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Reactions of 1,2-di(2-thienyl)-3,4-bis[(2,4,6-tri-*t*-butylphenyl)-phosphinidene]cyclobutene

Akitake Nakamura, Subaru Kawasaki, Kozo Toyota *, Masaaki Yoshifuji *,[1]

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba, Sendai 980-8578, Japan

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Abstract

Reactions of a sterically protected 1,2-di(2-thienyl)-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene were investigated. The diphosphinidenecyclobutene reacted with elemental sulfur or transition metal reagents to form a thiaphosphirane derivative or the corresponding transition metal complexes, respectively. Reactions of the di(2-thienyl)diphosphinidenecyclobutene with butyllithium followed by treatment with electrophiles afforded functionalized di(2-thienyl)diphosphinidenecyclobutene derivatives.

Keywords: Phosphaalkenes; Bidentate ligand; Steric and strain effects

1. Introduction

Sterically protected 3,4-diphosphinidenecyclobutenes (hereafter abbreviated to DPCB, Chart 1) [1], bearing an extremely bulky 2,4,6-tri-*t*-butylphenyl group (abbreviated to the Mes* group) [2], are unique ligands of interest [3,4], because of their relatively rigid framework containing the phosphorus–carbon π-bonds [5], as well as their dynamic behavior such as photo- or iodine-induced E/Z-isomerizations [1g]. We have prepared various transition metal complexes of DPCB [3] and some of them were used as homogeneous catalysts [4]. DPCB derivatives **1A**–**E** [1a,4b,4c,4d] and **2**–**4** [1c,1d,1e], containing aromatic substituents at the 1,2-positions, have been reported and we have recently described preparation of a 1,2-dithienyl derivative (*E*,*E*)-**5a** [1j].

The compounds (*E*,*E*)-**1B**-**E** were prepared from the corresponding phenylacetylene derivatives and not from straightforward substitution of the phenyl rings of (*E*,*E*)-**1A**: The straightforward introduction of substituents to the phenyl rings of (*E*,*E*)-**1A** seems to be difficult, because phosphorus–carbon π-bonds are relatively reactive. Indeed, reaction of (*E*,*E*)-**1A** with bromine (1.5 molar amount) in trimethyl phosphate at room temperature for 30 min led to the formation of a complex mixture of products containing (*E*,*Z*)-**1A** [1g] (Chart 2).

On the other hand, compound (*E*,*E*)-**5a** is a promising building block for construction of more elaborate DPCB derivatives, because introduction of a functional group (at the position α to the sulfur atom) is expected to be easy under mild conditions. Actually, we have prepared (*E*,*E*)-**5b** and (*E*,*E*,*E*,*E*)-**6** starting from (*E*,*E*)-**5a** [1j]. However, introduction of synthetically more useful functional groups is desired from viewpoint of materials science, in order to construct more sophisticated DPCB derivatives. We report here the reactions and functionalizations of (*E*,*E*)-**5a**.

2. Results and discussion

2.1. Preparation of 1,2-di(2-thienyl)-3,4-diphosphinidenecyclobutene

First, we prepared (thienylethynyl)phosphine **8** (Scheme 1) by the Corey–Fuchs reaction [6] but not by the reported

* Corresponding authors. Tel.: +81 22 795 6559; fax: +81 22 795 6562 (K. Toyota), Tel.: +1 205 348 0455; fax: +1 205 348 4704 (M. Yoshifuji).
E-mail addresses: toyota@mail.tains.tohoku.ac.jp (K. Toyota), yoshifuj@mail.tains.tohoku.ac.jp (M. Yoshifuji).
[1] Present address: Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487-0336, USA.

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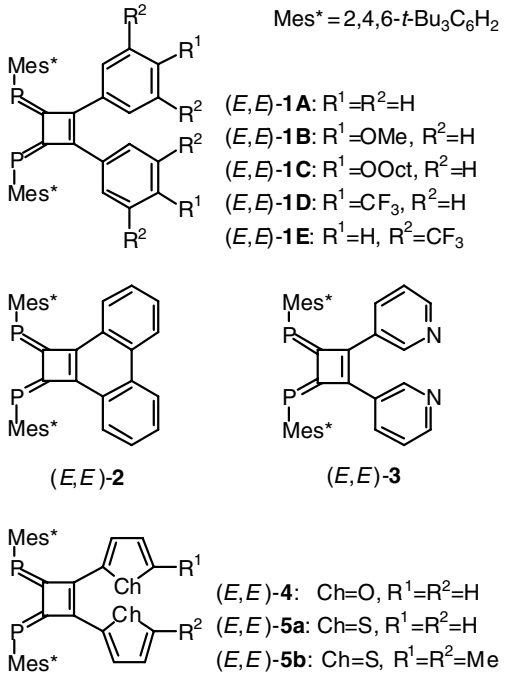
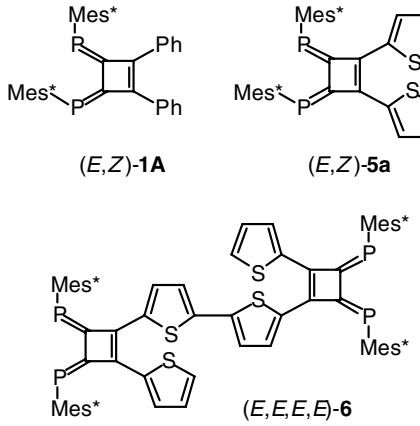


Chart 1.



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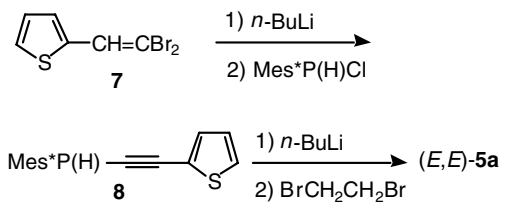


Scheme 1.

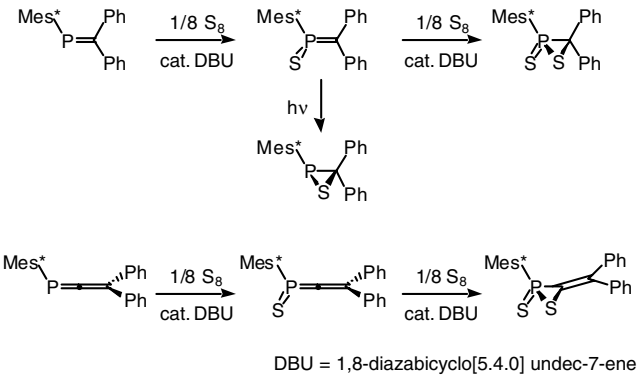
method [1j]: 2-(2′,2′-dibromovinyl)thiophene **7** [7] was prepared from thiophene via thiophene-2-carboxaldehyde. One pot reaction of **7** using butyllithium and chloro(2,4,6-tri-*t*-butylphenyl)phosphine [8] afforded **8**. The phosphine **8** was then converted to (*E*,*E*)-**5a** by a reported method [1j]. Compared with the previous method, the present method has an advantage: isolation of volatile thienylacetylene is not necessary. The compound obtained here was subjected to the following reactions (Sections 2.2.1, 2.2.2 and 2.3).

2.2. Reactions of 1,2-di(2-thienyl)-3,4-diphosphinidenecyclobutene at the phosphorus atom(s)

2.2.1. Reaction of 1,2-di(2-thienyl)-3,4-diphosphinidenecyclobutene with sulfur

Phosphorus–carbon double bonds are known to react with elemental sulfur at the phosphorus atoms [9] to give thiaphosphirane *P*-sulfides via phosphaethene *P*-sulfide intermediates. We have studied sulfurization of the Mes*-substituted phosphaethenes Mes*P = CR_2 in detail and we found a photo-induced isomerization of phosphaethene *P*-sulfide as shown in Scheme 2 [10]. A similar sulfurization reaction of 1-phosphaallene giving methylenethiaphosphirane *P*-sulfide has also been reported by us (Scheme 2) [11]. Here we have applied the sulfurization reaction to (*E*,*E*)-**5a** as follows.

An attempted reaction of (*E*,*E*)-**5a** with elemental sulfur at room temperature for 3 h resulted in the recovery of (*E*,*E*)-**5a**. However, in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), (*E*,*E*)-**5a** reacted with an excess amount of sulfur at room temperature for 10 days to give **11a** in 54% yield (Scheme 3). In order to prevent the photo-induced isomerization however, the reaction was performed in the dark. ^{31}P NMR spectrum of **11a** showed an AB pattern [δ_P (C_6D_6) −12.4 (d, $^3J_{PP}$ = 4.1 Hz) and 115.7 (d, $^3J_{PP}$ = 4.1 Hz)], which indicated the unsymmetrical structure of **11a**. ^{31}P NMR monitoring of the reaction mixture suggested a reaction pathway via **9a** and **10a** as shown in Scheme 3. Although the compounds **9a** and **10a** were not isolated in the pure form, signals assignable to these intermediates were observed during the reaction [**9a**: δ_P (C_6D_6) 107.4 (d, $^3J_{PP}$ = 5.0 Hz) and 200.5 (d, $^3J_{PP}$ = 5.0 Hz); **10a**: δ_P (C_6D_6) −8.8 and 197.9]. The steric hindrance seems to affect the reaction pathway. For example, signals due to bis(mono-sulfurized) derivative **12a** (Chart 3) or tetra-sulfurized derivative **13a** were not



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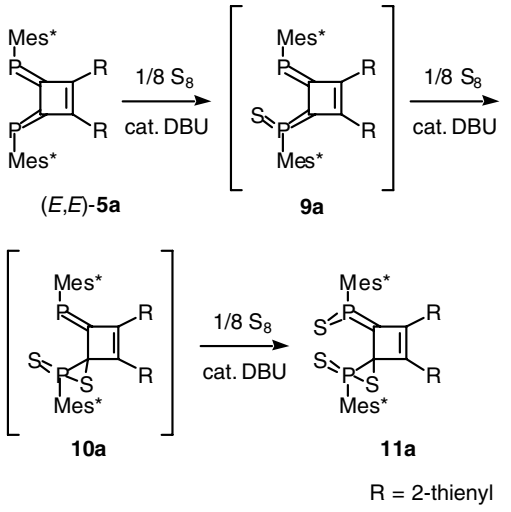

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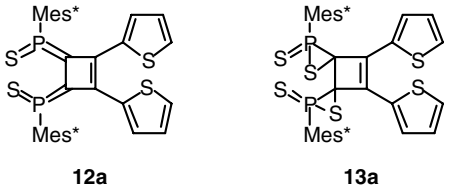
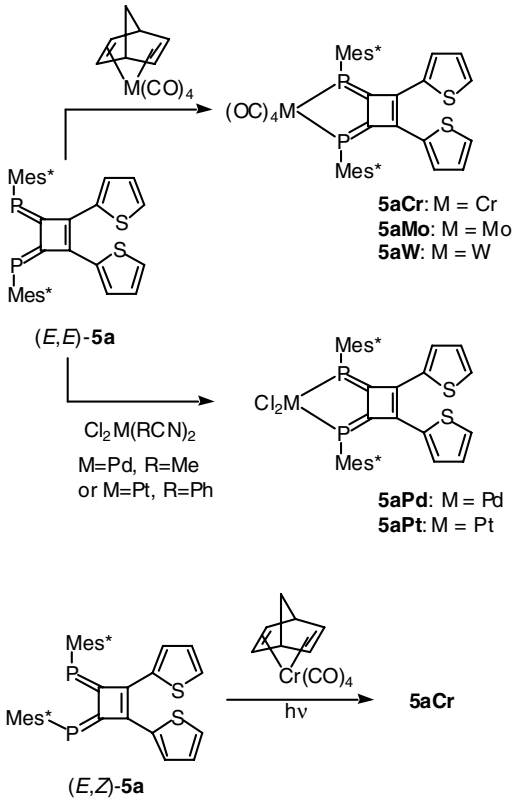


Chart 3.



Scheme 4.

observed at least as major signals during the ^{31}P NMR monitoring, even when more or less equivalents of sulfur were used. Unfortunately, an attempted X-ray crystallographic analysis of **11a** failed due to the lack of single crystal suitable for a diffraction experiment.

2.2.2. Reactions of 1,2-di(2-thienyl)-3,4-diphosphinidenecyclobutene with some transition metal reagents

Next, we studied transition metal complex formation of **5a** as follows (Scheme 4). Reaction of (*E*,*E*)-**5a** with [group(6) transition metal][(bicyclo[2.2.1]hepta-2,5-diene)-tetracarbonyl] complexes gave the corresponding tetracarbonylmetal complexes **5aCr** (quant.), **5aMo** (quant.), and **5aW** (37% yield). When (*E*,*E*)-**5a** was treated with $(MeCN)_2PdCl_2$ at room temperature in THF, complex **5aPd** was formed in 75% yield. Reaction of (*E*,*E*)-**5a** with $(PhCN)_2PtCl_2$ under similar conditions resulted in the recovery of (*E*,*E*)-**5a**. However, when the reaction was carried out at 50 °C for 2 days, complex **5aPt** was obtained in 19% yield.

It should be noted that an attempted reaction of (*E*,*E*)-**5a** with nickel complexes such as $NiBr_2$(dme) has been unsuccessful (recovery of (*E*,*E*)-**5a**, after 15 h-stirring in THF-d_8 at room temperature followed by an additional 3 h-stirring at 60 °C), probably because coordinating ability of lone pair of sp^2 hybridized phosphorus atom is weak compared to that of sp^3 hybridized phosphorus atom, due to less p-character of the lone pair.

Photo-induced isomerization and complex formation of (*E*,*Z*)-**5a** [12a] were confirmed as follows. The ^{31}P NMR spectroscopic monitoring of a reaction mixture of (*E*,*Z*)-**5a** with (bicyclo[2.2.1]hepta-2,5-diene)tetracarbonylchromium(0) in THF-d_8 did not show significant change in the dark at room temperature after 4 h, however, irradiation of the solution with a Xe lamp (300 W) for 24 h led to the formation of **5aCr**. A similar dynamic behavior of DPCB derivatives has been shown in a previous report [1g].

2.2.3. UV–Vis spectra and cyclic voltammograms of 1,2-di(2-thienyl)-3,4-diphosphinidenecyclobutene complexes

Fig. 1 shows UV–Vis spectra of compound (*E*,*E*)-**5a** and its complexes **5aCr**,**Mo**,**W**,**Pd**,**Pt**, while Fig. 2 shows UV–Vis spectra of compound (*E*,*E*)-**1A** and its complexes **1ACr**,**Mo**,**W**,**Pd**,**Pt**. Compared to the free ligand **5a**, bathochromic shifts of **5aPd** and **5aPt** were observed and wavelengths of the absorption bands for **5aPt** (ca. 390 and ca. 500 nm) were longer than the corresponding wavelengths of the bands of **5aPd**. A similar tendency was observed in the case of the complexes **1APd** and **1APt**. The group(6) metal complexes of **5a** and **1A** showed large bathochromic shifts, compared to the free ligands. As for the MLCT band at ca. 450 nm, the order of red shift is Cr > Mo ~ W for both **5a**-series and **1A**-series. This tendency was also shown in the cases of other DPCB derivatives such as 1,2-trimethylsilyl substituted DPCB [3a], probably because essentially the same molecular and atomic orbitals are concerned. When we compare the spectra of complexes of **5a**

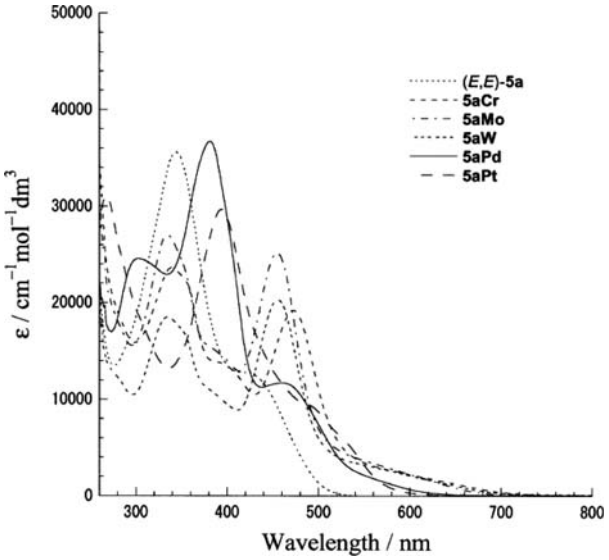


Fig. 1. UV–Vis spectra for **5a** and its complexes in CH_2Cl_2.

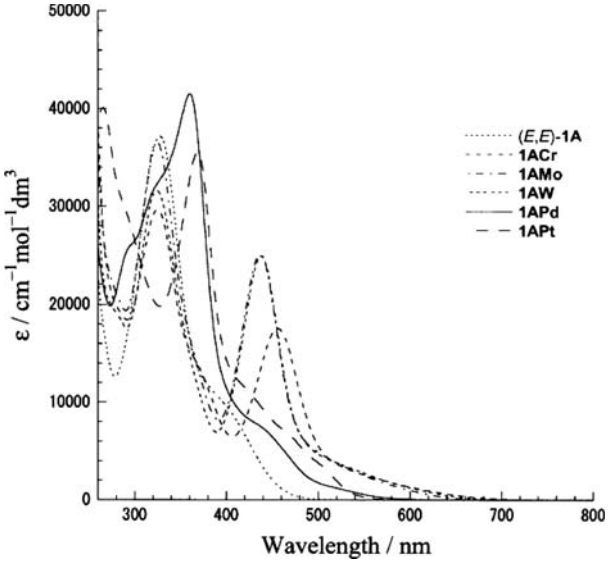


Fig. 2. UV–Vis spectra for **1A** and its complexes in CH_2Cl_2.

with those of the corresponding complexes of **1A**, complexes of **5a** show red shifts, as shown in the cases of the free ligands. Probably, the coplanarity of the cyclobutene ring with the 1,2-thiophene rings is better than that of the cyclobutene ring with the 1,2-phenyl rings.

Redox activity of assembled- or functionalized metal complexes attracts current interest [13] and reversible redox steps play an important role in the studies of these material-oriented complexes. Redox properties of the complexes of **5a** will give fundamental information about the behavior of the DPCB-transition metal complexes. Table 1 shows oxidation potentials of **5a** and its complexes. Although the first oxidation wave of the free ligand **5a** was irreversible, the group(6) metal carbonyl complexes **5aCr**,**Mo**,**W** showed reversible first oxidation waves, probably due to

Table 1
CV data for **5a** and its complexes[a]

Compound	E_1^{ox}	E_2^{ox}	E_1^{red}	E_2^{red}
(*E*,*E*)-**5a**	E_p 0.88			
5aCr	$E_{1/2}$ 0.44			
5aMo	$E_{1/2}$ 0.54	E_p 0.91	$E_{1/2}$ −1.69	
5aW	$E_{1/2}$ 0.51	E_p 0.88	$E_{1/2}$ −1.67	
5aPd	E_p 1.22		E_p −0.97	E_p −1.78
5aPt	E_p 1.17		E_p −1.31	E_p −1.47

[a] Conditions: 1 mM in CH_2Cl_2 with 0.1 M *n*-Bu_4NClO_4 as a support electrolyte. Working electrode: glassy carbon; counter electrode: Pt wire; reference electrode: Ag/0.01 M $AgNO_3$ in acetonitrile with 0.1 M *n*-Bu_4NClO_4 [$E_{1/2}$ (Fc/Fc^+) = 0.23 V]; scan rate: 100 mV/s.

oxidation of the metal(0) center, while the second oxidation (probably due to the phosphorus center) turned out to be irreversible. The complexes **5aMo** and **5aW** showed reversible first reduction waves. The reversible redox properties found here will lead to further investigation of complexes of the related DPCB ligands, as well as those of DPCB oligomers and polymers [1h,12].

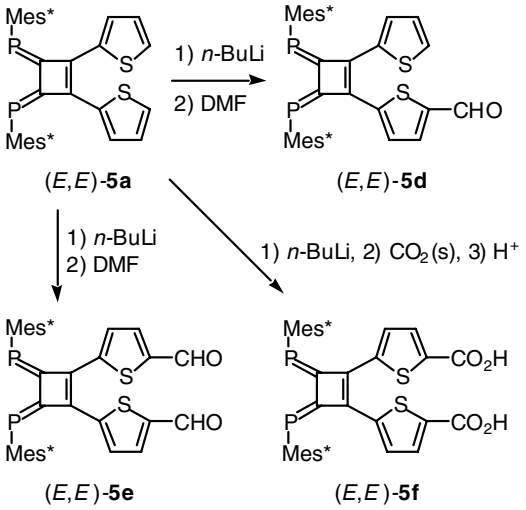
2.3. Reactions of 1,2-di(2-thienyl)-3,4-diphosphinidenecyclobutene on the thiophene ring(s)

2.3.1. Reactions of 1,2-di(2-thienyl)-3,4-diphosphinidenecyclobutene with some halogenating reagents

We then examined several reactions of **5a** on the thiophene rings. Iodination of thiophenes by *N*-iodosuccinimide (NIS) at the 2-position is an established method in the chemistry of thiophenes and oligothiophenes [14]. Thus, we first attempted iodination of (*E*,*E*)-**5a** with NIS. When a mixture of (*E*,*E*)-**5a** and NIS in chloroform was stirred in the dark at room temperature for 3 h, (*E*,*Z*)-**5a** was formed nearly quantitatively, probably because iodine (formed from NIS) caused the isomerization [1g] of (*E*,*E*)-**5a**. A similar result was obtained in the reaction of (*E*,*E*)-**5a** with NIS in the presence of acetic acid (normal conditions for iodination of thiophenes). In these reactions, iodonation of the thiophene rings of (*E*,*E*)-**5a** did not occur. These facts suggest that functionalization of the thienyl-DPCB is more difficult than that of normal thiophene compounds. In order to keep the (*E*,*E*)-geometry of DPCB, introduction of functional groups should be carried out in the absence of bromine or iodine molecules (it should be noted that addition of acetic acid to DPCB did not cause noticeable *E*,*Z*-isomerization at room temperature in 1 d).

2.3.2. Lithiation and functionalization of 1,2-di(2-thienyl)-3,4-diphosphinidenecyclobutene

We then investigated introduction of functional groups via lithiation of the thiophene moiety of **5a**. An attempted introduction of iodine by successive treatment of (*E*,*E*)-**5a** with butyllithium (2 equiv.) and ICl (2 equiv.) resulted in the formation of a complex mixture of products including (*E*,*Z*)-**5a** and some decomposed product. Lithiation of (*E*,*E*)-**5a** with butyllithium (1 equiv.), followed by reaction with DMF (1 equiv.), successfully afforded the corresponding



Scheme 5.

formyl derivative (*E*,*E*)-**5d** in 70% yield (Scheme 5). A large spin–spin coupling constant in the ^{31}P NMR spectrum of the product ($^{3}J_{PP} = 98.4$ Hz) is a characteristic of 1,2-unsymmetrically substituted (*E*,*E*)-DPCB [1e,1k]. When 2 equiv. of butyllithium and DMF were used, diformyl compound (*E*,*E*)-**5e** was obtained in 76% yield. Similarly, dicarboxylic acid (*E*,*E*)-**5f** was obtained (66% yield) by successive treatment of (*E*,*E*)-**5a** with butyllithium and dry ice and water.

These results indicate that the thienyl group is a promising substituent for introduction of various functional group near the DPCB center under basic conditions. It should be emphasized that decomposition or isomerization of the P=C bond was suppressed under these conditions.

3. Conclusion

Various reactions of the 1,2-dithienyl-3,4-diphsophinidenecyclobutene were curried out and the products were studied. Carbonyl functional groups such as formyl and carboxyl groups were successfully introduced to the thiophene ring without decomposition or isomerization of the phosphorus–carbon double bonds. Utilization of the thienyl group turned out to be a fairly useful method for introduction of functional groups into the proximity of the DPCB center under mild conditions. The DPCB derivatives obtained here will become good building blocks for construction of more elaborate ligands containing sp^2 hybridized phosphorus atoms. The findings described here will help development of DPCB-transition metal catalysts [4] and DPCB polymer-transition metal complexes [1h,12a]. Further investigation is in progress concerning conversions of the introduced functional groups of (*E*,*E*)-**5d-f**. These compounds are key building blocks for construction of DPCB oligomers and will give fertile chemistry of functionalized DPCB ligands and their complexes.

4. Experimental

4.1. General

Melting points were measured on a Yanagimoto MP-J3 micro-melting points apparatus and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 or a Bruker AM-600 spectrometer with TMS as the internal standard. ^{31}P NMR spectra were collected on a Bruker Avance-400 spectrometer using 85% H_3PO_4 as an external standard. UV–Vis spectra were measured on a Hitachi U-3210 spectrometer. IR spectra were obtained on a Horiba FT-300 spectrometer. FT-ICR-MS spectra were measured on a Bruker APEX III spectrometer. Cyclic voltammograms were recorded on a BAS-CV-50W voltammetric analyzer under nitrogen. Reactions were performed under an argon atmosphere, while work-up was carried out in air, unless otherwise specified. Complexes **1ACr**, **1AMo**, **1AW**, and **1APd** were prepared according to the literature [3d,4a] and their UV–Vis spectra were measured at room temperature in air.

4.2. (*E*,*E*)-1,2-Di(2-thienyl)-3,4-bis[(2,4,6-tri-t-butylphenyl)phosphinidene]cyclobutene (**5a**)

A mixture of (2,4,6-tri-*t*-butylphenyl)phosphine (7.498 g, 26.93 mmol) [15] and 2,2′-azobisisobutyronitrile (AIBN) (273.0 mg, 1.663 mmol) in carbon tetrachloride (72 mL) was refluxed for 4 h. The resulting mixture was concentrated and 50 mL of THF was added to chloro-(2,4,6-tri-*t*-butylphenyl)phosphine. To a solution of 2-(2′,2′-dibromovinyl)thiophene (**7**, 26.82 mmol) in THF (50 mL) was added 53.82 mmol of butyllithium (1.56 M solution in hexane) at −78 °C. The resulting solution was stirred for 1 h, allowed to warm to room temperature, and stirred for an additional 1 h. The solution was added to the above THF solution of the chlorophosphine and the combined mixture was stirred for 1 h and worked up using hexane and brine, and then the organic phase was dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was submitted to a silica-gel column chromatographic treatment (hexane) to give 7.650 g of **8** (74% yield based on the starting Mes*PH_2). The phosphine **8** was converted to (*E*,*E*)-**5a** by a method reported previously [1j].

4.3. Sulfurization reaction of (*E*,*E*)-**5a**

To a mixture of (*E*,*E*)-**5a** (98.1 mg, 0.128 mmol) and elemental sulfur (25.1 mg, 0.81 mg-atom) in dry benzene (10 mL) was added 0.03 mmol of DBU. The resulting solution was stirred in the dark at room temperature. The reaction was monitored by ^{31}P NMR spectroscopy (an appropriate amount of C_6D_6 was added to the sample solution). The reaction mixture was stirred for 2 days and DBU (0.03 mmol) was added. After additional 3 days-stirring, DBU (0.03 mmol) was added again, and the resulting

mixture was stirred for an additional 5 days. The solution was then passed through a short alumina column (eluent: $CHCl_3$) and the solvent was removed under reduced pressure. The residue was then separated by a column chromatography (Al_2O_3/CCl_4) to give 59.2 mg of **11a** (54% yield). Orange solid, m.p. 167–170 °C (dec.); ^{1}H NMR (600 MHz, CD_2Cl_2) $\delta = 1.19$ (9H, s, *p*-*t*-Bu), 1.29 (9H, s, *p*-*t*-Bu), 1.62 (9H, s, *o*-*t*-Bu), 1.66 (9H, s, *o*-*t*-Bu), 1.74 (9H, d, $^5J_{PH} = 0.6$ Hz, *o*-*t*-Bu), 1.82 (9H, s, *o*-*t*-Bu), 6.06 (1H, ddd, $^3J_{HH} = {}^5J_{PH} = 4.2$ Hz, $^4J_{HH} = 0.8$ Hz, 3-thiophene), 6.45 (1H, dd, $^3J_{HH} = 3.6$ Hz, $^4J_{HH} = 1.1$ Hz, 3-thiophene), 6.46 (1H, dd, $^3J_{HH} = 4.9$ Hz, $^3J_{HH} = 4.2$ Hz, 4-thiophene), 6.66 (1H, dd, $^3J_{HH} = 5.0$ Hz, $^3J_{HH} = 3.6$ Hz, 4-thiophene), 6.89 (1H, dd, $^4J_{PH} = 7.1$ Hz, $^4J_{HH} = 1.8$ Hz, *m*-Mes*), 6.93 (1H, ddd, $^3J_{HH} = 4.9$ Hz, $^6J_{PH} = 1.8$ Hz, $^4J_{HH} = 0.8$ Hz, 5-thiophene), 7.09 (1H, dd, $^4J_{HH} = 5.0$ Hz, $^4J_{HH} = 1.1$ Hz, 5-thiophene), 7.38 (1H, dd, $^4J_{PH} = 5.4$ Hz, $^4J_{HH} = 1.8$ Hz, *m*-Mes*), 7.42 (1H, dd, $^4J_{PH} = 5.4$ Hz, $^4J_{HH} = 1.8$ Hz, *m*-Mes*), and 7.49 (1H, dd, $^4J_{PH} = 5.5$ Hz, $^4J_{HH} = 1.8$ Hz, *m*-Mes*); ^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2) $\delta = 31.1$ (s, *p*-C*Me*$_3$), 31.2 (s, *p*-C*Me*$_3$), 33.6 (s, *o*-C*Me*$_3$), 34.0 (s, *o*-C*Me*$_3$), 34.6 (s,*o*-C*Me*$_3$), 34.8 (s, *o*-C*Me*$_3$), 35.0 (s, *p*-*C*Me$_3$), 35.6 (s, *p*-*C*Me$_3$), 39.6 (d, $^3J_{PC} = 2.6$ Hz, *o*-*C*Me$_3$), 40.1 (d, $^3J_{PC} = 2.3$ Hz, *o*-*C*Me$_3$), 40.2 (d, $^3J_{PC} = 2.6$ Hz, *o*-*C*Me$_3$), 41.7 (s, *o*-*C*Me$_3$), 61.1 (dd, $^1J_{PC} = 31.7$ Hz, $^2J_{PC} = 8.0$ Hz, PSC), 122.6 (d, $^3J_{PC} = 15.6$ Hz, *m*-Mes*), 124.0 (d, $^3J_{PC} = 13.8$ Hz, *m*-Mes*), 124.3 (d, $^3J_{PC} = 13.6$ Hz, *m*-Mes*), 125.4 (d, $^1J_{PC} = 81.1$ Hz, *ipso*-arom.), 126.7 (d, $^3J_{PC} = 14.3$ Hz, *m*-Mes*), 126.9 (s, thienyl), 127.09 (s, thienyl), 127.13 (s, thienyl), 127.4 (s, thienyl), 127.5 (d, $^4J_{PC} = 2.7$ Hz, thienyl), 128.7 (s, thienyl), 129.9 (d, $^1J_{PC} = 78.0$ Hz, *ipso*-Mes*), 131.6 (s, *ipso*-thienyl), 132.0 (d, $^3J_{PC} = 2.4$ Hz, *ipso*-thienyl), 137.1 (dd, $^2J_{PC} = 55.5$ Hz and $^3J_{PC} = 8.2$ Hz, P=C–*C*), 140.2 (dd, $^1J_{PC} = 134.5$ Hz and $^2J_{PC} = 3.8$ Hz, P=C), 141.9 (dd, $^2J_{PC} = {}^3J_{PC} = 12.9$ Hz, P–C–*C*), 153.3 (d, $^4J_{PC} = 3.5$ Hz, *p*-arom.), 154.1 (d, $^2J_{PC} = 12.8$ Hz, *o*-arom.), 154.8 (d, $^4J_{PC} = 3.5$ Hz, *p*-arom.), 154.9 (d, $^2J_{PC} = 6.0$ Hz, *o*-arom.), 155.0 (d, $^2J_{PC} = 7.3$ Hz, *o*-arom.), and 156.9 (d, $^2J_{PC} = 7.7$ Hz, *o*-arom.); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) $\delta = -12.3$ (d, $^3J_{PP} = 4.6$ Hz) and 115.1 (d, $^3J_{PP} = 4.6$ Hz); IR (KBr) 2960, 2908, 2866, 1595, 1477, 1400, 1363, 1236, 1213, 1124, 850, 777, and 700 cm^{-1}; UV–Vis (CH_2Cl_2) 270 (sh, log ε 4.39), 344 (3.96), and 430 nm (4.43). Found *m*/*z* 885.2975. Calc. for $C_{48}H_{64}NaP_2S_5$: M^++Na, 885.2979. Found: C, 66.70; H, 7.53; S, 18.43%. Calc. for $C_{48}H_{64}P_2S_5$: C, 66.78; H, 7.47; S, 18.57.

4.4. Transition metal complexes of *5a*

4.4.1. [1,2-Di(2-thienyl)-3,4-bis{(2,4,6-tri-t-butylphenyl)phosphinidene}cyclobutene]-tetracarbonylchromium(0) (*5aCr*)

A mixture of (*E*,*E*)-**5a** (87.0 mg, 0.113 mmol) and (bicyclo[2.2.1]hepta-2,5-diene)tetracarbonylchromium(0) (57.4 mg, 0.224 mmol) in THF (2 mL) was stirred at room temperature for 2 h. The solvent was removed under reduced pressure and the residue was treated with silica-gel column chromatography (hexane-$CHCl_3$, 5:1) to give the desired complex **5aCr** in nearly quantitative yield. **5aCr**. Black solid, m.p. > 125 °C (dec.); ^{1}H NMR (600 MHz, $CDCl_3$) $\delta = 1.41$ (18H, s, *p*-*t*-Bu), 1.67 (36H, s, *o*-*t*-Bu), 5.95 (2H, d, $^3J_{HH} = 3.6$ Hz, thiophene), 6.63 (2H, dd, $^3J_{HH} = 4.8$, 3.6 Hz, thiophene), 7.11 (2H, d, $^3J_{HH} = 4.8$ Hz, thiophene), and 7.50 (4H, s, *m*-Mes*); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) $\delta = 31.5$ (s, *p*-C*Me*$_3$), 33.9 (s, *o*-C*Me*$_3$), 35.3 (s, *p*-*C*Me$_3$), 38.8 (s, *o*-*C*Me$_3$), 122.7 (s, *m*-Mes*), 127.4 (s, thiophene), 128.2 (s, thiophene), 129.5 (s, thiophene), 132.4 (s, thiophene), 134.8 (d, $^1J_{PC} = 178.1$ Hz, *ipso*-Mes*), 143.8 (dd, $^2J_{PC} = 55.8$ Hz, $^3J_{PC} = 34.7$ Hz, P=C–*C*), 152.6 (s, *p*-Mes*), 157.6 (s, *o*-Mes*), 174.9 (dd, $^1J_{PC} = 28.7$ Hz, $^2J_{PC} = 22.6$ Hz, P=C), 220.0 (t, $^2J_{PC} = 17.4$ Hz, CO), and 228.0 (d, $^2J_{PC} = 5.1$ Hz, CO); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) $\delta = 189.2$; IR (KBr) 2962, 2910, 2871, 2013, 1957, 1923, 1892, 1593, 1473, 1414, 1404, 1363, 1240, 1211, 1126, 702, 667, 627, and 474 cm^{-1}; UV–Vis (CH_2Cl_2) 340 (log ε 4.37) and 472 nm (4.28). Found *m*/*z* 818.3332. Calc. for $C_{50}H_{64}CrP_2S_2$: M–4CO, 818.3324. Found: C, 63.90; H, 6.85; S, 6.52%. Calc. for $C_{52}H_{64}CrO_4P_2S_2 \cdot 3H_2O$: C, 63.40; H, 7.16; S, 6.51.

4.4.2. [1,2-Di(2-thienyl)-3,4-bis{(2,4,6-tri-t-butylphenyl)phosphinidene}cyclobutene]-tetracarbonylmolybdenum(0) (*5aMo*)

A mixture of (*E*,*E*)-**5a** (80.2 mg, 0.104 mmol) and (bicyclo[2.2.1]hepta-2,5-diene)tetracarbonylmolybdenum(0) (37.7 mg, 0.126 mmol) in THF (2 mL) was stirred at room temperature for 3 h. The solvent was removed under reduced pressure and the residue was treated with silica-gel column chromatography (hexane-$CHCl_3$, 75:1) to give the desired complex **5aMo** almost quantitatively. **5aMo**, dark brown solid, m.p. > 150 °C; ^{1}H NMR (600 MHz, $CDCl_3$) $\delta = 1.41$ (18H, s, *p*-*t*-Bu), 1.66 (36H, s, *o*-*t*-Bu), 5.98 (2H, d, $^3J_{HH} = 3.6$ Hz, thiophene), 6.71 (2H, dd, $^3J_{HH} = 5.4$, 3.6 Hz, thiophene), 7.11 (2H, d, $^3J_{HH} = 5.4$ Hz, thiophene), and 7.49 (4H, s, *m*-Mes*); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) $\delta = 31.5$ (s, *p*-C*Me*$_3$), 34.0 (s, *o*-C*Me*$_3$), 35.3 (s, *p*-*C*Me$_3$), 38.9 (s, *o*-*C*Me$_3$), 122.7 (s, *m*-Mes*), 127.4 (s, thiophene), 128.4 (s, thiophene), 129.1 (d, $^1J_{PC} = 6.0$ Hz, *ipso*-Mes*), 129.7 (s, thiophene), 132.2 (s, thiophene), 144.2 (dd, $^2J_{PC} = 55.8$ Hz, $^3J_{PC} = 34.7$ Hz, P=C–*C*), 152.5 (s, *p*-Mes*), 157.4 (s, *o*-Mes*), 175.3 (dd, $^1J_{PC} = 30.2$ Hz, $^2J_{PC} = 22.6$ Hz, P=C), 209.2 (t, $^2J_{PC} = 12.1$ Hz, CO), and 216.7 (dd, $^2J_{PC} = 41.5$, 11.4 Hz, CO); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) $\delta = 173.1$; IR (KBr) 2962, 2025, 1928, 1892, 704, 609, and 575 cm^{-1}; UV–Vis (CH_2Cl_2) 335 (log ε 4.43) and 454 nm (4.40). Found *m*/*z* 864.3001. Calc. for $C_{48}H_{64}MoP_2S_2$: M–4CO, 864.2977. Found: C, 60.38; H, 6.58; S, 6.15%. Calc. for $C_{52}H_{64}MoO_4P_2S_2 \cdot 3H_2O$: C, 60.69; H, 6.86; S, 6.23.

4.4.3. [1,2-Di(2-thienyl)-3,4-bis{(2,4,6-tri-t-butylphenyl)phosphinidene}cyclobutene](tetracarbonyl)tungsten(0) (**5aW**)

A mixture of (*E*,*E*)-**5a** (83.0 mg, 0.108 mmol) and (bicyclo[2.2.1]hepta-2,5-diene)tetracarbonyltungsten(0) (83.9 mg, 0.216 mmol) in THF (2 mL) was stirred at 50 °C for 1 day. The solvent was removed under reduced pressure and the residue was treated with silica-gel column chromatography (hexane-$CHCl_3$, 5:1) to give the desired complex **5aW** (42.7 mg, 37% yield). Black solid, m.p. > 180 °C (dec.); ^{1}H NMR (600 MHz, $CDCl_3$) $\delta = 1.42$ (18H, s, *p*-*t*-Bu), 1.67 (36H, s, *o*-*t*-Bu), 5.99 (2H, d, $^3J_{HH} = 3.6$ Hz, thiophene), 6.63 (2H, dd, $^3J_{HH} = 4.8$, 3.6 Hz, thiophene), 7.13 (2H, d, $^3J_{HH} = 4.8$ Hz, thiophene), and 7.51 (4H, s, *m*-Mes*); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) $\delta = 31.5$ (s, *p*-C*Me*$_3$), 34.1 (s, *o*-C*Me*$_3$), 35.3 (s, *p*-*C*Me$_3$), 39.0 (s, *o*-*C*Me$_3$), 122.8 (t, $^3J_{PC} = 3.0$ Hz, *m*-Mes*), 127.5 (s, thiophene), 128.2 (s, *ipso*-Mes*), 128.2 (s, thiophene), 129.6 (s, thiophene), 132.2 (s, thiophene), 142.8 (m, P=C–*C*), 152.7 (s, *p*-Mes*), 157.6 (s, *o*-Mes*), 174.9 (dd, $^1J_{PC} = 36.2$ Hz, $^2J_{PC} = 24.1$ Hz, P=C), 203.4 (t, $^2J_{PC} = 11.3$ Hz, CO), and 206.9 (m, CO); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) $\delta = 152.2$ (satellite d, $^1J_{PW} = 259.2$ Hz); IR (KBr) 2962, 2908, 2871, 2019, 1919, 1888, 1593, 1473, 1414, 1402, 1365, 1240, 1211, 1126, 704, 584, and 573 cm^{-1}; UV–Vis (CH_2Cl_2) 335 (log ε 4.27) and 455 nm (4.31). Found *m*/*z* 950.3413. Calc. for $C_{48}H_{64}P_2S_2W$: M–4CO, 950.3434. Found: C, 58.02; H, 6.33; S, 5.54%. Calc. for $C_{52}H_{64}O_4P_2S_2W \cdot H_2O$: C, 57.78; H, 6.15; S, 5.93.

4.4.4. Dichloro[1,2-di(2-thienyl)-3,4-bis{(2,4,6-tri-t-butylphenyl)phosphinidene}cyclobutene]-palladium(II) (**5aPd**)

A mixture of (*E*,*E*)-**5a** (89.7 mg, 0.117 mmol) and bis(acetonitrile)dichloropalladium(II) (36.4 mg, 0.140 mmol) in THF (2 mL) was stirred at room temperature for 3 h. The solvent was removed under reduced pressure and the residue was treated with silica-gel column chromatography (hexane–AcOEt, 2:1) to give the desired complex **5aPd** (83.0 mg, 75% yield). Brown solid, m.p. > 265 °C (dec.); ^{1}H NMR (600 MHz, $CDCl_3$) $\delta = 1.40$ (18H, s, *p*-*t*-Bu), 1.71 (36H, s, *o*-*t*-Bu), 6.26 (2H, br s, thiophene), 6.71 (2H, t, $^3J_{HH} = 4.2$ Hz, thiophene), 7.39 (2H, d, $^3J_{HH} = 4.8$ Hz, thiophene), and 7.63 (4H, s, *m*-Mes*); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) $\delta = 31.2$ (s, *p*-C*Me*$_3$), 34.7 (s, *o*-C*Me*$_3$), 35.5 (s, *p*-*C*Me$_3$), 39.5 (s, *o*-*C*Me$_3$), 121.4 (pseudo t, $J_{PC} = 4.5$ Hz, *ipso*-Mes*), 124.1 (t, $^3J_{PC} = 4.5$ Hz, *m*-Mes*), 128.2 (s, thiophene), 131.5 (s, thiophene), 131.7 (s, thiophene), 132.1 (s, thiophene), 140.4 (m, P=C–*C*), 155.5 (s, *p*-Mes*), 157.5 (s, *o*-Mes*), and 163.2 (dd, $^1J_{PC} = 46.0$ Hz, $^3J_{PC} = 41.5$ Hz, P=C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) $\delta = 149.4$; IR (KBr) 2962, 2906, 2870, 1589, 1473, 1412, 1369, 1267, 1240, 1213, 1124, 710, and 648 cm^{-1}; UV–Vis (CH_2Cl_2) 303 (log ε 4.39), 382 (4.57), and 461 nm (4.07). Found *m*/*z* 871.2879. Calc. for $C_{48}H_{63}P_2PdS_2$: M–2Cl–H, 871.2894. Found: C, 59.23; H, 6.91; Cl, 7.47; S, 6.32%. Calc. for $C_{48}H_{64}Cl_2P_2PdS_2 \cdot 2H_2O$: C, 58.80; H, 6.99; Cl, 7.23; S, 6.54.

4.4.5. Dichloro[1,2-di(2-thienyl)-3,4-bis{(2,4,6-tri-t-butylphenyl)phosphinidene}cyclobutene]platinum(II) (**5aPt**)

A mixture of (*E*,*E*)-**5a** (85.2 mg, 0.111 mmol) and bis(benzonitrile)dichloroplatinum(II) (104.6 mg, 0.222 mmol) in THF (2 mL) was stirred at 50 °C for 2 days. The solvent was removed under reduced pressure and the residue was treated with silica-gel column chromatography (hexane–AcOEt, 4:1) to give the desired complex **5aPt** (22.0 mg, 19% yield). Red solid, m.p. > 300 °C; ^{1}H NMR (600 MHz, $CDCl_3$) $\delta = 1.41$ (18H, s, *p*-*t*-Bu), 1.74 (36H, s, *o*-*t*-Bu), 6.30 (2H, br s, thiophene), 6.69 (2H, t, $^3J_{HH} = 4.2$ Hz, thiophene), 7.37 (2H, d, $^3J_{HH} = 4.8$ Hz, thiophene), and 7.67 (4H, s, *m*-Mes*); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) $\delta = 31.2$ (s, *p*-C*Me*$_3$), 34.6 (s, *o*-C*Me*$_3$), 35.5 (s, *p*-*C*Me$_3$), 39.6 (s, *o*-*C*Me$_3$), 119.1 (d, $^1J_{PC} = 31.7$ Hz, *ipso*-Mes*), 124.2 (t, $^3J_{PC} = 5.3$ Hz, *m*-Mes*), 128.2 (s, thiophene), 130.5 (s, thiophene), 131.4 (pseudo t, thiophene), 132.2 (s, thiophene), 139.1 (dd, $^2J_{PC} = 63.4$ Hz, $^3J_{PC} = 33.2$ Hz, P=C–*C*), 155.4 (s, *p*-Mes*), 158.1 (s, *o*-Mes*), and 161.0 (dd, $^1J_{PC} = 86.0$ Hz, $^2J_{PC} = 13.6$ Hz, P=C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) $\delta = 126.6$ (satellite d, $^1J_{PtP} = 4497.0$ Hz); IR (KBr) 2962, 2871, 1593, 1473, 1414, 1367, 1265, 1240, 710, and 650 cm^{-1}; UV–Vis (CH_2Cl_2) 268 (log ε 4.49) and 394 nm (4.47). Found *m*/*z* 959.3438. Calc. for $C_{48}H_{62}P_2PtS_2$: M–2Cl–2H, 959.3416. Found: C, 55.15; H, 6.54; Cl, 6.23; S, 5.58%. Calc. for $C_{48}H_{64}Cl_2P_2PtS_2 \cdot H_2O$: C, 54.85; H, 6.33; Cl, 6.75; S, 6.10.

4.4.6. Formation of **5aCr** from (*E*,*Z*)-**5a**

A mixture of (*E*,*Z*)-**5a** (35.2 mg, 0.046 mmol) and (bicyclo[2.2.1]hepta-2,5-diene)tetracarbonylchromium(0) (22.1 mg, 0.086 mmol) in THF-d_8 (0.74 mL) in an NMR sample tube was stored in the dark at room temperature for 4 h. The ^{31}P NMR spectrum of the solution showed that most of the starting (*E*,*Z*)-**5a** remained unchanged and that formation of **5aCr** was trace (probably due to room light during the operation). This solution was then irradiated with a Xe lamp (300 W) in an ice-bath for 2 h. Apparent formation of (*E*,*E*)-**5a** and **5aCr** was confirmed by ^{31}P NMR spectroscopy. After irradiation for an additional 22 h, the ratio of (*E*,*Z*)-**5a**:**5aCr** became 4:1.

4.5. Introduction of functional groups to the thiophene ring

4.5.1. (*E*,*E*)-1-(5-Formyl-2-thienyl)-2-(2-thienyl)-3,4-bis[(2,4,6-tri-t-butylphenyl)phosphinidene]cyclobutene (**5d**)

To a solution of (*E*,*E*)-**5a** (94.3 mg, 0.123 mmol) in THF (2 mL) was added 0.133 mmol of butyllithium (1.56 M solution in hexane) at −78 °C. The resulting solution was stirred at −78 °C for 30 min and 0.050 mL (0.643 mmol) of DMF was added. The mixture was stirred at −78 °C for 1 h, allowed to warm to room temperature, and the

solvent was evaporated under reduced pressure. The residue was treated with column chromatography (SiO_2/hexane-EtOAc) to give 69.6 mg (70% yield) of (*E*,*E*)-**5d**. Red solid, m.p. 189–192 °C (dec.); ^{1}H NMR (600 MHz, $CDCl_3$) $\delta = 1.38$ (9H, s, *p*-*t*-Bu), 1.38 (9H, s, *p*-*t*-Bu), 1.54 (18H, s, *o*-*t*-Bu), 1.56 (18H, s, *o*-*t*-Bu), 5.72 (1H, d, $^3J_{HH} = 4.1$ Hz, thiophene), 5.99 (1H, d, $^3J_{HH} = 3.8$ Hz, thiophene′), 6.58 (1H, dd, $^3J_{HH} = 4.9$ Hz, $^3J_{HH} = 3.8$ Hz, thiophene′), 7.09 (1H, d, $^3J_{HH} = 4.9$ Hz, thiophene′), 7.12 (1H, d, $^3J_{HH} = 4.1$ Hz, thiophene), 7.40 (2H, s, *m*-Mes*), 7.42 (2H, s, *m*-Mes*), and 9.69 (1H, s, CHO); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) $\delta = 32.0$ (s, C*Me*$_3$), 32.0 (s, C*Me*$_3$), 33.5 (s, C*Me*$_3$), 33.6 (s, C*Me*$_3$), 35.5 (s, *C*Me$_3$), 35.6 (s, *C*Me$_3$), 38.7 (s, *C*Me$_3$), 38.8 (s, *C*Me$_3$), 122.4 (s, *m*-Mes*), 122.6 (s, *m*-Mes*), 127.7 (s, thiophene), 129.4 (d, $J_{PC} = 3.0$ Hz, thiophene), 130.7 (d, $J_{PC} = 5.1$ Hz, thiophene), 130.8 (d, $J_{PC} = 4.9$ Hz, thiophene), 132.4 (s, thiophene), 134.3 (d, $^1J_{PC} = 43.1$ Hz, *ipso*-Mes*), 134.9 (d, $^1J_{PC} = 44.2$ Hz, *ipso*-Mes*), 135.9 (s, thiophene), 142.6 (s, thiophene), 143.7 (d, $J_{PC} = 3.0$ Hz, thiophene), 145.8 (dd, $^2J_{PC} = 40.7$ Hz, $^3J_{PC} = 27.7$ Hz, P=C–*C*), 149.1 (dd, $^2J_{PC} = 39.3$ Hz, $^3J_{PC} = 27.1$ Hz, P=C–*C*), 151.2 (s, *p*-Mes*), 151.2 (s, *p*-Mes*), 155.6 (s, *o*-Mes*), 155.7 (s, *o*-Mes*), 174.3 (dd, $^1J_{PC} = 22.8$ Hz, $^2J_{PC} = 12.5$ Hz, P=C), 174.8 (dd, $^1J_{PC} = 23.0$ Hz, $^2J_{PC} = 12.5$ Hz, P=C), and 183.0 (s, CHO); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) $\delta = 173.2$ (d, $^3J_{PP} = 98.4$ Hz) and 187.2 (d, $^3J_{PP} = 98.4$ Hz); IR (KBr) 2966, 2877, 2864, 1670, 1439, 1398, 1361, and 1215 cm^{-1}; UV–Vis (CH_2Cl_2) 345 (log ε 4.44) and 445 nm (4.10). Found *m*/*z* 793.3808. Calc. for $C_{49}H_{63}OP_2S_2$, M–H, 793.3795.

4.5.2. (*E*,*E*)-1,2-Bis(5-formyl-2-thienyl)-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene (**5e**)

To a solution of (*E*,*E*)-**5a** (134.8 mg, 0.176 mmol) in THF (2 mL) was added 0.38 mmol of butyllithium (1.58 M solution in hexane) at −78 °C. The resulting solution was stirred at −78 °C for 30 min and 0.070 mL (0.90 mmol) of DMF was added. The mixture was stirred at −78 °C for 1 h, allowed to warm to room temperature, and the solvent was evaporated under reduced pressure. The residue was then treated with column chromatography (SiO_2/hexane:EtOAc = 10:1) to give 110.0 mg (76% yield) of (*E*,*E*)-**5e**. Red solid, m.p. ca. 170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.42$ (18H, s, *p*-*t*-Bu), 1.59 (36H, s, *o*-*t*-Bu), 5.85 (2H, d, $^3J_{HH} = 4.0$ Hz, thiophene), 7.20 (2H, d, $^3J_{HH} = 4.0$ Hz, thiophene), 7.46 (4H, s, *m*-Mes*), and 9.74 (2H, s, CHO); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) $\delta = 32.0$ (s, C*Me*$_3$), 33.6 (s, C*Me*$_3$), 35.6 (s, *C*Me$_3$), 38.8 (s, *C*Me$_3$), 122.6 (s, *m*-Mes*), 131.0 (s, thiophene), 134.1 (pseudo *t*, $J_{PC} = 27.6$ Hz, *ipso*-Mes*), 135.9 (s, thiophene), 141.4 (s, thiophene), 144.7 (s, thiophene), 146.9 (pseudo *t*, $J_{PC} = 6.6$ Hz, P=C–*C*), 151.6 (s, *p*-Mes*), 155.6 (s, *o*-Mes*), 173.8 (dd, $^1J_{PC} = 17.6$ Hz, $^2J_{PC} = 9.6$ Hz, P=C), and 182.9 (s, CHO); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) $\delta = 189.4$; IR (KBr) 2966, 2924, 2900, 2866, 1674, 1471, 1452, 1415, 1396, 1362, 1215, and 810 cm^{-1}; UV–Vis (CH_2Cl_2) 357 (log ε 4.46) and 441 nm (4.13). Found *m*/*z* 821.3761. Calc. for $C_{50}H_{63}O_2P_2S_2$: M–H, 821.3744. Found: C, 71.55; H, 7.97; S, 7.32%. Calc. for $C_{50}H_{64}O_2P_2S_2 \cdot H_2O$: C, 71.40; H, 7.91; S, 7.62.

4.5.3. (*E*,*E*)-1,2-Bis(5-carboxy-2-thienyl)-3,4-bis[(2,4,6-tri-*t*-butylphenyl)phosphinidene]cyclobutene (**5f**)

To a solution of (*E*,*E*)-**5a** (81.0 mg, 0.106 mmol) in THF (1 mL) was added 0.23 mmol of butyllithium (1.58 M solution in hexane) at −78 °C. The resulting solution was stirred at −78 °C for 30 min, and an excess amount of dryice was added. The mixture was stirred at −78 °C for 1 h, allowed to warm to room temperature, and then the solvent was evaporated under reduced pressure. The residue was treated with column chromatography (SiO_2/hexane:EtOAc:HCO_2H = 100:20:1) to give 59.9 mg (66% yield) of (*E*,*E*)-**5f**. Red solid, m.p. 158–161 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.39$ (18H, s, *p*-*t*-Bu), 1.57 (36H, s, *o*-*t*-Bu), 5.66 (2H, d, $^3J_{HH} = 4.0$ Hz, thiophene), 7.24 (2H, d, $^3J_{HH} = 4.0$ Hz, thiophene), and 7.42 (4H, s, *m*-Mes*); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) $\delta = 32.0$ (s, C*Me*$_3$), 33.7 (s, C*Me*$_3$), 35.4 (s, *C*Me$_3$), 38.7 (s, *C*Me$_3$), 122.5 (s, *m*-Mes*), 131.0 (s, thiophene), 133.3 (s, thiophene), 133.7 (pseudo t, $J_{PC} = 27.5$ Hz, *ipso*-Mes*), 137.3 (s, thiophene), 137.7 (s, thiophene), 147.3 (pseudo t, P=C–*C*), 151.4 (s, *p*-Mes*), 155.3 (s, *o*-Mes*), 163.1 (s, CO_2H), and 173.8 (m, P=C); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) $\delta = 185.3$; IR (KBr) 13500 (br), 2951, 2921, 2871, 1678, 1518, 1454, 1425, 1398, 1284, and 1244 cm^{-1}; UV–Vis (DMF) 361 (log ε 4.44) and 450 nm (4.03). Found *m*/*z* 797.3031. Calc. for $C_{46}H_{55}O_4P_2S_2$: M–*t*-Bu, 787.3017. Found: C, 68.45; H, 7.73; S, 6.90%. Calc. for $C_{50}H_{64}O_4P_2S_2 \cdot H_2O$: C, 68.78; H, 7.62; S, 7.34.

4.6. Dichloro[1,2-diphenyl-3,4-bis{(2,4,6-tri-*t*-butylphenyl)phosphinidene}cyclobutene]platinum(II) (**1APt**)

A mixture of (*E*,*E*)-**1A** (103.5 mg, 0.137 mmol) and bis(benzonitrile)dichloroplatinum(II) (129.5 mg, 0.274 mmol) in THF (2.0 mL) was stirred at 50 °C for 2 days. The solvent was then removed under reduced pressure and the residue was treated with silica-gel column chromatography (hexane-EtOAc) to give **1APt** (75.9 mg, 54% yield). Orange solid, m.p. > 300 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.42$ (18H, s, *p*-*t*-Bu), 1.72 (36H, s, *o*-*t*-Bu), 6.89 (4H, d, $^3J_{HH} = 8.4$ Hz, *o*-Ph), 6.93 (4H, t, $^3J_{HH} = 7.8$ Hz, *m*-Ph), 7.21 (2H, t, $^3J_{HH} = 7.5$ Hz, *p*-Ph), and 7.64 (4H, d, $^4J_{PH} = 3.6$ Hz, *m*-Mes*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) $\delta = 31.5$ (s, *p*-C*Me*$_3$), 34.6 (s, *o*-C*Me*$_3$), 35.5 (s, *p*-*C*Me$_3$), 39.5 (s, *p*-*C*Me$_3$), 119.4 (m, *ipso*-Mes*), 124.2 (m, *m*-Mes*), 127.6 (s, Ph), 128.5 (s, Ph), 130.0 (s, Ph), 130.5 (s, Ph), 148.9 (dd, $^2J_{PC} = 61.2$ Hz, $^3J_{PC} = 31.0$ Hz, P=C–*C*), 155.1 (s, *p*-Mes*), 157.5 (s, *o*-Mes*), and 162.5 (m, P=C); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) $\delta = 129.2$ (satellite d, $^1J_{PtP} = 4499.2$ Hz); IR (KBr) 2962, 2908, 2871, 1595, 1473, 1448, 1400, 1362, 1240, 1211, 1126, 748, 690, and

677 cm^{-1}; UV–Vis (CH_2Cl_2) 265 (4.60) and 369 nm (4.55). Found: *m/z* 947.4264. Calc. for $C_{52}H_{66}P_2Pt$: M–2Cl–2H, 947.4284. Found: C, 59.99; H, 6.77; Cl, 7.14%. Calc. for $C_{52}H_{68}Cl_2P_2Pt \cdot H_2O$:C, 60.11; H, 6.79; Cl, 6.82.

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