Construction of Extended π-Conjugation Systems Utilizing Novel Multicarbene Complexes of Titanium

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Abstract: Titanium–multicarbene complexes, namely organotitanium species having a plurality of titanium–carbene complex substructures, were easily prepared by the reaction of aromatic nuclei possessing spatially separated thioacetal moieties with the titanocene(II) reagent $Cp_2Ti[P(OEt)_3]_2$. Reaction of these multicarbene complexes with aromatic ketones gave various highly conjugated compounds in good yields.

Key words: carbene complexes, conjugation, olefination, thioacetals, titanium

We have studied the preparation of various titanium–carbene complexes by the desulfurizative titanation of thioacetals with the low-valent titanium species $Cp_2Ti[P(OEt)_3]_2$ (**1**).[1] These titanium–carbene complexes, the typical Schrock-type metal carbenes, react with various carbonyl compounds to give olefins.[2] The major advantage of this olefination is that thioacetals are rather stable under basic and acidic conditions, and hence a variety of starting materials are readily available and can be transformed into the corresponding carbene complexes.

Although preparations of the Fischer-type monomolecular multicarbene complex arrays of tungsten,[3] rhodium,[4] and chromium[3a,5] have been reported, the Schrock-type congener has not appeared yet. In this communication, we describe the first generation of the Schrock-type multicarbene complexes **2** from multithioacetals **3** (Scheme 1) and their reactions with aromatic ketones to construct extended π-conjugation systems, which are basic skeletons of potential functional organic materials for electron luminescent devices, optical data storages, photovoltaic devices, and so on.[6]

Insertion of transition-metal carbene complexes into M–H bonds of group 14 metal hydrides R_3MH is a well-established process and employed as a prove for generation of a variety of carbene complexes.[7] We initially investigated the reaction of organotitanium species generated by the desulfurizative titanation of the multithioacetals **3** with dimethylphenylsilane. Treatment of the multithioacetals having a benzene or 1,3,5-triphenylbenezene core **3b**, **3c**, and **3g** with **1** in the presence of dimethylphenylsilane at 25 °C for one hour produced the bis- and tris(dimethylphenylsilylmethyl)arenes **4a**, **4b**, and **4c** in good yields, suggesting the formation of the corresponding multicarbene complexes **2** (entries 2, 3, and 4, Table 1).

In contrast, a similar treatment of **3a** having two adjacent thioacetal functions with dimethylphenylsilane gave no carbenoid-insertion-type product and instead the bissulfide **5** was obtained in moderate yield (entry 1, Table 1).

The formation of **5** is attributable to preferential generation of the benzotitanacyclopentane **6** and its hydrolysis during workup (Scheme 2). Indeed **6** was isolated as dark green crystals in 42% yield by the reaction carried out without aqueous workup.[8]

Therefore, it is of utmost importance for the successful generation of the multicarbene complexes **2** that thioacetal groups must be attached on a conformationally rigid molecular platform and are separated from each other. Synthetic utility of the multicarbene complexes **2** for the construction of extended π-conjugation systems was demonstrated in the preparation of **8a**–**n** by their reaction with aromatic ketones **7a**–**d** (Table 2).[9] In addition to the arene-cored carbene complexes, the multicarbene complexes having a silicon and heterocycle core were readily prepared and subjected to the reaction with benzophenone derivatives to produce extended π-conjugation compounds **8** in good to excellent yields.

Preparation of extended π-conjugation systems by multiple formations of phenylenevinylene substructures in one pot has been extensively investigated. Although various methods such as the Wittig and Horner–Wadsworth–Emmons reactions are employed for this purpose,[10] ketones are generally poor substrates as compared with aldehydes due to their steric hindrance.[11] Efficiency comparison between the present and reported methods is shown in Table 3. The reaction of the multicarbene complex generated from **3c** with benzophenone derivatives affords the polyaromatics **8b** and **8l** in better yields than the reaction using the bisphosphonate **9**.[11] Although extended π-conjugation systems can also be constructed by the double Hiyama coupling of certain vinylsilanes with diiodoarenes,[12] the yields of coupling products largely decrease when amino-substituted polyaromatics such as **8m** and **8n** are to be synthesized.

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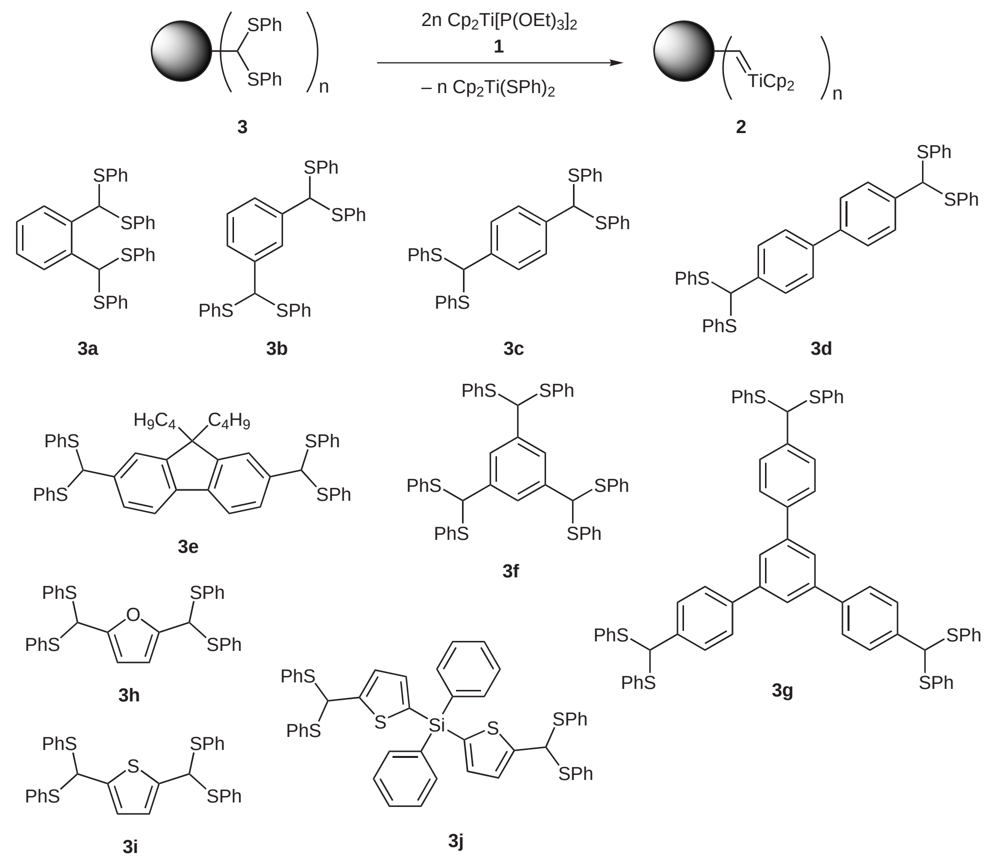


Scheme 1 Preparation of multicarbene complexes **2** from multithioacetals **3**

Table 1 Reaction of Multithioacetals **3** with Dimethylphenylsilane in the Presence of Titanocene(II) **1**

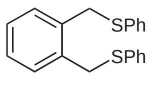
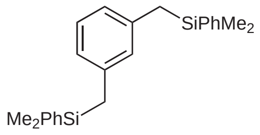
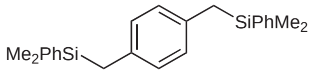
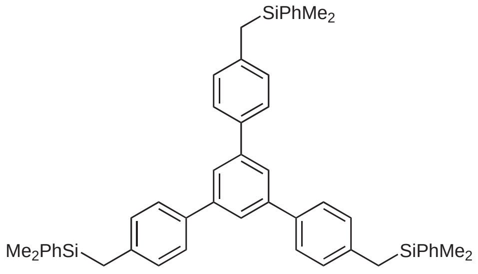
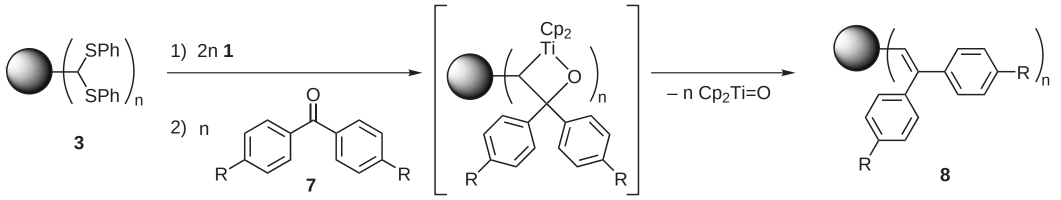
Entry	Thioacetal **3**	**1** (equiv)	Me_2PhSiH (equiv)	Product (yield, %)
1	**3a**	6	2.2	 **5** (41)
2	**3b**	6	2.2	 **4a** (70)
3	**3c**	6	2.2	 **4b** (72)
4	**3g**	9	3.3	 **4c** (53)

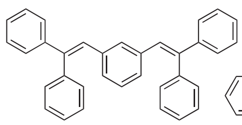
Table 2 Reaction of Multicarbene Complexes **2** with Benzophenone Derivatives **7**[a]



Entry	**3**	**7** (R)	**1** (equiv)	Temp (°C)	Time (h)	Product **8**	Yield (%)
1	**3b**	**7a** (H)	8	25	1	**8a**	64
2	**3c**	**7a** (H)	6	25	1	**8b**	66
3	**3d**	**7a** (H)	8	reflux	3	**8c**	90
4	**3f**	**7a** (H)	12	25	1	**8d**	49
5	**3g**	**7a** (H)	12	reflux	3	**8e**	64
6[b]	**3i**	**7a** (H)	8	0, then reflux	0.3, 3	**8f**	80
7[b]	**3j**	**7a** (H)	8	0, then reflux	0.3, 3	**8g**	56
8	**3c**	**7b** (BuO)	8	reflux	3	**8h**	64
9	**3d**	**7b** (BuO)	8	reflux	3	**8i**	80
10	**3e**	**7b** (BuO)	8	reflux	3	**8j**	58
11[b]	**3h**	**7b** (BuO)	8	0, then reflux	0.3, 3	**8k**	57
12	**3c**	**7c** (Ph_2N)	8	reflux	3	**8l**	61
13	**3b**	**7d** (Me_2N)	8	reflux	3	**8m**	62
14	**3c**	**7d** (Me_2N)	8	reflux	3	**8n**	72

[a] All reactions were performed with a similar procedure as described in the text, unless otherwise noted.

[b] The thioacetal **3** and the ketone **7** were added to a THF solution of **1** in one portion.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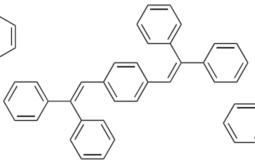
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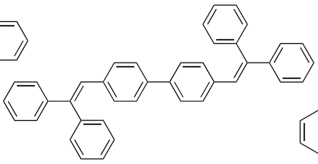
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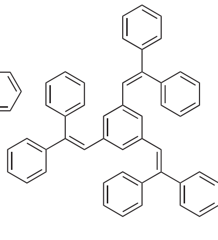
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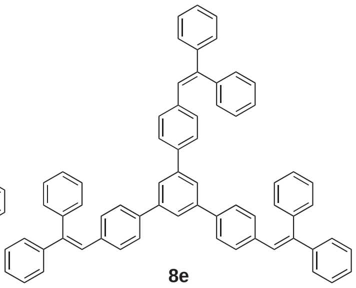
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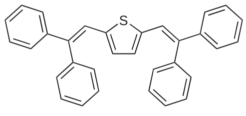
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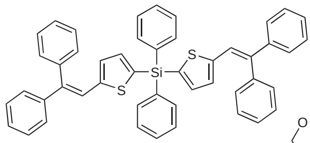

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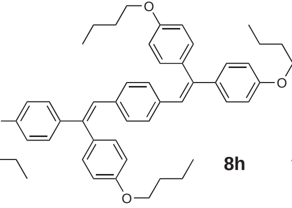

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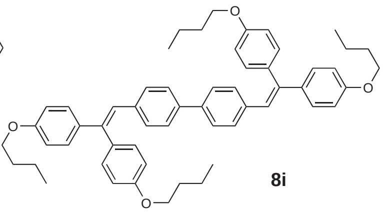

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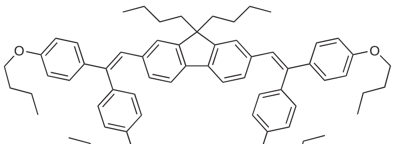

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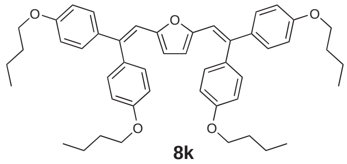

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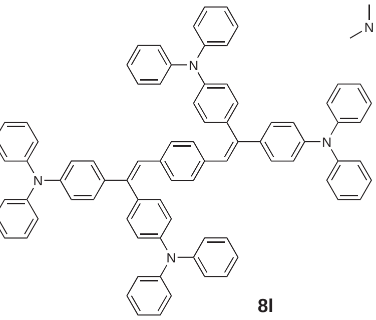

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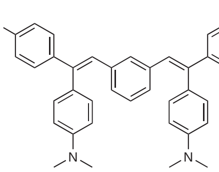

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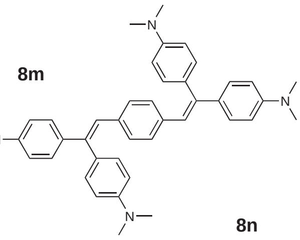

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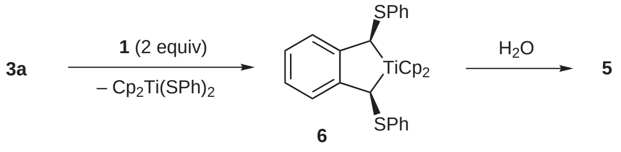
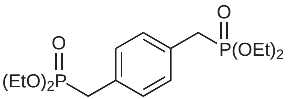


Scheme 2 Formation of titanacycle **6** from bisthioacetal **3a**

Table 3 Efficiency Comparison between the Present and Reported Reactions

Entry	Product	Yield (%)	
		Present reaction	Horner–Wadsworth–Emmons reaction using **9**
1	**8b**	66[a]	37,[11a] 27[11b]
2	**8l**	42,[b] 61[c]	17[11c]

[a] Carried out using **1** (6 equiv) and **7a** (2 equiv) at 25 °C for 1 h.
[b] Carried out using **1** (6 equiv), **3c** (1.1 equiv), and **7c** (2 equiv) under reflux for 3 h. The yield is based on the amount of **7c** used.
[c] Carried out using **1** (8 equiv) and **7** (4 equiv) under reflux for 3 h.



9

In conclusion, we have established the facile method for the preparation of titanium multicarbene complexes utilizing multithioacetals as starting materials. The mandatory requirement for the preparation of such unprecedented organotitanium species is that the thioacetal functionalities in a molecule must be arranged so as to be separated from each other, otherwise the titanacycle is formed. A variety of extended π-conjugation systems were constructed in one pot by the use of these multicarbene complexes.

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(8) (a) The titanacycle **6** was isolated by column chromatography over alumina gel (hexane–EtOAc, 98:2) under N_2, mp 85–87 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.88 (s, 2 H), 5.88 (s, 5 H), 6.44 (s, 5 H), 7.03–7.28 (m, 14 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 58.7, 114.6, 115.8, 123.0, 124.1, 125.0, 125.6, 128.7, 142.4, 146.1. IR (KBr): ν = 3057, 2914, 1579, 1476, 1439, 1085, 1022, 824, 739, 690 cm^{-1}.
Lappert and co-workers reported the preparation of 2-titanaindane[8b] and *meso*-1,3-bis(trimethylsilyl)-2-titanaindane[8c] complexes. The NMR signals of the Cp rings

of the latter titanacycle occur as two singlets at δ = 4.46 and 5.23 ppm. The spectrum of **6** shows the protons of two Cp rings as two singlets at δ = 5.88 and 6.44 ppm, suggesting that **6** has the *meso* configuration. (b) Bristow, G. S.; Lappert, M. F.; Martin, T. R.; Atwood, J. L.; Hunter, W. F. *J. Chem. Soc., Dalton Trans.* **1984**, 399. (c) Lappert, M. F.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1984**, 893.

(9) **General Procedure**
Cp_2TiCl_2 (398 mg, 1.6 mmol), magnesium turnings (43 mg, 1.76 mmol), and finely powdered 4 Å MS (128 mg) were placed in a flask and dried by heating with a heat gun in vacuo (2–3 mmHg). After cooling, THF (2.4 mL) and $P(OEt)_3$ (0.55 mL, 3.2 mmol) were added successively with stirring under argon. During the addition, the reaction mixture was cooled in a water bath so that the temperature was maintained between 20 °C and 30 °C. After stirring for 3 h at 25 °C, a THF (1.0 mL) solution of the thioacetal **3c** (108 mg, 0.2 mmol) was added. Then, a THF (4.0 mL) solution of **7b** (261 mg, 0.8 mmol) was added dropwise over 10 min and the reaction mixture was stirred for 3 h under reflux. The reaction was quenched by addition of 1 M NaOH and the insoluble materials were filtered off through Celite® and washed with $CHCl_3$. The layers were separated, and the aqueous layer was extracted with $CHCl_3$. After the combined organic extracts were dried with Na_2SO_4 and concentrated, the remaining triethyl phosphate, formed by the oxidation of triethyl phosphite, was removed by azeotropic distillation with MeOH. Purification of the residue by PTLC on silica gel (hexane–$CHCl_3$, 96:4) gave **8h** as yellow crystals (102 mg, 64%), mp 130–132 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.96 (t, *J* = 7.4 Hz, 6 H), 0.99 (t, *J* = 7.4 Hz, 6 H), 1.41–1.59 (m, 8 H), 1.67–1.85 (m, 8 H), 3.94 (t, *J* = 6.2 Hz, 4 H), 3.96 (t, *J* = 6.1 Hz, 4 H), 6.70 (s, 2 H), 6.75–6.89 (m, 12 H), 7.07 (d, *J* = 8.4 Hz, 4 H), 7.20 (d, *J* = 8.4 Hz, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8, 13.9, 19.2, 19.3, 31.3, 31.4, 67.6, 67.7, 114.1, 114.4, 125.8, 128.8, 129.0, 131.6, 136.0, 136.4, 141.6, 158.5, 158.8. IR (KBr): ν = 2956, 2932, 2871, 1604, 1570, 1509, 1467, 1390, 1284, 1247, 1175, 1146, 1111, 1070, 1027, 1010, 973, 834, 813, 617 cm^{-1}. Anal. Calcd for $C_{50}H_{58}O_4$: C, 83.06; H, 8.09. Found: C, 82.82; H, 8.12.

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