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Preparations and properties of polymers containing 3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]-1,2-di(2-thienyl)cyclobutene moieties

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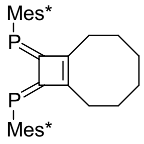
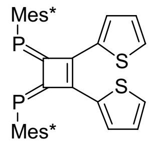
Abstract—Reaction of 1,8-bis[5-{(2,4,6-tri-*t*-butylphenyl)phosphinoethynyl}-2-thienyl]octane with butyllithium followed by treatment with 1,2-dibromoethane afforded a new polymer containing 3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]-1,2-di(2-thienyl)cyclobutene units. The polymer was allowed to react with bis(benzonitrile)dichloropalladium to give the polymer complex. A Sonogashira coupling reaction between ethynyltrimethylsilane and 4-bromonitrobenzene proceeded in DMF at 100 °C to give 4-nitro(trimethylsilylethynyl)benzene in the presence of the polymer complex, CuI, and triethylamine.

Sterically protected 3,4-diphosphinidenecyclobutenes (abbreviated as DPCB),[1] bearing an extremely bulky 2,4,6-tri-*t*-butylphenyl group[2] (hereafter abbreviated as Mes*), are unique ligands of interest,[3] because of their relatively rigid framework containing the phosphorus–carbon π-bond.[4] Various transition metal complexes of DPCB have been prepared[3] and some of them have been used as homogeneous catalysts.[5,6] In the course of our studies on DPCB derivatives, we have recently reported the preparations of DPCB derivatives **1a**,**b** as well as a DPCB polymer **2**.[1f,g,h] In contrast to successful application of phosphine complexes to polymer-supported catalysts such as polystyrene-supported triarylphosphine–palladium complex,[7] polymers containing double-bonded phosphorus[1f,8] are rare and their catalytic activities have remained unexplored. Preparations and applications of polymeric (or oligomeric) DPCB derivatives and their transition metal complexes are thus of interest, from the viewpoint of synthetic organic chemistry as well as materials science, because DPCB–metal complexes have unique catalytic activities, due to their remarkable π-back-donation character.[9] In addition, the DPCB-polymer metal complexes are expected to act as heterogeneous catalysts having the advantage of easy separation from the reaction product.[10] We now report here the preparation and properties of the first DPCB linear polymer and its dichloropalladium complex.

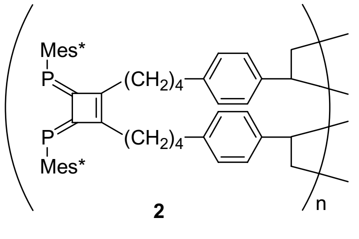


1a



1b

Mes* = 2,4,6-*t*-$Bu_3C_6H_2$



2

At first, in the preparation of **1a**,[1g] we found that a small amount (ca. 5% yield) of oligomeric DPCB derivative **3**

Keywords: Polymers; Steric and strain effects; Phosphaalkenes.

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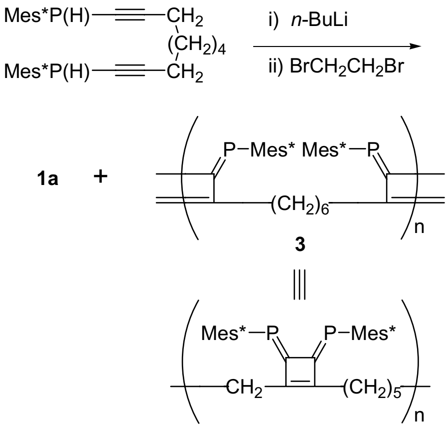
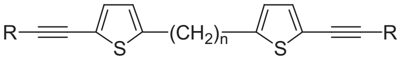


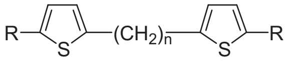
Scheme 1.

[$M_n = 2300$, $M_w = 2700$][11] was formed as by-product (Scheme 1). In this reaction, intramolecular coupling dominated, probably because formation of eight-membered rings are energetically favored, to give **1a** (8% isolated yield) with the normal reaction mechanism for DPCB formation, via a di(phosphaallene) intermediate.[1]

We then planned an polymer formation, in order to increase the yield and average molecular weight of the polymers: introduction of rigid moieties, such as aromatic rings, into methylenes may limit the conformational flexibility of the alkyl chain and consequently prevent intramolecular coupling. We thus investigated coupling reactions of α,ω-bis[5-{(2,4,6-tri-*t*-butylphenyl)phosphinoethynyl}-2-thienyl]alkanes **4** as follows: α,ω-di(2-thienyl)alkanes **5A–C**[12] were allowed to react with *N*-iodosuccinimide or *n*-BuLi/I_2 to give **6A–C**. The diiodo derivatives **6A–C** were converted to **7A–C** by Sonogashira coupling, and then to **8A–C** by desilylation reaction of **7A–C** with KOH. Metallation of **8A–C** with ethylmagnesium bromide followed by reaction with chloro-(2,4,6-tri-*t*-butylphenyl)phosphine[13] afforded α,ω-bis[5-{(2,4,6-tri-*t*-butylphenyl)phosphinoethynyl}-2-thienyl]alkane **4A–C**. The compound **4A**[14] was oily and soluble in chloroform and EtOAc, while the solids **4B**,**C**, once formed, were sparingly soluble in common solvents, such as chloroform and DME. Attempted polymerizations of **4B**,**C** thus failed.

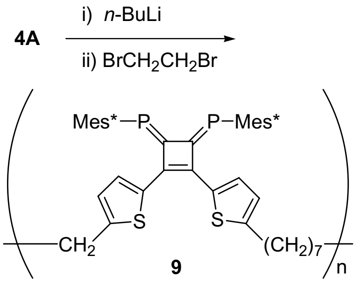


4A: n=8, R=Mes*PH; **4B**: n=6, R=Mes*PH;
4C: n=4, R=Mes*PH
7A: n=8, R=Tms; **7B**: n=6, R=Tms; **7C**: n=4, R=Tms
8A: n=8, R=H; **8B**: n=6, R=H; **8C**: n=4, R=H



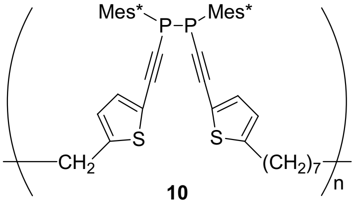
5A: n=8, R=H; **5B**: n=6, R=H; **5C**: n=4, R=H
6A: n=8, R=I; **6B**: n=6, R=I; **6C**: n=4, R=I

In contrast, polymers of **4A** were successfully obtained as follows (Scheme 2): Lithiation of the diphosphane **4A** with butyllithium (2 molar ratio) followed by treatment with 1,2-dibromoethane (1 molar ratio) afforded a mixture containing polymer **9**, probably via **10** and **11**, a cyclic DPCB derivative **12** ($\delta_P = 164.1$), and phosphaallene **13** [$\delta_P = 80.6$ (d, $^3J_{PH} = 26.6$ Hz)].[15]



Scheme 2.

Table 1 shows the results of the polymerization reactions. The reaction in DME (entry 6) gave the best result, taking the distribution of molecular weight of the polymer into account. The crude product obtained in entry 6 was then separated by GPC. From an early fraction a highest-molecular-weight-polymer **9′** was obtained (ca. 9% isolated yield, $M_n = 58{,}000$, $M_w/M_n = 7.8$) and used for evaluation of properties.[16]



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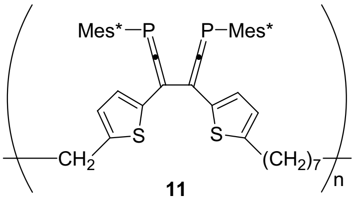

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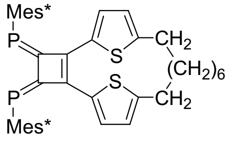
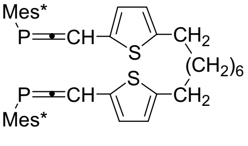


12



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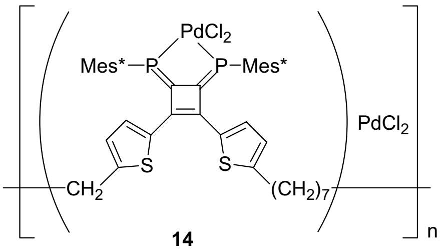


14

The ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of **9′** (Fig. 1) indicated that most of the DPCB units in the polymer

Table 1. Result of polymerization reaction of **4A**

Entry	Solvent	Concn ($mol\,dm^{-3}$)	Ratio of product[a]			
			9	**12**	**13**	**4A** (Recov.)
1	THF	0.1	48	24	29	0
2	THF	0.5	83[b]	17	0	0
3	THF	1.0	43	9	48	0
4	THF + HMPA	0.5	35	10	3	52
5	2-Methyltetrahydrofuran	0.5	55[c]	17	22	6
6	DME	0.5	53[d]	18	26	3
7	1,4-Dioxane	0.5	42	11	47	0
8	Et_2O	0.5	30	1	15	54
9	Toluene	0.5	14	0	85	1

[a] Estimated based on ^{31}P NMR peak heights.

[b] $M_n = 1400$, $M_w/M_n = 6.4$, based on GPC (gel permeation chromatography) analysis ($CHCl_3$, polystyrene standard).

[c] $M_n = 21{,}000$, $M_w/M_n = 23$, based on GPC analysis.

[d] $M_n = 27{,}400$, $M_w/M_n = 33$, based on GPC analysis.

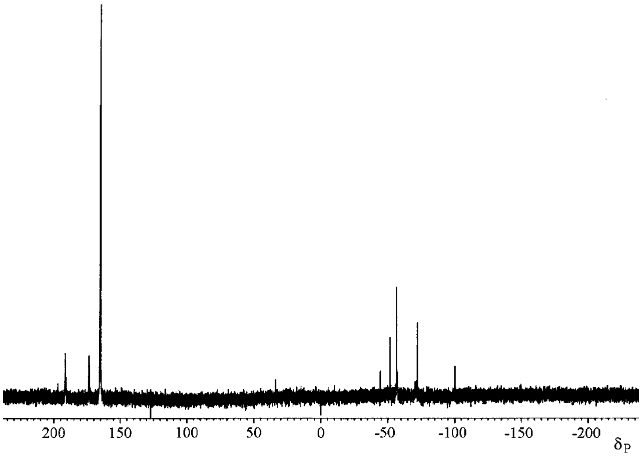


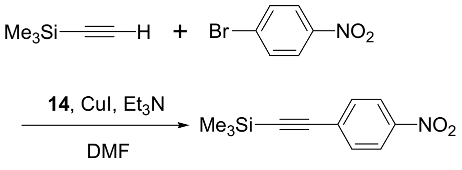
Figure 1. $^{31}P\{^1H\}$ NMR spectrum of **9′** in $CDCl_3$.

adopt (*E*,*E*)-configuration: The spectrum showed a major signal due to phosphorus atoms in the (*E*,*E*)-DPCB units (δ_P 165), two weak signals due to the (*E*,*Z*)-DPCB units (δ_P 174 and 191, J_{PP} is not clear because of broadening), and some high-field signals (−44, −51, −57, −72, −100) probably due to the phosphorus atoms in the terminal moieties. It is likely that the partial *E*/*Z*-isomerization of the DPCB units in **9′** occurred after formation of the polymer by light or a trace of Lewis acid,[17] because the reactions of ethynylphosphines with butyllithium and 1,2-dibromoethane generally proceed stereospecifically to give only the (*E*,*E*)-isomers.[1b]

We then investigated the preparation of a DPCB-polymer transition-metal complex and its catalytic activity. Dichloropalladium complexes of some monomeric DPCB derivatives have been known to catalyze the Sonogashira reaction of trimethylsilylacetylene and 4-bromonitrobenzene.[5a] Thus we prepared a DPCB-polymer palladium complex and applied it to the Sonogashira reaction, as follows: The polymer **9′** was allowed to react with $PdCl_2(PhCN)_2$, in a 1:1 mixture of THF and dichloromethane at ambient temperature for 1 day, to give a brown solid insoluble in common solvents. Elemental analysis of this solid [Found: C, 47.92; H, 5.69; Cl, 12.74; S, 5.50%. Calcd for $(C_{56}H_{78}Cl_4P_2Pd_2S_2)_n$: C, 54.60; H, 6.38; Cl, 11.51; S, 5.21%] showed relatively good agreement with the calculated value of ideal polymer composition **14** containing DPCB moieties and $PdCl_2$ moieties in 1:2 ratio. The result of elemental analysis also indicates that nitrogen atoms derived from benzonitrile in the starting $PdCl_2(PhCN)_2$ did not remain in the polymer complex. Although no information about the coordination state in the polymer has been obtained due to the insolubility, we assume incorporation of $PdCl_2$ in addition to the normal chelate coordination of $PdCl_2$ at the sp^2-phosphorus atoms.

For the purpose of testing the catalytic activity of the DPCB-polymer palladium complex (**14**), the coupling reaction between 4-bromonitrobenzene (61 mg, 0.30 mmol) and ethynyltrimethylsilane (0.60 mol) was tried, in the presence of **14** (5 mg), CuI (0.018 mmol), and triethylamine (0.13 mL) in DMF (1.5 mL) at 100 °C for 24 h to give 4-nitro(trimethylsilylethynyl)benzene in 83% yield (average of two runs, Scheme 3). It should be noted that **14** acted essentially as a heterogeneous catalyst because it is insoluble in DMF at 100 °C, while its activity was comparable to that of the homogeneous monomeric **1b**–$PdCl_2$ catalyst [71% yield of 4-nitro(trimethylsilylethynyl)benzene under similar conditions].[18] The complex **14** is easily removed from reaction media in work-up, which merits application of **14**.

In summary, we have prepared a new DPCB polymer and its dichloropalladium complex. The catalytic activities of the DPCB-polymer Pd-complex have been preliminarily shown. Further investigations on preparations, structures, and applications of DPCB-polymer Pd-complexes are now in progress.



Scheme 3.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2004.08.108. Experimental procedures and spectroscopic data for compounds (*E*,*Z*)-**1b**, **4A**–**C**, **6A**–**C**, **7A**–**C**, **8A**–**C**, **9′**, **12**, and **14**.

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11. Molecular weight was determined by GPC (solvent: $CHCl_3$) using a polystyrene standard.
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14. Selected data for **4A**: brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.21–1.68$ (12H, m, CH_2), 1.34 (18H, s, *p-t*-Bu), 1.68 (36H, s, *o-t*-Bu), 2.73 (4H, t, $^3J_{HH} = 7.5$ Hz, CH_2), 5.96 (2H, d, $^1J_{PH} = 249.5$ Hz, PH), 6.58 (2H, d, $^3J_{HH} = 3.6$ Hz, thiophene), 6.95 (2H, d, $^3J_{HH} = 3.6$ Hz, thiophene), and 7.51 (4H, s, arom.); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta = 28.8$, 29.0, 30.0, 31.2, 31.4, 33.6, 35.0, 38.4, 91.4 (d, $^1J_{PC} = 22.3$ Hz, C≡C), 96.0 (s, C≡C), 120–127, 132.2, 148.1, 150.5, and 155.5 (d, $^2J_{PC} = 10.6$ Hz); ^{31}P NMR (162 MHz, $CDCl_3$) $\delta = -100.1$ (d, $^1J_{PH} = 249.5$ Hz). FAB-MS *m*/*z* 877 ($M^+ - 1$) and 275 ($Mes^*P^+ - 1$). Found: *m*/*z* 878.5171. Calcd for $C_{56}H_{80}P_2S_2$: M, 878.5173.
15. The coupling reaction of lithium phosphide (generated by the reaction of **4A** with *n*-BuLi) seemed to be rather complicated, because the lithium (thienylethynyl)phosphide isomerized to phosphaallenyllithium species, which also formed DPCB derivative by treatment with 1,2-dibromoethane.[1h] This may be the reason for the large M_w/M_n ratio.
16. Selected data for **9′**: brown solid; UV (CH_2Cl_2) 247, 293, 344, and 445 (sh) nm; IR (KBr) 2951, 2158, 1589, 1462, 1394, 1360, 1238, 1207, 1174, 1120, 874, and 798 cm^{-1}. Found: C, 73.22; H, 8.59; S, 7.33%. Calcd for $(C_{56}H_{78}P_2S_2)_n$: C, 76.67; H, 8.96; S, 7.31%.
17. In fact, monomeric (*E*,*E*)-**1b** was converted to (*E*,*Z*)-**1b** by photo-irradiation or addition of a catalytic amount of iodine. (*E*,*Z*)-**1b**: δ_P 177.9 and 195.9, AB, $^3J_{PP} = 17.2$ Hz.
18. Similarly to the cases of the previously reported DPCB–$PdCl_2$ complexes,[5a] the catalytic activities of **14** and **1b**-$PdCl_2$ are not as high as that of $(Ph_3P)_2PdCl_2$ complex, which works at room temperature in the Sonogashira reaction.