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Interaction of cyclic thiadiynes with CpCo(COD) — selectivity and reactivity

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Dedicated to Professor Marianne Baudler on the occasion of her 80th birthday

Abstract

The reaction of CpCo(COD) with several cyclic thiadiynes leads to selective product formation; according to their ring size either (2,5)[2.2]thiophenophanes or CpCo-stabilized cyclobutadienes were formed. The outcome of the reaction can be attributed to the geometry in the transition states, **6** and **11**. X-ray structure analyses of the reacting thiacycles and the isolated CpCo compounds are given and correlated with the tautness of the cobaltols. © 2002 Elsevier Science B.V. All rights reserved.

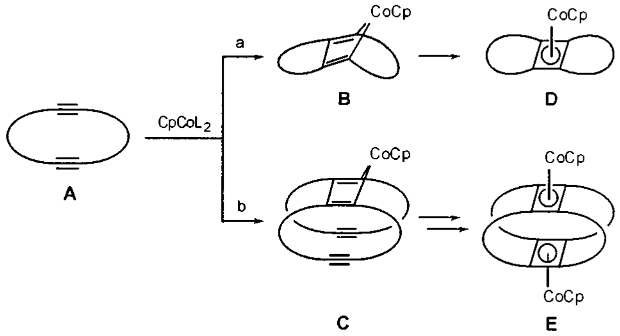
Keywords: Thiacyclodiyne; Cobaltol; Thiophenophane; Intra- and intermolecular cyclobutadiene formation

1. Introduction

The metal supported oligomerizations of alkynes to cyclooctatetraene-, benzene- or metal-stabilized cyclobutadiene (cbd) derivatives are widely used reactions in chemistry [1]. It is believed that a metallacyclopentadiene [2] is formed as an intermediate which either reacts further in a catalytic cycle to yield a trimer or tetramer or it reacts to cbd stabilized by a metal fragment. In the case of cyclic diynes, only two products are found in reactions with [(η^5-cyclopentadiene)cobalt] reagents, $CpCoL_2$. Either an intra- (path a) or an intermolecular (path b) reaction is found as shown in Scheme 1 [3].

If there are more than three methylene units between the triple bonds, the intramolecular reaction product **D** prevails. In cyclodeca-1,6-diyne [10] or in compounds with ethano- or tetramethyldisilyl-bridges the superphane **E** is the main outcome[3].

The latter result can be rationalized by assuming that the metallacycle **B** is more strained than the intermediate **C**. To test this conception further, we reacted thiacyclodiynes such as **1** (Scheme 2) with the sulfur atom in the propargylic position. We thought that the sulfur might stabilize the intermediate metallacycle **6**. To our surprise, a product **8** was obtained [4] for which we found a (2,5)[2.2]thiophenophane structure; instead of yielding an intramolecular cbd product, the sulfur and the CpCo-fragment exchanged places giving rise to the thiophenophane **8**. This was also observed with **2** and **3** [5].



Scheme 1.

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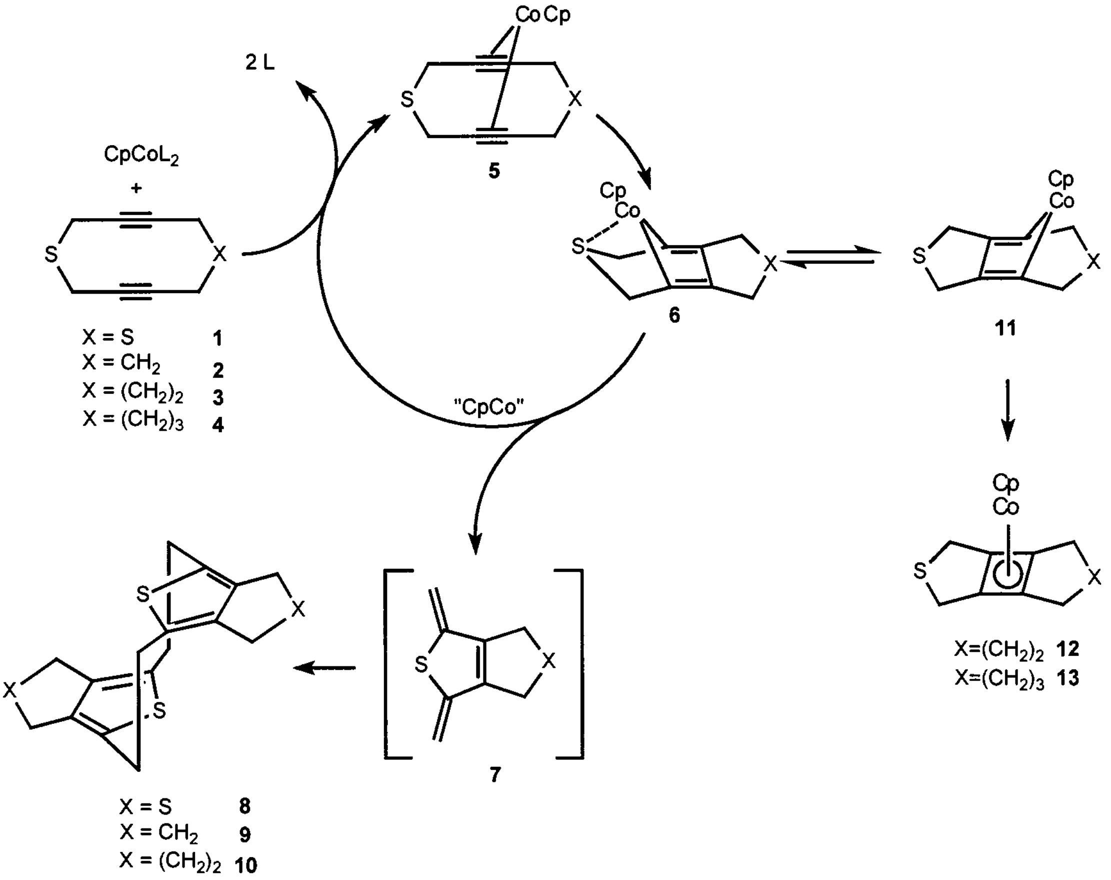


Scheme 2.

2. Results

The proposed mechanism (Scheme 2) implements an equilibrium between the two cobaltol species **6** and **11**, which can be expected in the reaction of a thiacyclodiyne with the $CpCoL_2$ reagent. The stability of these intermediates depends mainly on the sulfur–cobalt interaction, which might favor **6**, and the steric hindrance in these transition states. The ease of forming **11** should, therefore, be connected to the tautness of the non-sulfur containing ring in this cobaltol.

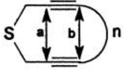
To substantiate this concept of selective cobaltol formation we synthesized several thiacyclodiynes and determined the triple bond distances by X-ray structure analysis (Table 1). Since the cobaltol intermediates **6** and **11** cannot be isolated, we correlated the geometry of the non-sulfur containing rings in the transition states with the triple bond distances of the starting materials.

Our results suggest that in cycles with sulfur in propargylic position for $b > 350$ pm the metallacycle **11** is favored, whereas for smaller b-values either **6** is predominant or an intermolecular pathway (e.g. **14**) is preferred.

Compound **14** was prepared in 20% yield by phase transfer catalysis with sodium sulfide in a methylene chloride–water mixture. Compounds **3** [5b] and **4** [6] have been described previously; changing the workup strategy led to crystallization. The structural analysis of **2** has been reported elsewhere [7].

Reaction of **2** with the $CpCoL_2$ reagent yielded the corresponding thiophenophane in 34% [5]. Widening of the triple bond distances by reacting the nine-membered disilathiacyclodiyne **14** produced the superphane **15** in 15% yield. Although we expected the sulfur to stabilize cobaltol **6** there is no reaction pathway to form the

Table 1
Comparison of triple bond distances in **2**, **3**, **4** and **14**

thiacycle	n	cmpd.	a [pm]	b [pm]
	$(CH_2)_3$	**2**[7]	307	298
	$(Si(CH_3)_2)_2$	**14**	313	326
	$(CH_2)_4$	**3**[5b]	323	351
	$(CH_2)_5$	**4**[6]	346	398

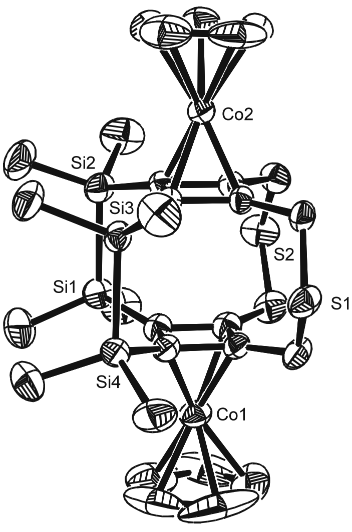


Fig. 1. Side view of the molecular structure of **15**. The hydrogen atoms, a second independent molecule and two molecules of the solvent are omitted for the sake of clarity. The plots are presented at 50% probability of the thermal ellipsoids.

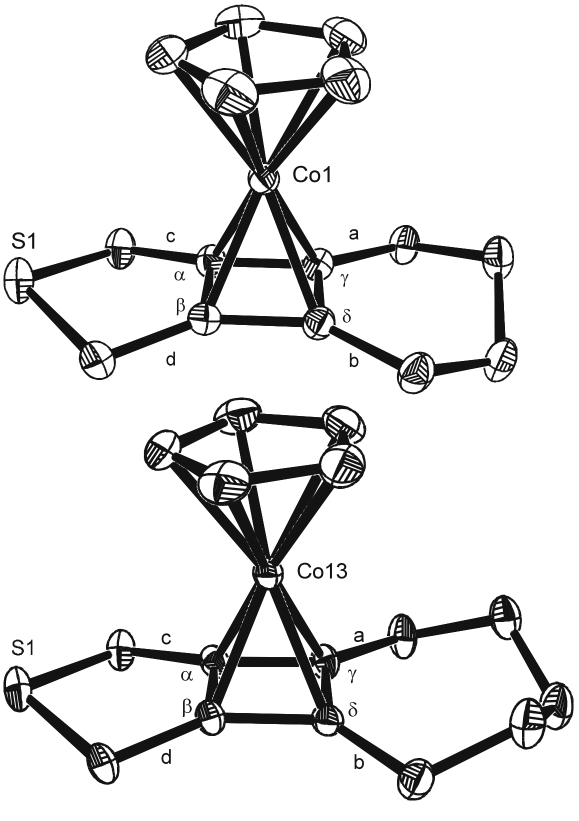


Fig. 2. Comparison between the molecular structures of **12** (top) and **13** (bottom). The hydrogen atoms are omitted for the sake of clarity. The plots are presented at 50% probability of the thermal ellipsoids.

metallacycle **B** (Scheme 1), since a highly strained disilacyclobutene ring would have to be formed and, therefore, **14** follows path b. The X-ray structure shows that only the C_{2v} isomer with the sila- and the thiachains in the *syn* position is produced (Fig. 1). This *syn*-selectivity of the bulky tetramethyldisilyl bridges has been encountered previously [8]. It was attributed to steric effects in the transition state to the cobaltol intermediate **C** (Scheme 1) and to the electronic effects [3a,12].

The reaction of thiacyclododeca-3,10-diyne (**4**) with CpCo(COD) yielded 51% of the intramolecular product **13**. We assume that the least strained metallacycle intermediate **11** is favored (Scheme 2), sulfur might no longer stabilize the metallacycle and no thiophenophane is obtained.

Reacting thiacycloundeca-3,9-diyne (**3**) with the CpCo reagent afforded the previously reported (2,5)[2.2]thiophenophane **10** in 12% yield [5b] and also the CpCo-stabilized cbd complex **12** in 15% yield. This result clearly indicates an equilibrium between **6** and **11**. The special geometry in **3** does not favor one of the cobaltol intermediates to be formed and therefore giving rise to a product mixture of **10** and **12**.

A comparison of the X-ray analyses of **12** and **13** is presented in Fig. 2. The average C–C bond length of the cbd units is 145 pm. The tautness of the non-sulfur containing side chain is reflected in the δ- and γ-bond angles, as shown in Fig. 2. Shortening this side chain by one methylene unit decreases the bond angles by about 8°. Further selected bond angles and bond lengths are given in Table 2.

3. Conclusions

To test our hypothesis of an equilibrium between two cobaltols with (**6**) and without (**11**) a cobalt–sulfur interaction, we reacted various cyclic thiadiynes with the sulfur atom in propargylic position to the triple bonds. In those cases (**1**–**3**) where, for geometric reasons, the cobaltol **6** was likely to occur, the corresponding thiophenophane derivatives **8**–**10** could be isolated. In those ring systems (**4**, **14**) where the cobaltol **11** was preferred, an intramolecular cbd complex **13** or an intermolecular reaction product **15** emerged. In the case of thiaundeca-3,9-diyne (**3**) both anticipated products, **10** and **12**, resulted.

Table 2
Selected structural data for **12** and **13**

Data	**12**	**13**
α (°)	116.3	117.2
β (°)	116.7	117.0
δ (°)	125.1	133.6
γ (°)	124.2	131.9
a (pm)	149.1	149.3
b (pm)	149.4	148.6
c (pm)	148.9	149.6
d (pm)	149.3	148.6

4. Experimental

4.1. General remarks

All melting points are uncorrected. The NMR spectra were measured with a Bruker Avance 500 (^{1}H-NMR at 500 MHz and ^{13}C-NMR at 125.77 MHz) using the solvent as internal standard (δ). The mass spectra refer to data from a JEOL JMS-700 instrument. IR spectra were recorded with a Bruker Vector 22. UV light absorption data were recorded using a Hewlett Packard 8452A spectrometer. All reactions with CpCo(COD) were carried out in a dried glassware under Ar atmosphere using dried and oxygen-free solvents.

4.2. Syntheses of cyclic thiadiynes

4.2.1. 5,5,6,6-Tetramethyl-1-thia-5,6-disilacyclonona-3,7-diyne (**14**)

To a solution of 1.0 g 1,8-dibrom-4,4,5,5-tetramethyl-4,5-disilaocta-2,6-diyne [9] and 0.29 g nBu$_4$NBr in 130 ml methylene chloride was added 0.82 g $Na_2S\cdot9H_2O$ in 175 ml water. The mixture was vigorously stirred for 20 h. After separating the two phases, the aqueous layer was extracted with methylene chloride (3 × 50 ml). The combined organic layers were washed with water (2 × 100 ml). After drying ($MgSO_4$), the solvent was removed and the crude product was purified by flash column chromatography on silica (light petroleum–methylene chloride 4:1) to yield 170 mg (28%) of the desired product as a light yellow solid. Further purification was achieved by means of kugelrohr distillation at 0.04 mbar/110 °C to yield 130 mg (20%) of **14** as colorless needles suitable for X-ray structure analysis. M.p. 81 °C. ^{1}H-NMR (CDCl$_3$): δ 0.25 (s, 12H, CH$_3$), 3.45 (s, 4H, CH$_2$). ^{13}C-NMR (CDCl$_3$): δ -2.6 (CH$_3$), 23.6 (CH$_2$), 90.3, 109.4 (C). HRMS (EI) Anal. Calc. for [$C_9H_{13}SSi_2$]: 209.0276. Found: 209.0279. IR (KBr, cm^{-1}): 2954, 2895, 2158, 1757, 1632, 1401. Elemental analysis: Calc.: C, 53.52; H, 7.18. Found: C, 53.68; H, 7.47%.

4.2.2. Thiacycloundeca-3,9-diyne (**3**)

The synthesis was carried out according to the procedure reported in the literature [6] except for the workup; flash column chromatography on silica was done with methylene chloride–light petroleum 1:1 and the crude product was recrystallized from Et$_2$O–light petroleum to afford **3** as colorless plates suitable for X-ray structure analysis. M.p. 42 °C. HRMS (EI) Anal. Calc. for [$C_{10}H_{11}S$]: 163.0582. Found: 163.0585.

4.2.3. Thiacyclododeca-3,10-diyne (**4**)

The synthesis was carried out according to the procedure reported in the literature [6] except for the workup; column chromatography was done on silica with methylene chloride–light petroleum 1:7 and the crude solid product was recrystallized from Et$_2$O–light petroleum to afford **4** as a white powder. Further purification was achieved by means of kugelrohr distillation at 0.09 mbar/145 °C to yield colorless needles suitable for X-ray structure analysis. M.p. 49 °C. HRMS (EI) Anal. Calc. for [$C_{11}H_{13}S$]: 177.0737. Found: 177.0723.

4.3. Reactions with CpCo(COD)

4.3.1. Superphane **15**

A solution of 100 mg of 5,5,6,6-tetramethyl-1-thia-5,6-disilacyclonona-3,7-diyne (**14**) and 104 mg CpCo(COD) in 7 ml cyclooctane was heated for 55 h at 150 °C. The resulting dark mixture was directly put on an alumina column (neutral, grade III), conditioned with light petroleum. After excess CpCo(COD) was eluted, the product **15** was isolated in 15% yield as yellow oxygen sensitive needles suitable for X-ray structure analysis. M.p. 220 °C. ^{1}H-NMR (CDCl$_3$): δ 0.11 (s, 12H, Si(CH$_3$)), 0.26 (s, 12H, Si(CH$_3$)), 3.09 (bd, 4H, CH$_2$S), 3.52 (bd, 4H, CH$_2$S), 4.73 (s, 10H, CpH). ^{13}C-NMR (CDCl$_3$): δ -1.0 (SiCH$_3$), -0.2 (SiCH$_3$), 29.7 (CH$_2$S), 67.3 (cbd–C), 79.3 (Cp), 80.2 (cbd–C). HRMS (EI) Anal. Calc. for [$C_{30}H_{42}S_2Si_4Co_2$]: 696.0465. Found: 696.0461. IR (KBr, cm^{-1}): 2945, 2895, 1627, 1473, 1403.

4.3.2. ({1,2,6,7-η^4}-Tricyclo-[7.3.0.0^{2,6}]-4-thiadodeca-1,6-dien)(η^5-cyclopentadienyl)cobalt(I) (**13**)

A solution of 504 mg of thiacyclododeca-3,10-diyne (**4**) and 656 mg CpCo(COD) in 50 ml cyclooctane was heated for 93 h at 140 °C. The resulting dark mixture was directly put on an alumina column (neutral, grade III), conditioned with light petroleum–methylene chloride 30:1. After excess CpCo(COD) was eluted the product **13** was obtained in 51% yield as yellow needles suitable for X-ray structure analysis. M.p. 105 °C. ^{1}H-NMR (CDCl$_3$): δ 0.69–0.80 (m, 1H, CH$_2$), 1.39–1.59 (m, 4H, CH$_2$), 1.79–1.92 (m, 5H, CH$_2$), 3.12 (d, 2H, SCH$_2$), 3.20 (d, 2H, SCH$_2$), 4.70 (s, 5H, CpH). ^{13}C-NMR (CDCl$_3$): δ 29.1 (CH$_2$), 30.8 (CH$_2$), 31.0 (CH$_2$), 32.3 (SCH$_2$), 73.5 (cbd–C), 80.5 (Cp), 80.9 (cbd–C). HRMS (EI) Anal. Calc. for [$C_{16}H_{19}SCo$]: 302.0558. Found: 302.0539. IR (KBr, cm^{-1}): 3098, 2919, 2835, 1628, 1435. Elemental analysis: Calc.: C, 63.57; H, 6.33; S, 10.61. Found: C, 63.66; H, 6.31; S, 10.77%.

4.3.3. ({1,2,6,7-η^4}-Tricyclo-[6.3.0.0^{2,6}]-4-thiaundeca-1,6-dien)(η^5-cyclopentadienyl)cobalt(I) (**12**) and (2,5)[2.2](3,4-tetramethylene)thiophenophane (**10**)

A solution of 157 mg of thiacycloundeca-3,9-diyne (**3**) and 244 mg CpCo(COD) in 10 ml cyclooctane was heated for 4 h at 140 °C. The resulting dark mixture was directly put on an alumina column (neutral, grade

III), conditioned with light petroleum. After excess CpCo(COD) was eluted a mixture of **12** and **10** was obtained. Separation was carried out by kugelrohr distillation at 0.07 mbar/175 °C to yield 15% of **12** as yellow needles suitable for X-ray structure analysis. The residue yields the thiophenophane **10** in 13% [5]. Analytical data of **12**: m.p. 118 °C. ^{1}H-NMR (C_6D_6): δ 1.26–1.30 (m, 2H, CH_2), 1.54–1.59 (m, 2H, CH_2), 1.71–1.81 (m, 2H, CH_2), 2.09–2.16 (m, 2H, CH_2), 3.08 (d, 2H, SCH_2), 3.17 (d, 2H, SCH_2), 4.61 (s, 5H, CpH). ^{13}C-NMR (C_6D_6): δ 23.5 (t, CH_2), 23.8 (t, CH_2), 31.9 (t, SCH_2), 68.8 (s, cbd–C), 80.5 (s, cbd–C), 81.4 (d, Cp). HRMS (FAB) Anal. Calc. for [$C_{15}H_{17}SCo$]: 288.0383. Found: 288.0384. IR (KBr, cm^{-1}): 2926, 2895, 2832, 2021, 1629, 1432. Elemental analysis: Calc.: C, 62.49; H, 5.94; S, 11.12. Found: C, 62.49; H, 6.03; S, 11.15%.

4.4. X-ray crystallography and structure solution

The crystallographic data were recorded with a Siemens Smart CCD diffractometer at 200 K for **3**, **4**, **12**, **14** and **15** and a Nonius-CAD4 diffractometer at 173 K for **13**. Relevant crystal and data collection parameters are given in Table 3. The structures were solved by using direct methods, least-squares refinement, and Fourier techniques. Structure solution and refinement were performed with SHELXTL [11].

Table 3
Crystal data and structure refinement parameters for **3**, **4**, **12**, **13**, **14** and **15**

Compound	**3**	**4**	**12**	**13**	**14**	**15**
Empirical formula	$C_{10}H_{12}S$	$C_{11}H_{14}S$	$C_{15}H_{17}CoS$	$C_{16}H_{19}CoS$	$C_{10}H_{16}SSi_2$	$C_{30}H_{42}Co_2S_2Si_4$
Formula weight	164.26	178.28	288.28	302.30	224.47	696.05
Temperature (K)	200	200	200	173	200	200
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	*Pbca*	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1$	$P\bar{1}$
Crystal color	Colorless	Colorless	Yellow	Yellow	Colorless	Yellow
Crystal shape	Polyhedron	Irregular	Polyhedron	Irregular	Polyhedron	Polyhedron
Crystal size (mm)	0.47 × 0.24 × 0.07	0.52 × 0.11 × 0.08	0.32 × 0.26 × 0.13	0.33 × 0.20 × 0.05	0.42 × 0.32 × 0.13	0.34 × 0.28 × 0.26
Unit cell dimensions						
a (Å)	12.2965(8)	14.8403(2)	6.2471(2)	8.827(3)	8.6622(3)	15.6317(3)
b (Å)	8.0618(4)	4.7368(1)	8.6403(3)	21.032(9)	11.6122(3)	16.3619(2)
c (Å)	18.3228(11)	15.7533(2)	11.9886(4)	8.044(2)	13.0695(4)	17.4940(3)
α (°)	90	90	88.735(1)	90	90	71.172(1)
β (°)	90	115.620(1)	81.393(1)	115.68(1)	90.663(1)	71.161(1)
γ (°)	90	90	74.735(1)	90	90	82.354(1)
V (Å^3)	1816.37(18)	998.51(3)	617.14(4)	1345.9(8)	1324.54(7)	4006.0(1)
Z	8	4	2	4	4	4
D_{calc} (g cm^{-3})	1.201	1.186	1.55	1.49	1.134	1.28
Absorption coefficient μ (mm^{-1})	0.288	0.267	1.53	1.41	0.389	1.08
θ Range for data collection (°)	2.22–23.55	1.52–26.35	1.7–27.5	2.6–28.0	1.56–25.58	1.8–27.5
Index ranges	$-5<h<13$, $-8<k<8$, $-20<l<20$	$-18<h<18$, $-5<k<5$, $-19<l<19$	$-8<h<8$, $-11<k<11$, $-15<l<15$	$0<h<11$, $0<k<27$, $-10<l<9$	$-9<h<10$, $-13<k<14$, $-15<l<14$	$-20<h<20$, $-21<k<21$, $-22<l<22$
Reflections collected	4535	8906	6339	3434	9677	41 436
Independent reflections	1323	2020	2803	3239	4198	18 305
Max/min transmission	0.98, 0.70	0.98, 0.74	0.85, 0.69	0.87, 0.76	0.96, 0.87	0.74, 0.32
Observed data/parameters	1323/100	2020/165	2803/163	2386/239	4198/243	18 305/746
$R(F)$	0.040	0.025	0.022	0.049	0.021	0.062
$R_w(F^2)$	0.105	0.058	0.056	0.108	0.055	0.158
Goodness-of-fit on F^2	1.08	0.96	1.07	1.05	1.05	1.01
$(\Delta\rho)_{max}$ and $(\Delta\rho)_{min}$ (e Å^{-3})	0.50 and −0.29	0.18 and −0.18	0.35 and −0.20	0.66 and −1.14	0.20 and −0.14	0.78 and −0.51

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 162011, 162012, 162013, 162014, 162015 and 162016 for compounds **3**, **4**, **12**, **13**, **14** and **15**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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