrawing groups **1c** were also subjected to the reaction with *t*-butyl isocyanide followed by the treatment with iodomethane, from which the corresponding cobalticinium-containing polymers (**3b** and **3c**) were obtained in 81 and 96% yields, respectively, by the precipitation with MeOH (Table 1). From their ^{1}H-NMR spectra, the unit ratios were found to be ca. 65:20:15 and 55:25:20, respectively. These results indicate that the conversion of **1** to **2** proceeds quantitatively. However, the following alkylation does not occur in a quantitative fashion, most probably because the polymers produced by the alkylation have ionic structures and their solubility in the reaction system was not sufficient [10].

2.3. Physical properties of polymers

UV–vis spectra of the cobalticinium-containing polymer **3a** and its model compound **7** are shown in Fig. 4. The two absorption maxima at 334 and 484 nm were observed in a benzene–MeOH solution of **7**. The corresponding absorption bands could be also observed in the case of **3a**, although the intensity of the absorption at longer wavelength was relatively weaker, simply because of the density of the cobalticinium units in **3a** (ca. 70% of the repeating units of **3a** has the cobalticinium structure).

The redox behavior of the cobalticinium compound **7** and the polymer **3a** was examined by cyclic voltammetry, using a 1 mM–0.1 M Bu_4NBF_4–CH_3CN solution and precast film in 0.1 M Bu_4NBF_4–CH_3CN on a Pt electrode, respectively, at the scan rate of 50 mVs^{-1} (Fig. 5). In the case of **7** (Fig. 5(a)), the cyclic voltammogram (CV) revealed four reversible redox potentials at −1.73, −0.82, 0.28, and 0.63 V versus SCE, while the polymer **3a** exhibited two reversible oxidation peaks at 0.28 and 0.64 V, a quasi-reversible reduction at −0.8 V, and two irreversible reductions at −1.57 and −1.77 V (Fig. 5(b,c)). In the case of **3a**, the current of the first oxidation is dependent upon the redox history where the peak intensity became stronger when the measurement was started from the reduction side. The increased oxidation current might be originated from oxidation of the cobalt moieties and the higher voltage shift of the oxidation might be due to the stabilization of the reduced form of cobalticinium moiety in the polymer **3a** in comparison with that of **7**.

The thermal properties of the iminocyclopentadienecobalt- and cobalticinium-containing polymers (**2a** and **3a**, respectively), were estimated by thermogravimetric analyses (TGA) (Fig. 6). The 10% weight loss (Td_{10}) of **2a** and **3a** was observed at 453 and 364°C, respectively, while the organocobalt polymer **1a** had Td_{10} at 240°C [11]. The degradation of **2a** and **3a** below 500°C might be originated from the decomposition of the lateral alkyl moieties because their weight losses observed at 500°C are approximately equal to the weights of their soft segments.

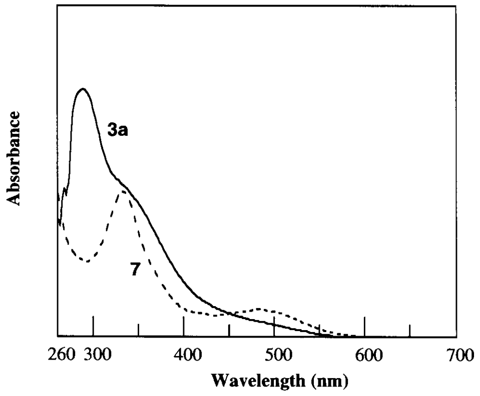


Fig. 4. UV–vis absorption spectra of **7** (5×10^{-5} M methanol solution) and **3a** (5×10^{-5} M methanol–benzene (v/v = 50/50) solution).

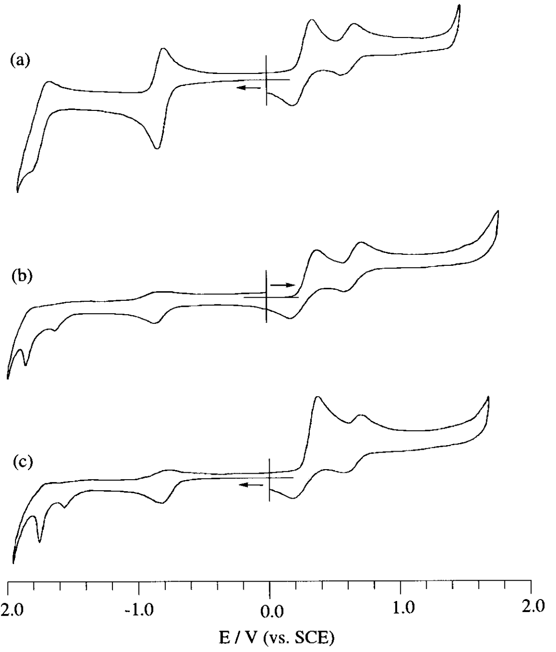


Fig. 5. CVs of **7** as a 1 mM–0.1 M Bu_4NBF_4–CH_3CN solution (a) and **3a** as a precast film immersed in 0.1 M Bu_4NBF_4–CH_3CN measured on a Pt electrode (b and c) at the scan rate of 50 mVs^{-1}.

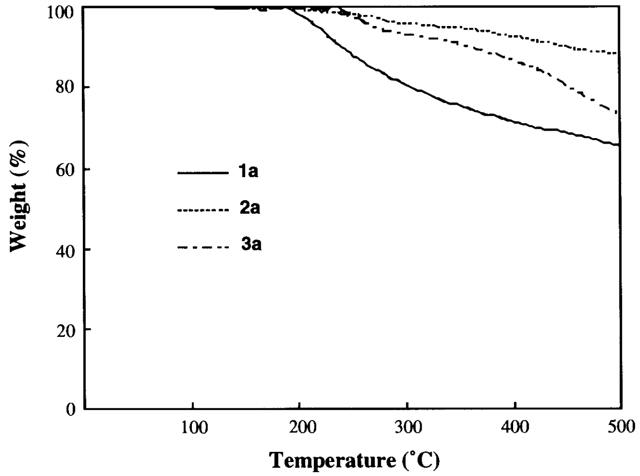


Fig. 6. TGA traces of **1a**, **2a**, and **3a** under nitrogen (10°C min^{-1}).

3. Experimental

^1H- and ^{13}C-NMR spectra were recorded on a JNM-EX400 spectrometer (400 and 100 MHz, respectively) in C_6D_6 and/or CD_3OD (tetramethylsilane as internal standard). IR spectra were obtained on a JASCO FT/IR-5300 spectrometer. UV–vis spectra were recorded on a Shimadzu UV-2100 spectrometer in $CHCl_3$. Cyclic voltammetry experiments were performed with a potentiostat/galvanostat (Hokuto Denko Model HA-301) and a function generator (Hokuto Denko Model HB-104) equipped with an X-Y Riken Denshi F-35C recorder at a scanning rate of 50 mVs^{-1}. The working, auxiliary, and reference electrodes were 1 cm^2 Pt plate, 2 cm^2 Pt plate, and SCE, respectively. A 0.1 M acetonitrile solution of Bu_4NBF_4 was used as electrolyte. Thermogravimetric analyses (TGA) were carried out on a Seiko TG/DTA 220 instrument at a heating rate of 10°C min^{-1} under nitrogen.

Organocobalt polymers **1a**–**1c** [2c] and a cobaltacyclopentadiene **4** [1a] were obtained as previously described. *t*-Butyl isocyanide was prepared according to the literature procedure [12]. Benzene was dried over sodium and distilled under nitrogen. Iodomethane and other reagents were used as received.

*3.1. Synthesis of (η^5-cyclopentadienyl)(η^4-N-t-butyliminotetra-phenylcyclopentadiene)cobalt (**5**)*

To a test tube were added **4** (1.486 g, 2.00 mmol), five equivalents of *t*-butyl isocyanide (1 ml, 10 mmol), and benzene (15 ml) under nitrogen and the mixture was kept stirring at 70°C for 1 day. After the reaction, the product **5** was obtained in 88% yield as black crystals by recrystallization from *n*-hexane. From the remaining solution after the recrystallization, no side product such as **6** nor the starting **4** was detected.

5: ^1H-NMR (δ, ppm, C_6D_6): 1.28 ($-C(CH_3)_3$, s, 9H), 4.68 ($-C_5H_5$, s, 5H), 6.80–7.10 ($-C_6H_5$, m, 20H). ^{13}C-NMR (δ, ppm, C_6D_6): 32.10 ($-CH_3$), 53.55 (−NC≡), 84.31 ($-C_5H_5$), 126.54, 126.99, 127.10, 127.51, 132.41, 135.30 ($-C_6H_5$, $-C_5N$). IR (KBr, cm^{-1}): 3054, 2955, 1638, 1599, 1584, 1493, 1443, 1200, 1073, 1028, 756, 702.

5′: ^1H-NMR (δ, ppm, $C_6D_6 + CD_3OD$): 1.00 ($-C(CH_3)_3$, s, 9H), 5.41 ($-C_5H_5$, s, 5H), 6.92–7.46 ($-C_6H_5$, m, 20H). ^{13}C-NMR (δ, ppm, $C_6D_6 + CD_3OD$): 30.09 ($-CH_3$), 54.95 (−NC≡), 87.31 ($-C_5H_5$), 96.53, 123.82, 127.79, 128.23, 128.55, 128.63, 128.90, 129.49, 130.95. 131.55($-C_6H_5$, $-C_5N$). IR (NaCl, in MeOH cm^{-1}): 3056, 2961, 1630, 1543, 1481, 1443, 1194, 1076, 1026, 758, 698.

*3.2. Synthesis of (η^5-cyclopentadienyl)(η^5-N-t-butyl-N-methylamino-tetraphenylcyclopentadienyl)cobalticinium iodide (**7**)*

To a test tube were added **4** (0.148 g, 0.200 mmol), five equivalents of *t*-butyl isocyanide (100 μl, 1 mmol), and benzene (10 ml) under nitrogen and the mixture was kept stirring at 70°C for 1 day. Iodomethane (1 ml) was added to the reaction mixture and kept stirring at room temperature (r.t.) for 1 h. The product was obtained as a red powder in 98% yield (0.137 g, 1.95 mmol) by precipitation into benzene.

7: ^1H-NMR (δ, ppm, CD_3OD): 1.01 ($-C(CH_3)_3$, s, 9H), 2.77 ($-CH_3$, s, 3H), 5.87 ($-C_5H_5$, s, 5H), 7.00–7.55 ($-C_6H_5$, m, 20H). ^{13}C-NMR (δ, ppm, CD_3OD): 29.45

($-CH_3$), 42.18 ($-CH_3$), 59.57 ($-NC\equiv$), 89.61 ($-C_5H_5$), 97.35, 99.26, 129.23, 129.27, 129.69, 129.94, 130.11, 130.60, 131.37, 133.09, 133.33 ($-C_6H_5$, $-C_5N$). IR (NaCl, cm^{-1}): 3057, 2930, 1630, 1478, 1445, 1402, 1159, 1074, 1030, 754, 700.

*3.3. Synthesis of iminocyclopentadienecobalt-containing polymer (**2a**)*

To a test tube were added **1a** ($M_n = 6800$, $M_w/M_n = 1.5$, 0.148 g, 0.200 mmol unit), five equivalents of *t*-butyl isocyanide (100 μl, 1 mmol), and benzene (10 ml) under nitrogen and the mixture was kept stirring at 70°C for 1 day. To the reaction mixture was added dried *n*-hexane (50 ml). The resulting pale brown powdery precipitate was collected by filtration under nitrogen, washed with dried *n*-hexane, and then dried in vacuo to give 0.099 g (0.180 mmol unit) of **2a**.

2a: ^{1}H-NMR (δ, ppm, C_6D_6): 1.20–1.50 ($-C(CH_3)_3$, br, 9H × 0.85), 4.50–4.60 ($-C_5H_5$, br, 5H × 0.15), 4.65–4.85 ($-C_5H_5$, br, 5H × 0.85), 6.80–8.20 ($-C_6H_4-$, $-C_6H_5$, br, 18H).

2a′: ^{1}H-NMR (δ, ppm, $C_6D_6 + CD_3OD$): 0.90–1.30 ($-C(CH_3)_3$, br, 9H × 0.85), 4.50–4.60 ($-C_5H_5$, br, 5H × 0.15), 5.50–5.70 ($-C_5H_5$, br, 5H × 0.85), 6.90–7.90 ($-C_6H_4-$, $-C_6H_5$, br, 18H). ^{13}C-NMR (δ, ppm, $C_6D_6 + CD_3OD$): 30.34, 30.50, 55.67, 88.08, 128.84, 129.13, 129.64, 130.23, 131.02, 132.45, 132.81, 133.01, 133.58, 134.31. IR (KBr, cm^{-1}, under air): 3057, 2969, 1601, 1543, 1501, 1445, 1395, 1370, 1192, 1073, 1005, 758, 700.

*3.4. Synthesis of cobalticinium-containing polymers (**3**) (typical procedure for **3a**)*

To a test tube were added **1a** ($M_n = 9800$, $M_w/M_n = 1.7$, 0.148 g, 0.200 mmol unit), five equivalents of *t*-butyl isocyanide (100 μl, 1 mmol), and benzene (10 ml) under nitrogen and the mixture was kept stirring at 70°C for 1 day. To the reaction mixture was added an excess of iodomethane (1 ml) and stirred overnight at r.t. The orange powder was precipitated with *n*-hexane, washed with benzene and MeOH, and then dried in vacuo to give 0.114 g (0.176 mmol unit) of **3a**. Polymers **3b** and **3c** were prepared under the similar conditions.

3a: ^{1}H-NMR (δ, ppm, $C_6D_6 + CD_3OD$): 0.80–1.30 ($-NC(CH_3)_3$, br, 9H × 0.85), 2.60–2.80 ($-NCH_3$, br, 3H × 0.70), 4.50–4.60 ($-C_5H_5$, br, 5H × 0.15), 5.50–5.70 ($-C_5H_5$, br, 5H × 0.85), 6.90–7.90 ($-C_6H_4-$, $-C_6H_5$, 18H). ^{13}C-NMR (δ, ppm, $C_6D_6 + CD_3OD$): 30.58, 42.63, 62.97, 88.30, 89.06, 119.20, 127.41, 128.16, 128.52, 128.82, 129.06, 130.35, 130.81, 131.35, 132.90, 133.56, 135.50. IR (KBr, cm^{-1}): 3054, 2970, 2926, 1603, 1578, 1543, 1501, 1443, 1393, 1188, 1074, 1005, 758, 700.

3b: yield 81% (0.163 g, 0.161 mmol unit): red powder. ^{1}H-NMR (δ, ppm, $C_6D_6 + CD_3OD$): 0.80–1.80 ($-CH_2-$, $-CH_3$, $-NC(CH_3)_3$, br, 46H + 9H × 0.85), 2.60–2.85 ($-NCH_3$, br, 3H × 0.65), 3.60–4.00 ($-OCH_2-$, br, 4H), 4.40–4.50 ($-C_5H_5$, br, 5H × 0.15), 5.40–5.70 ($-C_5H_5$, br, 5H × 0.85), 6.50–8.10 ($-C_6H_4-$, $-C_6H_4O-$, 16H). ^{13}C-NMR (δ, ppm, $C_6D_6 + CD_3OD$): 14.67, 23.49, 26.87, 29.60, 30.49, 32.30, 32.80, 44.83, 57.49, 65.61, 68.88, 88.43, 88.56, 89.20, 89.27, 108.14, 115.17, 120.49, 134.09, 154.49, 169.35. IR (KBr, cm^{-1}): 3038, 2924, 2853, 1607, 1572, 1514, 1468, 1391, 1290, 1250, 1177, 1074, 1007, 833, 577.

3c: yield 96% (0.202 g, 0.192 mmol unit). reddish brown powder. ^{1}H-NMR (δ, ppm, $C_6D_6 + CD_3OD$): 0.80–1.70 ($-CH_2-$, $-CH_3$, $-NC(CH_3)_3$, br, 46H + 9H × 0.80), 2.65–2.85 ($-NCH_3$, br, 3H × 0.55), 4.10–4.60 ($-CO_2CH_2-$, br, 4H + $-C_5H_5$, br, 5H × 0.20), 5.50–5.80 ($-C_5H_5$, br, 5H × 0.80), 6.80–8.40 ($-C_6H_4-$, $-C_6H_4CO_2-$, 16H). ^{13}C-NMR (δ, ppm, $C_6D_6 + CD_3OD$): 15.30, 23.21, 24.13, 26.95, 27.35, 30.02, 30.68, 30.82, 31.10, 31.46, 33.36, 49.09, 66.78, 89.16, 90.19, 101.93, 126.07, 130.99, 132.91, 133.78, 134.28, 149.40, 167.14, 167.45, 179.76, 197.81. IR (KBr, cm^{-1}): 3032, 2926, 2853, 1719, 1607, 1547, 1466, 1391, 1271, 1179, 1107, 1005, 826, 579.

References

[1] (a) Y. Wakatsuki, H. Yamazaki, J. Organomet. Chem. 139 (1977) 157. (b) P. Hong, H. Yamazaki, Synthesis (1977) 50. (c) Y. Wakatsuki, H. Yamazaki, J. Chem. Soc. Dalton Trans. (1978) 1278. (d) F. W. Grevels, Y. Wakatsuki, H. Yamazaki, J. Organomet. Chem. 141 (1977) 331. (e) Y. Wakatsuki, H. Yamazaki, J. Organomet. Chem. 149 (1978) 385.

[2] (a) I. Tomita, A. Nishio, T. Igarashi, T. Endo, Polym. Bull. 30 (1993) 179. (b) J.-C. Lee, A. Nishio, I. Tomita, T. Endo, Macromolecules 30 (1997) 5205.

[3] (a) I. Tomita, A. Nishio, T. Endo, Macromolecules 28 (1995) 3042. (b) J.-C. Lee, I. Tomita, T. Endo, Polym. Bull. 39 (1997) 415. (c) J.-C. Lee, I. Tomita, T. Endo, Macromolecules 31 (1998) 5916.

[4] (a) I. Tomita, A. Nishio, T. Endo, Macromolecules 27 (1994) 7009. (b) I.L. Rozhanskii, I. Tomita, T. Endo, Macromolecules 29 (1996) 1934.

[5] For example, ferrocene-containing oligomers and polymers have been reported to show interesting electronic properties originating from the metallic centers. See S. Barlow, D. O'Hare, Chem. Rev. 97 (1997) 637.

[6] (a) H. Yamazaki, Y. Wakatsuki, Bull. Chem. Soc. Jpn. 52 (1979) 1239. (b) K. Yasufuku, A. Hamada, K. Aoki, H. Yamazaki, J. Am. Chem. Soc. 102 (1980) 4363. (c) J.-C. Lee, I. Tomita, T. Endo, Chem. Lett. (1998) 121.

[7] The ^{1}H-NMR spectrum of **7** in a mixed solvent of C_6D_6 and CD_3OD revealed a peak for the Cp at 5.87 ppm, much lower than that of **5** in the same solvent system, probably because **7** does not have any equilibrium as proposed for **5**.

[8] The organocobalt polymer **1a** containing ca. 85% of the cobaltacyclopentadiene moieties was used for this reaction. The remaining 15% was the cyclobutadienecobalt units contaminated during the synthetic step of **1a**. See Ref. [2b].

[9] Under air, the pale brown-colored polymer **2a** turned into pale orange less soluble material, probably by oxidation.

[10] As mentioned in the model experiments, attempts to use solvents with higher polarity for the alkylation failed to result in the recovery of the starting polymer.

[11] The decomposition of **1a** originates from the elimination of triphenylphosphine ligand by the rearrangement to the cyclobutadienecobalt-containing polymer. See Ref. [4].

[12] S.R. Sandler, W. Karo, Organic Functional Group Preparations, vol. III, second ed., Academic, San Diego, 1989 Chapter 5.