Tetrahedron 67 (2011) 1530–1535

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Cyclodimerization and cyclotrimerization of isocyanates promoted by one praseodymium benzenethiolate complex [$Pr(SPh)_3(THF)_3$]

He-Ming Wang [a], Hong-Xi Li [a], Xiang-Yang Yu [a], Zhi-Gang Ren [a], Jian-Ping Lang [a,b,*]

[a] College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 210032, PR China

ARTICLE INFO

Article history:
Received 3 October 2010
Received in revised form 16 December 2010
Accepted 24 December 2010
Available online 8 January 2011

Keywords:
Praseodymium
Thiolate
Amide
Catalysis
Phenyl isocyanate

ABSTRACT

The cyclotrimerization of aryl isocyanates and the cyclodimerization of alkyl isocyanates initiated by one praseodymium benzenethiolate complex [$Pr(SPh)_3(THF)_3$] were investigated. Comparative runs with [$Pr(SPh)_3(THF)_3$] and its precursor $Pr[(Me_3Si)_2N]_3$ showed that the former has the advantages of a higher selectivity toward isocyanates, easy preparation, low catalyst loading, high conversion as well as mild reaction conditions.

1. Introduction

Investigation of catalysts that can selectively catalyze the cyclodimerization, cyclotrimerization, or polymerization of isocyanates is one active topic of organic chemistry.[1] Isocyanurates are employed in the preparation of copolymer resins that require water-resistance, transparency, and impact resistance,[2] and a novel optically active isocyanurate has been used for chiral discrimination of enantiomeric amino acid units.[3] Triaryl isocyanurates are useful activators for anionic polymerization of ϵ-caprolactams to nylon-6 and are known to substantially enhance the stability of polyurethane networks and coating materials with respect to thermal resistance, flame retardation, chemical resistance, and film-forming characteristics.[4] The isocyanate cyclodimerized products could readily eliminate one CO molecule to result in the formation of organic ureas, which have industrial and academic applications as agrochemicals, dyes for cellulose fibers, antioxidants in gasoline, resin precursors, and synthetic intermediates.[5] The most common catalysts for the cyclodimerization, cyclotrimerization, or polymerization of isocyanates include phosphines,[6] *N*-heterocyclic carbenes,[7] calcium carbene complexes,[8] amines,[9] potassium phthalimide,[10] fluoride anions,[11] and alkoxyalkenes.[12] Metal-containing cyclotrimerization catalysts include organotin[13] and zirconium compounds,[14] organozinc halides and alkoxides,[15] copper and nickel halides,[10] palladium(0) complexes,[16] and organolanthanide complexes.[17–19] Among organolanthanide complexes, lanthanide amide complexes $(MeC_5H_4)_2LnN^iPr_2(THF)$ (Ln=Y, Er, Yb)[17] were reported to exhibit good catalytic performance for phenyl isocyanate polymerization, while $(MeC_5H_4)_2LnCl/n$-BuLi[18] systems were excellent catalysts for the cyclotrimerization of phenyl isocyanate. These results showed that ancillary ligands play an important role on the selectivity of the catalysts. Recently, we found that lanthanide thiolate complexes[20] displayed excellent catalytic performances on the ring-opening polymerization of ϵ-caprolactone, which may be due to the fact that the Ln–S bond disruption enthalpy is smaller than those of Ln–C and Ln–N bonds.[21] Do the lanthanide thiolate complexes show the catalytic activity and selectivity for cyclodimerization, cyclotrimerization, or polymerization of isocyanates? With this question in mind, we prepared one praseodymium benzenethiolate complex [$Pr(SPh)_3(THF)_3$] from the protonlysis reactions of its triamide complex $Pr[(Me_3Si)_2N]_3$ with benzenthiol and carried out their catalytic reactions of various isocyanates. [$Pr(SPh)_3(THF)_3$] does show good activity and selectivity for the cyclodimerization and cyclotrimerization of isocyanates. All these results will be described in this article.

2. Results and discussion

Lanthanide tri(dimethylsilyl)amide complex $Ln[(Me_3Si)_2N]_3$[22] could be used to prepare its corresponding thiolate complex

* Corresponding author. Tel.: +86 512 6588 2865; fax: +86 512 6588 0089; e-mail address: jplang@suda.edu.cn (J.-P. Lang).

0040-4020/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2010.12.069

through its protonolysis reaction with a thiol because thiol has an acidity stronger than that of $HN(SiMe_3)_2$ and could protonate the $(Me_3Si)_2N^-$ anion to give lanthanide thiolate complex.[20,23] Therefore, treatment of $Pr[(Me_3Si)_2N]_3$ with 3 equiv of benzenethiol in toluene followed by a standard workup produced $[Pr(SPh)_3(THF)_3]$ in 92% yield. The elemental analysis was consistent with its chemical formula. Attempts to grow its single crystals for determining its crystal structure always failed. This product was quite unstable and very sensitive to air and moisture. To examine the reactivity of this complex toward isocyanates, $[Pr(SPh)_3(THF)_3]$ was mixed with phenyl isocyanate (**1a**) in a 1/100 M ratio and stirred at 20 °C for 12 h. After hydrolysis by water and extraction by diethyl ether, the filtrate was concentrated to dryness in vacuo. The solid was re-crystallized with hot toluene/THF to give colorless crystals of one cyclotrimerized product 1,3,5-trisphenyl-1,3,5-triazinane-2,4,6-trione (**2a**) in 54% yield. To our knowledge, it represents the first example to employ lanthanide thiolate complexes to catalyze the cyclotrimerization of isocyanates.

To optimize the above reaction conditions, different solvents, temperatures, and catalyst loading were explored. Table 1 lists the results for the cyclotrimerization of phenyl isocyanate (**1a**) catalyzed by $[Pr(SPh)_3(THF)_3]$. Four different solvents (toluene, THF, *n*-hexane, and MeCN) were used to evaluate their influence on the catalytic performance for the cyclotrimerization of phenyl isocyanate. We observed a strong solvent dependence of the cyclotrimerization. In *n*-hexane or toluene, $[Pr(SPh)_3(THF)_3]$ did not catalyze phenyl isocyanate cyclodimerization, cyclotrimerization, polymerization at 20 °C. In MeCN, it could catalyze the cyclotrimerization of phenyl isocyanate in a low activity. Whereas the same reaction in THF afforded the product 1,3,5-triphenyl-[1,3,5] triazinane-2,4,6-trione (**2a**) in 54% yield within 12 h at 20 °C. As shown in Table 1, the temperature did exert a great impact on the catalytic activity of $[Pr(SPh)_3(THF)_3]$. The catalytic activity in THF increased as the temperature was raised. For example, when the temperature was raised from 20 °C to 40 °C to 60 °C, the cyclotrimerization reaction conducted in the presence of 1 mol % catalyst in THF after 12 h, afforded the cyclotrimerized product in 54%, 87%, and 99% yields, respectively. In the last example, the amount of catalyst used to initiate the reaction efficiently was examined. As shown in Table 1 (entries 4, 7, and 8), increasing the catalyst loading resulted in an obvious increase of the product yield. For example, the outputs of the reactions increased dramatically from 54% to 63% to 98% when the catalyst loading was changed from 1 mol % to 2 mol % to 3 mol % in THF at 20 °C. To this end, the optimal reaction conditions for the cyclotrimerization of phenyl isocyanate were achieved by using catalyst loading: 1 mol % of $[Pr(SPh)_3(THF)_3]$; solvent: THF; reaction time: 12 h; and reaction temperature: 60 °C.

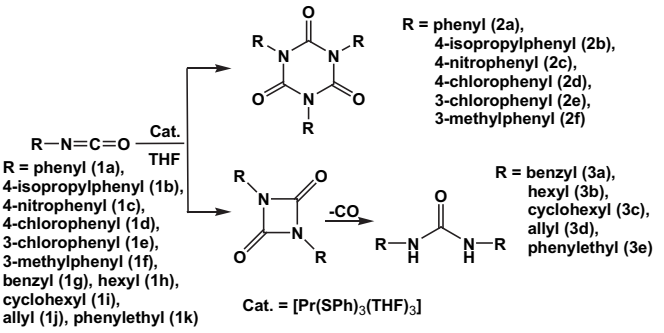
Table 1
Catalytic activity of $[Pr(SPh)_3(THF)_3]$ on the cyclotrimerization of phenyl isocyanate (**1a**)

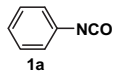
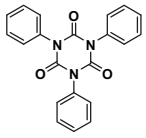
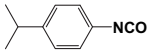
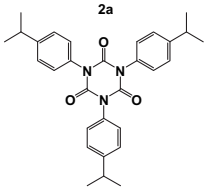
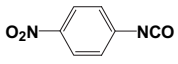
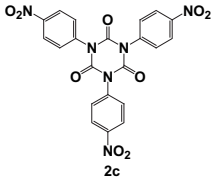
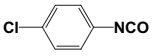
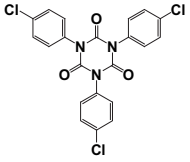
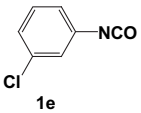
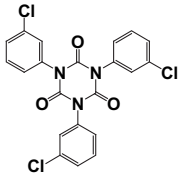
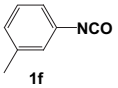
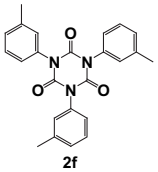
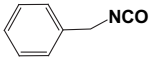
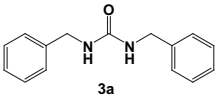
Entry[a]	Cat./**1a** (%)	Temp (°C)	Solvent	Yield[b] (%)
1	1	20	*n*-Hexane	0
2	1	20	Toluene	0
3	1	20	MeCN	18
4	1	20	THF	54
5	1	40	THF	87
6	1	60	THF	99
7	2	20	THF	63
8	3	20	THF	98

[a] Reaction time: 12 h.
[b] Isolated yield.

The scope of substrates was then investigated by using this catalytic system under the optimized reaction conditions. The results are presented in Table 2. It can be seen that this catalyst exhibited high catalytic activity for the cyclotrimerization of aryl isocyanates,

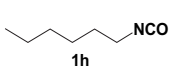
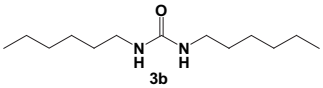
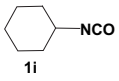
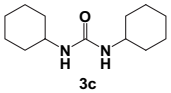
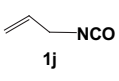
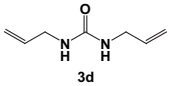
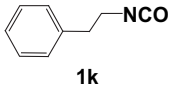
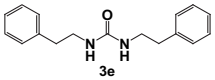
Table 2
Data for the $[Pr(SPh)_3(THF)_3]$-catalyzed cyclodimerization or cyclotrimerization of different isocyanates



Entry[a]	Isocyanate	Product	Yield[b] (%)
1	 **1a**	 **2a**	99
2	 **1b**	 **2b**	97
3	 **1c**	 **2c**	100
4	 **1d**	 **2d**	92
5	 **1e**	 **2e**	99
6	 **1f**	 **2f**	91
7	 **1g**	 **3a**	97

(*continued on next page*)

Table 2 (*continued*)

Entry[a]	Isocyanate	Product	Yield[b] (%)
8	 1h	 3b	94
9	 1i	 3c	99
10	 1j	 3d	85
11	 1k	 3e	93

[a] Catalyst: $[Pr(SPh)_3(THF)_3]$, catalyst/isocyanate=1/100.
[b] Isolated yield.

such as phenyl isocyanate, 4-isopropylphenyl isocyanate, 4-nitrophenyl isocyanate, 4-chlorophenyl isocyanate, 3-chlorophenyl isocyanate, 3-methylphenyl (Table 2, entries 1–6) in nearly quantitative yields. However, when alkyl isocyanates, such as benzyl isocyanate, hexyl isocyanate, cyclohexyl isocyanate, allyl isocyanate, and phenylethyl isocyanate were employed under the same conditions, no cyclotrimerized products were isolated from the HRMS and ^1H NMR results of the reaction products. Instead, the corresponding substituted ureas, *N*,*N*′-dibenzylurea, *N*,*N*′-dihexylurea, *N*,*N*′-dicyclohexylurea, *N*,*N*′-diallylurea, and *N*,*N*′-diphenylethylurea, were isolated from the corresponding reactions (Table 2, entries 7–11). The formation of the substituted ureas is assumed to proceed through the hydrolysis of the corresponding isocyanate cyclodimerized products. These results are different from those of $(MeC_5H_4)_2LnN^iPr_2(THF)$ (Ln=Y, Er, Yb)[17] and $(MeC_5H_4)_2LnCl/n$-BuLi,[18] suggesting that ancillary ligands on lanthanide centers greatly influence the selectivity of the catalysts. The structure of product **3a** (Fig. 1) were determined for the clear identification of their identities.

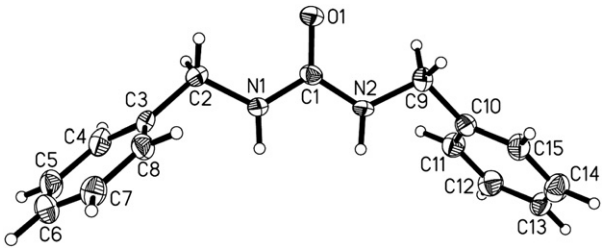
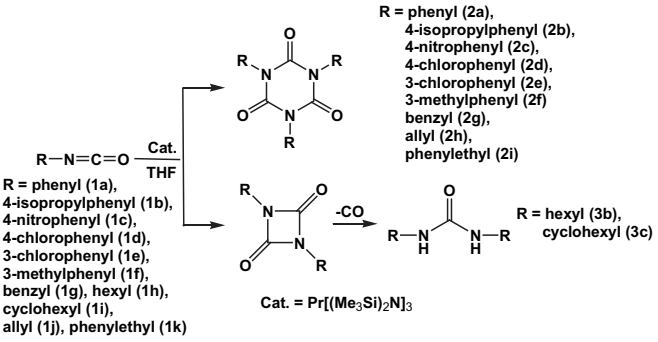
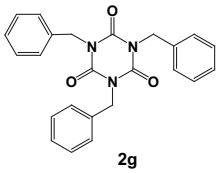
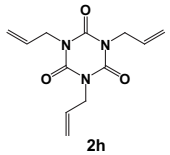
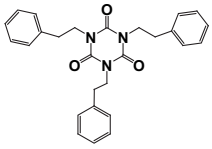


Fig. 1. View of the molecular structure of **3a**.

For comparison, the catalytic activity of the precursor $Pr[(Me_3Si)_2N]_3$ on the cyclotrimerization or cyclodimerization of isocyanate was also studied (Table 3). The results are listed in Table 3. This complex also exhibited a relatively high selectivity on cyclotrimerization of aryl isocyanates. When it was used to initiate the cyclotrimerization of alkyl isocyanates, only benzyl isocyanate, allyl isocyanate, and phenylethyl isocyanate gave rise to the corresponding cyclotrimerized products. However, the hexyl isocyanate, cyclohexyl isocyanate produced the substituted ureas, which might be derived from the corresponding cyclodimerized products. Comparative runs with $Pr[(Me_3Si)_2N]_3$ showed that $[Pr(SPh)_3(THF)_3]$ initiated a higher selectivity. It is found that $[Pr(SPh)_3(THF)_3]$ exhibited a relatively higher catalytic activity on the cyclotrimerization or cyclodimerization of the corresponding isocyanates than $Pr[(Me_3Si)_2N]_3$. For example, when cyclotrimerization of 4-isopropylphenyl isocyanate, a 74% yield of the cyclotrimerization product catalyzed by $Pr[(Me_3Si)_2N]_3$ can be obtained, while the conversion of the 4-isopropylphenyl isocyanate to cyclotrimer catalyzed by $[Pr(SPh)_3(THF)_3]$ system can be raised to 97% under the same conditions. As discussed below, the mechanism of $[Pr(SPh)_3(THF)_3]$ on the cyclotrimerization or cyclodimerization of isocyanate may be the similar to that of $Pr[(Me_3Si)_2N]_3$. But their corresponding intermediates are different, which result in the different catalytic activity and selectivity of $[Pr(SPh)_3(THF)_3]$ and $Pr[(Me_3Si)_2N]_3$ on the cyclotrimerization or cyclodimerization of isocyanate.

Table 3
Data for the $Pr[(Me_3Si)_2N]_3$-catalyzed cyclodimerization or cyclotrimerization of different isocyanates

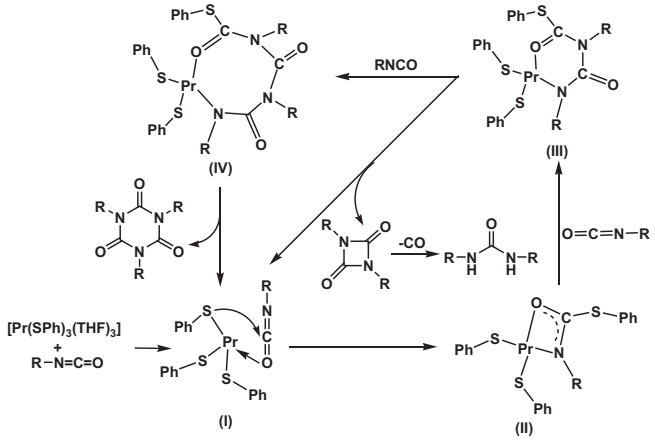


Entry[a]	Isocyanate	Product	Yield[b] (%)
1	**1a**	**2a**	99
2	**1b**	**2b**	74
3	**1c**	**2c**	83
4	**1d**	**2d**	81
5	**1e**	**2e**	79
6	**1f**	**2f**	76
7	**1g**	 **2g**	75
8	**1h**	**3b**	74
9	**1i**	**3c**	72
10	**1j**	 **2h**	69
11	**1k**	 **2i**	75

[a] Catalyst: $Pr[(Me_3Si)_2N_3]$, catalyst/isocyanate=1/100.
[b] Isolated yield.

For the above cyclodimerization and cyclotrimerization of isocyanate initiated by $[Pr(SPh)_3(THF)_3]$, we suggested the following possible mechanism (Scheme 1). Coordination of the isocyanate to the central metal atom of $[Pr(SPh)_3(THF)_3]$ through replacement of the coordinated THF molecules may form an isocyanate-coordinated intermediate I '$[Pr(SPh)_3(RNCO)_n]$', which may be the first step of the catalytic cycle. Insertion of one isocyanate into the Ln–S

bond may lead to the formation of the intermediate II, which reacts with another isocyanate molecule to give the intermediate III. This intermediate may proceed in two different ways. One is that it may be converted into the cyclodimerized product, when the alkyl isocyanate is present. The other is that the intermediate III may further combine one isocyanate molecule, forming the intermediate IV, when the aryl isocyanate is used. The intermediate IV then converted into the cyclotrimerized product and the intermediate I. The electronic properties of different isocyanates may lead to different reactivity of the intermediate III, which may cause its different selectivity. A series of experiments were conducted to understand the insertion mechanism. Reaction of $[Pr(SPh)_3(THF)_3]$ with 3 equiv of PhNCO in THF did not produce the expected insertion product '$[Pr(OC(SPh)NPh)_3]$' but the cyclotrimerized product **2a**. When we directly added PhNCO to the mixture containing $Pr[(Me_3Si)_2N]_3$ and 3 equiv of PhSH in THF, a standard workup produced colorless crystals of phenyl-thiocarbamic acid *S*-phenyl ester (**4**) (Fig. 2), in which the intermediate II should be formed but hydrolyzed by $(Me_3Si)_2NH$ released in the reaction system. Although we were unable to isolate any intermediate complexes, the identification of **4** supported our initial assumption that $[Pr(SPh)_3(THF)_3]$ was formed and isocyanate was inserted into the Pr–S bond.



Scheme 1. Proposed catalytic mechanism.

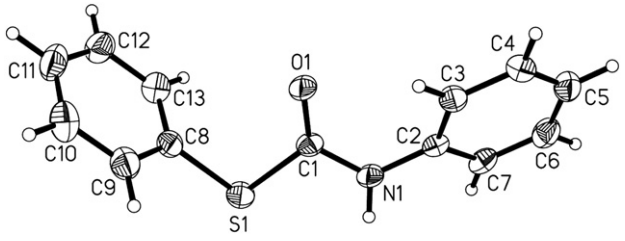


Fig. 2. View of the molecular structure of **4**.

3. Conclutions

In summary, we have demonstrated the preparation of one praseodymium benzenethiolate complex $[Pr(SPh)_3(THF)_3]$ from protonolysis reactions of $Pr[(Me_3Si)_2N]_3$ with benzenthiol. Comparative runs with $Pr[(Me_3Si)_2N]_3$ showed that $[Pr(SPh)_3(THF)_3]$ exhibited a higher catalytic activity and selectivity on cyclotrimerization of aryl isocyanates and cyclodimerization of alkyl isocyanates. In addition, this catalyst has the advantages of easy preparation, low catalyst loading, high conversion, mild reaction conditions, and compatibility with different substrates. To our knowledge, it represents the first example to employ lanthanide thiolate complexes to catalyze the cyclodimerization of isocyanates. It is anticipated that other lanthanide thiolate complexes may also be prepared to catalyze the above reactions and other organic reactions with better catalytic activities. Studies on these respects are underway in our laboratory.

4. Experimental

4.1. General

All manipulations were carried out under argon using standard Schlenk-techniques. Solvents were dried by distillation from sodium/benzophenone (THF, toluene, hexane) or P_2O_5 (MeCN) under argon prior to use. $Pr[(Me_3Si)_2N]_3$[22] was prepared according to the literature methods. The PhSH ligand and phenyl isocyanate, 4-isopropylphenyl isocyanate, 4-nitrophenyl isocyanate, 4-chlorophenyl isocyanate, 3-chlorophenyl isocyanate, 3-methylphenyl benzyl isocyanate, hexyl isocyanate, cyclohexyl isocyanate, allyl isocyanate, phenylethyl isocyanate were purchased from Aldrich. ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a Varian UNITYplus-400 spectrometer. ^1H NMR and ^{13}C NMR chemical shifts were referenced to the solvent signal in $CDCl_3$ or DMSO-d_6. Elemental analyses were performed on a Carlo-Erbo CHNO–S microanalyzer. The IR spectra (KBr disc) were recorded on a Nicolet MagNa-IR550 FT-IR spectrometer (4000–400 cm^{-1}). The uncorrected melting points were measured on a Mel-Temo II apparatus.

4.2. Preparation of $[Pr(SPh)_3(THF)_3]$

To a solution of $Pr[(Me_3Si)_2N]_3$ (0.728 g, 1.172 mmol) in toluene (30 mL) was slowly added a solution of PhSH (0.387 g, 3.520 mmol) in THF (10 mL). A large amount of yellow precipitate was observed to form within minutes. After the mixture was stirred at room temperature for 12 h, it was evaporated to remove all the volatile species under vacuum. The resulting yellow solid was washed with toluene (2×10 mL) and dried in vacuum. Yield 0.736 g (92%, based on Pr). Anal. Calcd for $C_{30}H_{39}O_3S_3Pr$: C 52.62, H 5.74, S 14.05; found: C 52.21, H 6.18, S 14.49. Mp: 59.0–61.0 °C. IR (KBr disk): 3056(w), 2982(s), 2870(m), 1629(m), 1473(w), 1400(m), 1260(m), 1192(w), 1082(s), 920(w), 767(m), 689(m), 601(m) cm^{-1}.

4.3. General procedure for the cyclotrimerization or cyclodimerization of isocyanates catalyzed by $[Pr(SPh)_3(THF)_3]$ (2a as an example)

To a 30 mL Schlenk tube under dried argon were added $[Pr(SPh)_3(THF)_3]$ (0.0137 g, 0.02 mmol), THF (10 mL), and phenyl isocyanate (0.216 mL, 2.00 mmol). When the resulting mixture was stirred at 60 °C for 12 h, it was hydrolyzed by water (1 mL), extracted with diethyl ether (3×10 mL), dried over anhydrous $MgSO_4$, and filtered. After removal of the solvent from the extract under the reduced pressure, the solid was re-crystallized in THF and toluene and filtered off. The filtrate was allowed to stand at −18 °C for several days, forming colorless crystals of 1,3,5-trisphenyl-1,3,5-triazinane-2,4,6-trione (**2a**) in 97% yield.

*4.3.1. 1,3,5-Trisphenyl-1,3,5-triazinane-2,4,6-trione (**2a**).* Mp: 280.5–281.6 °C. IR (KBr disk): 3067, 1709, 1593, 1490, 1414, 1219, 1072, 1028, 918, 753, 689, 590, 506 cm−1. ^1H NMR ($CDCl_3$, ppm): δ 7.529–7.159 (15H, m, aromatic CH). ^{13}C NMR ($CDCl_3$, ppm) δ 148.9, 133.9, 129.6, 128.7. HRMS (EI) *m*/*z*: calcd for $C_{21}H_{15}N_3O_3$ 357.11; found: 357.11.

*4.3.2. 1,3,5-Tris(4-isopropylphenyl)-1,3,5-triazinane-2,4,6-trione (**2b**).* White solid. Mp: 287.8–288.3 °C. IR (KBr disk): 3046, 2961, 2929, 2869, 1707, 1605, 1551, 1511, 1409, 1308, 1222, 1183, 1056, 1019, 830, 756, 706, 568, 446 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): δ 7.477–7.254 (12H, m, aromatic CH), 3.132–3.026 (3H, m, CH),

1.397–1.380 (18H, d, CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 150.1, 149.1, 131.3, 128.3, 127.5, 34.0, 24.0. HRMS (EI) *m*/*z*: calcd for $C_{30}H_{33}N_3O_3$ 483.25; found: 483.25.

*4.3.3. 1,3,5-Tris(4-nitrophenyl)-1,3,5-triazinane-2,4,6-trione (**2c**).* Yellow solid. Mp: 410.5–411.0 °C. IR (KBr disk): 3080, 1728, 1688, 1617, 1552, 1527, 1493, 1432, 1407, 1351, 1016, 865, 806, 757, 691, 756, 494 cm^{-1}. ^1H NMR (DMSO-d_6, ppm): δ 8.436–7.766 (12H, m, aromatic CH). ^{13}C NMR (DMSO-d_6, ppm): δ 148.0, 147.6, 139.6, 130.4, 124.6. HRMS (EI) *m*/*z*: calcd for $C_{21}H_{12}N_6O_9$ 492.07; found: 492.07.

*4.3.4. 1,3,5-Tris(4-chlorophenyl)-1,3,5-triazinane-2,4,6-trione (**2d**).* White solid. Mp: 342.0–342.5 °C. IR (KBr disk): 3050, 1706, 1605, 1491, 1426, 1234, 1169, 1087, 1014, 812, 758, 519, 426 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): δ 7.490–7.314 (12H, m, aromatic CH). ^{13}C NMR ($CDCl_3$, ppm): δ 148.3, 135.7, 131.9, 129.9. HRMS (EI) *m*/*z*: calcd for $C_{21}H_{12}N_3O_3Cl_3$ 458.9944; found: 458.9944.

*4.3.5. 1,3,5-Tris(3-chlorophenyl)-1,3,5-triazinane-2,4,6-trione (**2e**).* White solid. Mp: 229.8–230.3 °C. IR (KBr disk): 3087, 1721, 1694, 1591, 1476, 1409, 1224, 1075, 1034, 1003, 880, 782, 760, 694, 595, 557 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): δ 7.481–7.296 (12H, m, aromatic CH). ^{13}C NMR ($CDCl_3$, ppm): δ 148.1, 135.1, 134.3, 130.6, 130.1, 129.0, 126.9. HRMS (EI) *m*/*z*: calcd for $C_{21}H_{12}N_3O_3Cl_3$ 458.99; found: 459.00.

*4.3.6. 1,3,5-Trim-tolyl-1,3,5-triazinane-2,4,6-trione (**2f**).* White solid. Mp: 280.8–281.3 °C. IR (KBr disk): 3033, 2956, 2921, 2867, 1708, 1609, 1490, 1409, 1409, 1251, 1188, 1089, 1054, 1003, 876, 785, 738, 692, 602, 553 cm^{-1}. ^1H NMR (DMSO-d_6, ppm): δ 7.411–7.252 (12H, m, aromatic CH), 2.367 (9H, s, CH_3). ^{13}C NMR (DMSO-d_6, ppm): δ 148.9, 138.4, 134.7, 129.4, 129.2, 128.7, 125.9. HRMS (EI) *m*/*z*: calcd for $C_{24}H_{21}N_3O_3$ 399.16; found: 399.16.

*4.3.7. 1,3,5-Tribenzyl-1,3,5-triazinane-2,4,6-trione (**2g**).* White solid. Mp: 160.3–160.8 °C. IR (KBr disk): 3036, 2980, 2969, 1686, 1586, 1495, 1452, 1364, 1325, 1205, 1075, 1030, 885, 822, 748, 697, 599, 516 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): δ 7.454–7.225 (15H, m, aromatic CH), 5.018 (6H, s, CH_2). ^{13}C NMR ($CDCl_3$, ppm): δ 149.3, 136.0, 129.3, 128.9, 128.4, 46.5. HRMS (EI) *m*/*z*: calcd for $C_{24}H_{21}N_3O_3$ 399.16; found: 399.16.

*4.3.8. 1,3,5-Triallyl-1,3,5-triazinane-2,4,6-trione (**2h**).* White solid. Mp: 24.5–25.0 °C. IR (KBr disk): 3070, 2932, 2856, 1710, 1645, 1462, 1392, 1346, 1318, 1090, 993, 918, 669, 582 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): δ 5.872–5.778 (3H, m, C=C–H), 5.187–5.144 (3H, d, C=C–H), 5.080–5.055 (3H, d, C=C–H), 4.411 (6H, s, CH_2). ^{13}C NMR ($CDCl_3$, ppm): δ 149.8, 132.6, 117.7, 45.5. HRMS (EI) *m*/*z*: calcd for $C_{12}H_{15}N_3O_3$ 249.11; found: 249.11.

*4.3.9. 1,3,5-Triphenethyl-1,3,5-triazinane-2,4,6-trione (**2i**).* White solid. Mp: 133.0–133.5 °C. IR (KBr disk): 3061, 3026, 2968, 2933, 2878, 1689, 1615, 1576, 1461, 1371, 1337, 1236, 1133, 1078, 1029, 952, 825, 748, 700, 608, 488 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): δ 7.308–7.155 (15H, m, aromatic CH), 3.406–3.372 (6H, t, CH_2), 2.786–2.751(6H, t, CH_2). ^{13}C NMR ($CDCl_3$, ppm): δ 158.3, 139.4, 129.1, 128.9, 126.7, 41.9, 36.6. HRMS (EI) *m*/*z*: calcd for $C_{27}H_{27}N_3O_3$ 441.21; found: 441.21.

*4.3.10. 1,3-Dibenzylurea (**3a**).* White solid. Mp: 167.8–168.3 °C. IR (KBr disk): 3321, 3030, 2919, 2873, 1627, 1572, 1492, 1453, 1246, 1062, 1026, 909, 751, 696, 591, 490 cm^{-1}. ^1H NMR ($CDCl_3$, ppm) δ 7.319–7.227 (10H, m, aromatic CH); 4.873 (2H, s, NH); 4.338 (4H, s, CH_2). ^{13}C NMR ($CDCl_3$, ppm) δ 158.7, 139.3, 128.9, 127.7, 127.6, 44.8. HRMS (EI) *m*/*z*: calcd for $C_{15}H_{16}N_2O$ 240.13; found: 240.13.

*4.3.11. 1,3-Dihexylurea (**3b**).* White solid. Mp: 74.5–75.2 °C. IR (KBr disk): 3334, 2956, 2931, 2856, 1616, 1578, 1468, 1384, 1299, 1251, 1221, 728, 629, 441 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): 5.158 (2H, s, NH), 2.911–2.867 (4H, t, CH_2), 1.294–1.156 (4H, m, CH_2), 1.062 (12H, s, CH_2), 0.673–0.636 (6H, t, CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 158.8, 39.8, 31.3, 30.1, 26.4, 22.3, 13.8. HRMS (EI) *m*/*z*: calcd for $C_{13}H_{28}N_2O$ 228.22; found:228.22.

*4.3.12. 1,3-Dicyclohexylurea (**3c**).* White solid. Mp: 231.8–232.3 °C. IR (KBr disk): 3326, 2928, 2850, 1629, 1580, 1535, 1436, 1311, 1271, 1244, 1186, 1088, 1045, 892, 641, 454 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): δ 4.058 (2H, s, NH), 3.496–3.463 (2H, m, CH), 2.007–1.917 (4H, m, CH_2), 1.707–1.613 (8H, m, CH_2), 1.403–1.293 (4H, m, CH_2), 1.155–1.041 (4H, m, CH_2). ^{13}C NMR ($CDCl_3$, ppm): δ 156.9, 49.5, 34.3, 25.9, 25.2. HRMS (EI) *m*/*z*: calcd for $C_{13}H_{24}N_2O$ 224.19; found: 224.19.

*4.3.13. 1,3-Diallylurea (**3d**).* White solid. Mp: 91.7–92.2 °C. IR (KBr disk): 3331, 3082, 2913, 2864, 1627, 1586, 1460, 1419, 1384, 1252, 1060, 991, 917, 672, 435 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): δ 5.871–5.779 (2H, m, C=C–H), 5.582 (2H, s, NH), 5.186–5.143 (2H, d, C=C–H), 5.079–5.054 (2H, d, C=C–H), 3.756 (4H, s, CH_2). ^{13}C NMR ($CDCl_3$, ppm): δ 159.1, 135.8, 115.5, 43.0. HRMS (EI) *m*/*z*: calcd for $C_7H_{12}N_2O$ 140.10; found: 140.10.

*4.3.14. 1,3-Diphenethylurea (**3e**).* White solid. Mp: 140.0–140.5 °C. IR (KBr disk): 3337, 3061, 3026, 2933, 2879, 1616, 1575, 1503, 1475, 1449, 1384, 1305, 1237, 1081, 1034, 911, 746, 700, 486 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): δ 7.3 16–7.154 (10H, m, aromatic CH), 4.484 (2H, s, NH), 3.406–3.360 (4H, t, CH_2), 2.791–2.745 (4H, t, CH_2). ^{13}C NMR ($CDCl_3$, ppm): δ 158.3, 139.4, 129.1, 128.8, 126.7, 41.9, 36.7. HRMS (EI) *m*/*z*: calcd for $C_{17}H_{20}N_2O$ 268.16; found: 268.16.

4.4. Synthesisof phenyl-thiocarbamic acid *S*-phenyl ester (4)

To a solution of HSPh (0.3104 mL, 2.82 mmol) was added a solution of $Pr[(Me_3Si)_2N]_3$ (0.5732 g, 0.924 mmol) in THF (15 mL). The reaction mixture was stirred overnight. At ambient temperature, PhNCO (0.345 g, 2.901 mmol) in THF (10 mL) solution was added into the mixture. The resulting mixture was stirred for 12 h and then was concentrated to dryness in vacuo. The resulting solid was extracted with toluene (20 mL) and then filtered. The filtrate was kept at −18 °C for several days and colorless crystals of **4** were formed. Yield: 0.477 g (74%). Mp: 125.0–125.5 °C. IR (KBr disk): 3253, 3052, 1661, 1596, 1536, 1499, 1441, 1306, 1240, 1164, 1088, 1024, 918, 880, 756, 689, 642, 575, 580, 506, 452 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): δ 7.635–7.616 (2H, m, aromatic CH), 7.484–7.471 (3H, m, aromatic CH), 7.387–7.376 (2H, d, aromatic CH), 7.327–7.288 (2H, t, aromatic CH), 7.135–7.098 (1H, t, aromatic CH), 7.056(1H, s, NH). ^{13}C NMR ($CDCl_3$, ppm): δ 164.8, 137.7, 135.8, 130.1, 129.7, 129.3, 128.2, 124.8, 119.8. HRMS (EI) *m*/*z*: calcd for $C_{13}H_{11}NOS$ 229.06; found: 229.06.

Acknowledgements

This work was supported by the National Nature Science Foundation of China (Nos. 20871088, 20871038, and 90922018), the Nature Science Key Basic Research of Jiangsu Province for Higher Education (09KJA150002), the NSF of the Education Committee of Jiangsu Province (No. 07KJD150182), the State Key Laboratory of Organometallic Chemistry of Shanghai Institute of Organic Chemistry (08-25), the Qin-Lan Project of Jiangsu Province, and the *SooChow* Scholar Program and Program for Innovative Research Team of Suzhou University.

Supplementary data

Crystal data and refinement parameters for **3a** (CCDC No. 789447) and **4** (CCDC No. 789448). The ^1H and ^{13}C NMR spectra for

cyclotrimerized products **2a**–**i** and substituted ureas **3a**–**e**. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.12.069.

References and notes

1. Raders, S. M.; Verkade, J. G. *J. Org. Chem.* **2010**, *75*, 5308–5311.
2. Tang, J.; Mohan, T.; Verkade, J. G. *J. Org. Chem.* **1994**, *59*, 4931–4938.
3. Sugimoto, H.; Yamane, Y.; Inoue, S. *Tetrahedron: Asymmetry* **2000**, *11*, 2067–2075.
4. (a) Tang, J. S.; Verkade, J. G. *Angew. Chem., Int. Ed.* **1993**, *32*, 896–898; (b) Foley, S. R.; Zhou, Y.; Yap, G. P. A.; Richeson, D. S. *Inorg. Chem.* **2000**, *39*, 924–929.
5. Gabriele, B.; Salerno, G.; Mancuso, R.; Costa, M. *J. Org. Chem.* **2004**, *69*, 4741–4750.
6. Liu, X.; Bai, Y.; Verkade, J. G. *J. Organomet. Chem.* **1999**, *582*, 16–24.
7. Duong, H. A.; Cross, M. J.; Louie, J. *Org. Lett.* **2004**, *6*, 4679–4681.
8. Orzechowski, L.; Harder, S. *Organometallics* **2007**, *26*, 2144–2148.
9. Tagachi, Y.; Shibaya, I.; Yasumoto, Y.; Ynoemoto, K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3486–3489.
10. Moghaddam, F. M.; Dekamin, M. G.; Koozehgari, G. R. *Lett. Org. Chem.* **2005**, *2*, 734–738.
11. Nambu, Y.; Endo, T. *J. Org. Chem.* **1993**, *58*, 1932–1934.
12. Mizuya, J.; Yokozawa, T.; Endo, T. *J. Polym. Sci., Polym. Chem.* **1991**, *29*, 1544–1550.
13. (a) Bloodworth, A. J.; Davies, A. G. *J. Chem. Soc.* **1965**, 6858–6863; (b) Foley, S. R.; Yap, G. P. A.; Richeson, D. S. *Organometallics* **1999**, *18*, 4700–4705.
14. Li, Y.; Matsumura, H.; Yamanaka, M.; Takahashi, T. *Tetrahedron* **2004**, *60*, 1393–1400.
15. Noltes, J. G.; Boersma, J. *J. Organomet. Chem.* **1967**, *7*, 6–8.
16. Paul, F.; Moulin, S.; Piechaczyk, O.; Le Floch, P.; Osborn, J. A. *J. Am. Chem. Soc.* **2007**, *129*, 7294–7304.
17. Mao, L. S.; Shen, Q.; Xue, M. Q.; Sun, J. *Organometallics* **1997**, *16*, 3711–3714.
18. Zhou, X. G.; Zhang, L. B.; Zhu, M.; Cai, R. F.; Weng, L. H. *Organometallics* **2001**, *20*, 5700–5706.
19. (a) Wu, Y. J.; Wang, S. W.; Zhu, X. C.; Yang, G. S.; Wei, Y.; Zhang, L. J.; Song, H. B. *Inorg. Chem.* **2008**, *47*, 5503–5511; (b) Zhu, X. C.; Fan, J. X.; Wu, Y. J.; Wang, S. W.; Zhang, L. J.; Yang, G. S.; Wei, Y.; Yin, C. W.; Zhu, H.; Wu, S. H.; Zhang, H. T. *Organometallics* **2009**, *28*, 3882–3888.
20. (a) Li, H. X.; Ren, Z. G.; Zhang, Y.; Zhang, W. H.; Lang, J. P.; Shen, Q. *J. Am. Chem. Soc.* **2005**, *127*, 1122–1123; (b) Li, H. X.; Cheng, M. L.; Ren, Z. G.; Zhang, W. H.; Lang, J. P.; Shen, Q. *Inorg. Chem.* **2006**, *45*, 1885–1887; (c) Li, H. X.; Zhang, Y.; Ren, Z. G.; Cheng, M. L.; Wang, J.; Lang, J. P. *Chin. J. Chem.* **2005**, *23*, 1499–1503; (d) Cheng, M. L.; Li, H. X.; Zhang, W. H.; Ren, Z. G.; Zhang, Y.; Lang, J. P. *Eur. J. Inorg. Chem.* **2007**, 1889–1896.
21. Nolan, S. P.; Stern, D.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7844–7853.
22. Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *J. Chem. Soc., Dalton Trans.* **1973**, 1021–1023.
23. (a) Aspinall, H. C.; Bradley, D. C.; Hursthouse, M. B.; Sales, K. D.; Walker, N. P. C. *J. Chem. Soc., Chem. Commun.* **1985**, 1585–1586; (b) Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Smith, R. G. *J. Chem. Soc., Chem. Commun.* **1992**, 932–934; (c) Aspinall, H. C.; Cunningham, S. A.; Maestro, P.; Macaudiere, P. *Inorg. Chem.* **1998**, *37*, 5396–5398; (d) Pernin, C. G.; Ibers, J. A. *Inorg. Chem.* **2000**, *39*, 1216–1221; (e) Niemeyer, M. *Eur. J. Inorg. Chem.* **2001**, 1969–1981.