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Synthesis of dialkyl(aryl)cyclobutenylphosphine oxides

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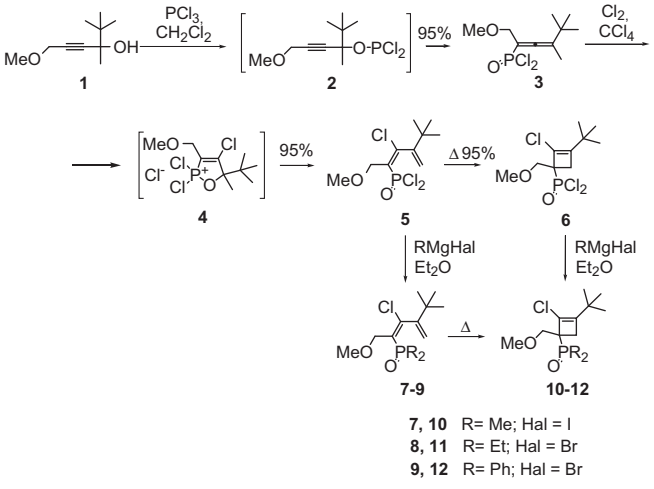
ABSTRACT

Dialkyl(aryl)cyclobutenylphosphine oxides are obtained via two routes: from the corresponding cyclobutenylphosphonic dichlorides using organomagnesium chemistry and from 1,3-dienylphosphine oxides by thermal electrocyclic ring closure.

Cyclobutene derivatives are difficult to prepare and their properties remain vastly underexplored. Methods for the synthesis of cyclobutenes are based mainly on catalytic [2+2] cycloaddition reactions between alkenes and acetylenes,[1–3] and expansion of cyclopropane rings with subsequent transformations.[4,5] Substituted cyclobutenes have been obtained by intramolecular Wittig reaction using the vinyltriphenylphosphonium salt.[6] It was reported[7,8] that in some cases, 1-substituted 2-chloro-3-*tert*-butyl-1,3-butadiene-1-phosphonic dichlorides readily undergo butadiene-cyclobutene thermal isomerization. This approach has allowed the synthesis of a variety of cyclobutenyl dichlorophosphonates and can be used as a generic pathway to phosphorus-containing cyclobutenes.[9]

However, cyclobutenylphosphine oxides, which are interesting compounds for the study of their subsequent transformations and for practical applications, are not readily available. Herein, we report the synthesis of several previously undescribed 1,3-dienyl- and cyclobutenylphosphine oxides. The cyclobutenylphosphine oxides were prepared in two ways: (1) by the replacement of a halogen with an alkyl(aryl) group in the corresponding cyclobutenyl dichlorophosphonates, and (2) through thermal, solvent-free 1,3-butadiene-cyclobutene isomerization of 1,3-dienylphosphine oxides. These general routes to the synthesis of substituted dialkyl(aryl)cylobutenylphosphine oxides are described in Scheme 1.

Methyl propargyl ether was prepared by the reaction of propargyl alcohol with dimethyl sulfate using a known method.[10] The acetylenic alcohol **1** was prepared by the reaction of methyl propargyl ether with pinacolone in the presence of freshly prepared potassium *tert*-butoxide similar to the method described by Miyamoto et al.[11] Alcohol **1** was reacted with phosphorus trichloride to form intermediate **2**, which underwent spontaneous isomerization to allene **3**.[12] Hydrogen chloride formed during this reaction was efficiently removed with a stream of nitrogen. Next, allene **3** was chlorinated with a solution of chlorine in carbon tetrachloride to give unstable salt **4**, which liberated hydrogen chloride upon heating to form 1,3-diene **5**. This isomerized on



Scheme 1. Synthesis of dialkyl(aryl)cyclobutenylphosphine oxides.

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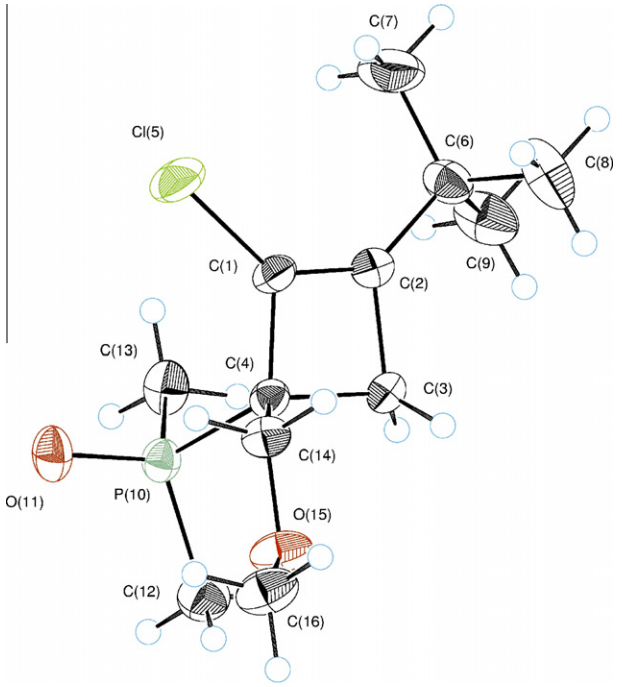

Figure 1. X-ray crystal structure (ORTEP) of **10**.

Table 1
Synthesis of cyclobutene derivatives **10**–**12** by cyclization of 1,3-dienes **7**–**9**

1,3-Diene	Time (h)		*T* (°C)	Ratio[a]	Isolated yield[b]
7	2		150	13:87	**10** (84%)
8	2		150	17:83	**11** (79%)
9	2.5	0.5	150	20:80	**12** (70%)
		2	200	25:75	

[a] Ratio of diene/cyclobutene, determined by ^{1}H NMR spectroscopy.
[b] Yield obtainted via method B.[13]

heating to give cyclobutene **6**, which was purified by distillation under reduced pressure.[7,8]

Typically, phosphine oxides **7**–**12**[13] were prepared by organomagnesium synthesis from **6**. The crude products were purified either by flash chromatography on silica gel (dichloromethane/methanol 97/3; compounds **7**–**9**, **12**) or by distillation under vacuum (compounds **10** and **11**). The structure of compound **10** was confirmed by X-ray crystal structure analysis (Fig. 1).[14]

Successful butadiene-cyclobutene isomerization of phosphine oxides on heating (conversions of **5** into **6** and **7**–**9** in **10**–**12**) shows that the formation of the cyclobutene isomer is determined mainly by steric requirements (Table 1), rather than the polarization of the parent 1,3-diene molecule.

In conclusion, we have reported the synthesis of several previously undescribed cyclobutenylphosphine oxides, obtained by the cyclization of the corresponding 1,3-dienyl-phosphine oxides. There is reason to suppose that similar cyclizations can be carried out using a variety of sterically hindered 1,3-dienes, and not necessarily bearing a phosphorus-containing group.

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2012.02.042. These data include MOL files and InChiKeys of the most important compounds described in this article.

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12. Macomber, R. S.; Kennedy, E. R. *J. Org. Chem.* **1976**, *41*, 3191–3197.
13. *General procedure for the synthesis of phosphine oxides* **7**–***12*** *(method A)*: To a stirred solution of phosphonic dichloride **5** or **6** (7.64 g, 25 mmol) in Et_2O (25 ml) was added dropwise at −10 °C a solution of the corresponding Grignard reagent (0.05 M) in Et_2O over 1 h. The mixture was allowed to warm to room temperature over 1 h with stirring. Formation of a white precipitate was observed. The mixture was refluxed for another 2 h, then cooled and treated with a saturated solution of NH_4Cl. The ethereal layer was separated, the aqueous layer extracted with $CHCl_3$ (2 × 10 ml), and the combined extracts dried over Na_2SO_4. The solvent was removed by rotary evaporation. The crude product was purified either by flash chromatography (SiO_2, CH_2Cl_2/MeOH, 97:3; compounds **7**–**9**, **12**) or by distillation under vacuum (compounds **10** and **11**). *Method B (for* ***10***–***12*** *only)*. Compounds **10**–**12** were obtained from corresponding 1,3-dienes **7**–**9** by thermal, solvent-free electrocyclic ring closure. The products were separated from the starting compounds by flash chromatography (SiO_2, CH_2Cl_2/MeOH, 97:3). See Table 1 for details. *3-tert-Butyl-2-chloro-1-methoxymethyl-1-dimethylphosphoryl-1,3-butadiene (****7****)*: Yield 3.85 g (58%), pale yellow oil, R_f = 0.37 (CH_2Cl_2/MeOH, 95:5). IR (KBr, cm^{-1}): 3415, 2965, 2890, 2820, 1590, 1460, 1358, 1175, 1100, 955, 906, 758, 710. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26 (s, 9H, C(CH_3)$_3$), 1.63 (d, 6H, CH_3P, $^2J_{HP}$ 12.0 Hz), 3.36 (s, 3H, CH_3O), 4.21 (dd, 1H, CH_3OCH_2, $^2J_{HH}$ 12.0 Hz, $^3J_{HP}$ 8.0 Hz), 4.43 (dd, 1H, CH_3OCH_2, $^2J_{HH}$ 12.0 Hz, $^3J_{HP}$ 16.0 Hz), 5.22 (s, 1H, =CH_2), 5.29 (s, 1H, =CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ 18.2 (d, CH_3P, $^1J_{CP}$ 115.7 Hz), 19.7 (d, CH_3P, $^1J_{CP}$ 124.3 Hz), 30.7 (s, C(CH_3)$_3$), 35.0 (s, *C*(CH_3)$_3$), 57.9 (s, CH_3O), 70.6 (s, CH_3OCH_2), 116.5 (s, =CH_2), 129.0 (d, =CP, $^1J_{CP}$ 83.1 Hz), 150.4 (d, *C*=CP, 11.6 Hz), 157.0 (s, *C*=CH_2). ^{31}P NMR (81 MHz, $CDCl_3$): δ 33.8. HRMS *m/z*: 265.1115 found (calcd for $C_{12}H_{23}ClO_2P$, (M+H)$^+$ requires 265.1124). *3-tert-Butyl-2-chloro-1-methoxymethyl-1-diethylphosphoryl-1,3-butadiene (****8****)*: Yield 3.34 g (46%), pale yellow oil, R_f = 0.41 (CH_2Cl_2/MeOH, 95:5). IR (KBr, cm^{-1}): 3410, 2963, 2889, 2824, 1593, 1458, 1362, 1177, 1099, 957, 907, 760, 710. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (dt, 3H, CH_3CH_2P, $^3J_{HH}$ 7.9 Hz, $^3J_{HP}$ 17.2 Hz), 1.10 (dt, 3H, CH_3CH_2P, $^3J_{HH}$ 7.9 Hz, $^3J_{HP}$ 15.6 Hz), 1.20 (s, 9H, C(CH_3)$_3$), 1.75 (q, 2H, CH_3CH_2P, $^3J_{HH}$ 7.9 Hz, $^2J_{HP}$ 11.2 Hz), 1.78 (q, 2H, CH_3CH_2P, $^3J_{HH}$ 7.9 Hz, $^2J_{HP}$ 10.0 Hz), 3.29 (s, 3H, CH_3O), 4.04 (dd, 1H, CH_3OCH_2, $^2J_{HH}$ 12.0 Hz, $^3J_{HP}$ 9.8 Hz), 4.26 (dd, 1H, CH_3OCH_2, $^2J_{HH}$ 12.0 Hz, $^3J_{HP}$ 14.6 Hz), 5.07 (s, 1H, =CH_2), 5.18 (s, 1H, =CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ 5.70 (s, CH_3CH_2P), 22.0 (d, CH_3CH_2P, $^1J_{CP}$ 135.2 Hz), 23.4 (d, CH_3CH_2P, $^1J_{CP}$ 135.9 Hz), 30.8 (s, C(CH_3)$_3$), 34.9 (s, *C*(CH_3)$_3$), 58.1 (s, CH_3O), 70.8 (s, CH_3OCH_2), 116.0 (s, =CH_2), 127.4 (d, =CP, $^1J_{CP}$ 75.9 Hz), 151.5 (d, *C*=CP, $^2J_{CP}$ 14.2 Hz), 156.6 (s, *C*=CH_2). ^{31}P NMR (81 MHz, $CDCl_3$): δ 43.2. HRMS *m/z*: 293.1429 found (calcd for $C_{14}H_{27}ClO_2P$, (M+H)$^+$ requires 293.1437). *3-tert-Butyl-2-chloro-1-methoxymethyl-1-diphenylphosphoryl-1,3-butadiene (****9****)*: Yield 2.5 g (26%), colorless crystals, mp 110–112 °C, R_f = 0.46 (CH_2Cl_2/MeOH, 95:5). IR (KBr, cm^{-1}): 3059, 2963, 2889, 2824, 1651, 1589, 1474, 1458, 1439, 1366, 1188, 1111, 988, 961, 725, 702, 552. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27 (s, 9H, C(CH_3)$_3$), 2.98 (s, 3H, CH_3O), 4.04 (dd, 1H, CH_3OCH_2, $^2J_{HH}$ 12.0 Hz, $^3J_{HP}$ 9.8 Hz), 4.26 (dd, 1H, CH_3OCH_2, $^2J_{HH}$ 12.0 Hz, $^3J_{HP}$ 14.6 Hz), 4.71 (s, 1H, =CH_2), 4.98 (s, 1H, =CH_2), 7.40–7.53 (m, 6H, 4*m*-H, 2*p*-H), 7.65 (dd, 2*o*-H, $^3J_{HH}$ 7.26 Hz, $^3J_{HP}$ 11.65 Hz), 7.90 (dd, 2*o*-H, $^3J_{HH}$ 6.54 Hz, $^3J_{HP}$ 12.37 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.7 (s, C(CH_3)$_3$), 35.0 (s, *C*(CH_3)$_3$), 58.1 (s, CH_3O), 70.4 (d, CH_3OCH_2, $^2J_{CP}$ 9.6 Hz), 117.6 (s, =CH_2), 128.0 (d, 2*m*-C, $^3J_{CP}$ 12.1 Hz), 128.3 (d, 2*m*-C, $^3J_{CP}$ 12.8 Hz), 128.5 (d, =CP, $^1J_{CP}$ 92.2 Hz), 131.5 (d, 2*p*-C, $^4J_{CP}$ 8.10 Hz), 131.8 (d, 4*o*-C, $^2J_{CP}$ 9.4 Hz), 133.5 (d, *ipso*-C, $^1J_{CP}$ 106.4 Hz), 134.2 (d, *ipso*-C, $^1J_{CP}$ 106.4 Hz), 154.5 (d, C=CP, $^2J_{CP}$ 16.8 Hz), 155.8 (d, *C*=CH_2, $^3J_{CP}$ 3.4 Hz). ^{31}P NMR (81 MHz, $CDCl_3$): δ 28.4. HRMS *m/z*: 389.1411 found (calcd for $C_{22}H_{27}ClO_2P$, (M+H)$^+$ requires 389.1437). Spin–spin coupling between germinal protons of terminal methylene group (compounds **7**–**9**) is not observed. *2-Chloro-1-dimethylphosphoryl-1-methoxymethyl-3-tert-butyl-*

cyclobut-2-ene (***10***): Yield 4.2 g (63%, method A), colorless hygroscopic crystals, mp 62–63 °C, bp 110–112 °C (0.006 Torr). IR (KBr, cm^{-1}): 3429, 2963, 2932, 2882, 2824, 1655, 1474, 1366, 1304, 1177, 1103, 934, 868, 745, 718. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (s, 9H, $C(CH_3)_3$), 1.37 (d, 3H, CH_3P, $^2J_{HP}$ 12.8 Hz), 1.45 (d, 3H, CH_3P, $^2J_{HP}$ 13.2 Hz), 2.22 (dd, 1H, =CCH_2, $^2J_{HH}$ 12.4 Hz, $^3J_{HP}$ 2.2 Hz), 2.44 (dd, 1H, =CCH_2, $^2J_{HH}$ 12.4 Hz, $^3J_{HP}$ 6.2 Hz), 3.27 (s, 3H, CH_3O), 3.62 (t, 1H, CH_3OCH_2, $^2J_{HH}$ 10.4 Hz, $^3J_{HP}$ 10.4 Hz), 3.70 (t, 1H, CH_3OCH_2, $^2J_{HH}$ 10.4 Hz, $^3J_{HP}$ 10.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2 (d, CH_3P, $^1J_{CP}$ 174.8 Hz), 14.9 (d, CH_3P, $^1J_{CP}$ 172.9 Hz), 27.5 (s, $C(CH)_3$), 30.9 (s, =CCH_2), 33.0 (s, $C(CH_3)_3$), 51.7 (q, CH_2CP, $^1J_{CP}$ 71.6 Hz), 59.2 (s, CH_3O), 72.5 (s, CH_3OCH_2), 117.0 (d, C=CH_2, $^3J_{CP}$ 5.8 Hz), 152.6 (d, =CCl, $^2J_{CP}$ 1.12 Hz). ^{31}P NMR (81 MHz, $CDCl_3$): δ 44.3. HRMS *m*/*z*: 265.1109 found (calcd for $C_{12}H_{23}ClO_2P$, $(M+H)^+$ requires 265.1124). *2-Chloro-1-diethylphosphoryl-1-methoxymethyl-3-tert-butylcyclobut-2-ene* (***11***): Yield 3.81 g (52%, method A), pale yellow oil, bp 120–122 °C (0.005 Torr). IR (KBr, cm^{-1}): 3395, 2966, 2882, 2827, 1655, 1458, 1366, 1281, 1173, 1107, 1030, 1003, 980, 949, 764. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07 (s, 9H, $C(CH_3)_3$), 1.13 (dt, 3H, CH_3CH_2P, $^3J_{HH}$ 8.4 Hz, $^3J_{HP}$ 16.8 Hz), 1.15 (dt, 3H, CH_3CH_2P, $^3J_{HH}$ 8.4 Hz, $^3J_{HP}$ 15.6 Hz), 1.77 (q, 2H, CH_3CH_2P, $^3J_{HH}$ 8.4 Hz, $^2J_{HP}$ 15.2 Hz), 1.80 (q, 2H,CH_3CH_2P, $^3J_{HH}$ 8.4 Hz, $^2J_{HP}$ 15.0 Hz), 2.26 (dd, 1H, =CCH_2, $^3J_{HP}$ 2.2 Hz, $^2J_{HH}$ 11.9 Hz), 2.57 (dd, 1H, =CCH_2, $^3J_{HP}$ 6.0 Hz, $^2J_{HH}$ 11.9 Hz), 3.31 (s, 3H, CH_3O), 3.62 (t, 1H, CH_3OCH_2, $^2J_{HH}$ 9.9 Hz, $^3J_{HP}$ 9.9 Hz), 3.73 (t, 1H, CH_3OCH_2, $^2J_{HH}$ 9.9 Hz, $^3J_{HP}$ 9.9 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 5.8 (d, CH_3CH_2P, $^2J_{CP}$ 9.6 Hz), 18.9 (d, CH_3CH_2P, $^1J_{CP}$ 64.7 Hz), 19.7 (d, CH_3CH_2P, $^1J_{CP}$ 64.1 Hz), 27.6 (s, $C(CH_3)_3$), 31.3 (s, =CCH_2), 33.0 (s, $C(CH_3)_3$), 52.4 (d, CH_2CP, $^1J_{CP}$ 65.7 Hz), 59.2 (s, CH_3O), 72.8 (s, CH_3OCH_2), 116.9 (d, C=CH_2, $^3J_{CP}$ 6.7 Hz), 152.7 (d, =CCl, $^2J_{CP}$ 9.11 Hz). ^{31}P NMR (81 MHz, $CDCl_3$): δ 50.4. HRMS *m*/*z*: 293.1423 found (calcd for $C_{14}H_{27}ClO_2P$, $(M+H)^+$ requires 293.1437). *2-Chloro-1-diphenylphosphoryl-1-methoxymethyl-3-tert-butylcyclobut-2-ene* (***12***): Yield 3.3 g (34%, method A), colorless crystals, mp 113–114.5 °C, R_f = 0.66 (CH_2Cl_2/MeOH 95:5). IR (KBr, cm^{-1}): 3437, 3055, 2963, 2928, 2870, 2827, 1651, 1474, 1458, 1439, 1366, 1281, 1192, 1115, 984, 756, 725, 698, 548. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.78 (s, 9H, $C(CH_3)_3$), 2.39 (dd, 1H, =CCH_2, $^3J_{HP}$ 7.0 Hz, $^2J_{HH}$ 12.2 Hz), 2.61 (dd, 1H, =CCH_2, $^3J_{HP}$ 3.3 Hz, $^2J_{HH}$ 12.2 Hz), 3.26 (s, 3H, CH_3O), 3.77 (dd, 1H, CH_3OCH_2, $^2J_{HH}$ 11.0 Hz, $^3J_{HP}$ 7.4 Hz), 3.82 (dd, 1H, CH_3OCH_2, $^2J_{HH}$ 11.0 Hz, $^3J_{HP}$ 5.4 Hz), 7.40–7.53 (m, 6H, 4*m*-H, 2*p*-H), 7.87 (dd, 4*o*-H, $^3J_{HH}$ 11.4 Hz, $^3J_{HP}$ 19.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.4 (s, $C(CH_3)_3$), 31.2 (s, =CCH_2), 32.9 (s, $C(CH_3)_3$), 53.5 (d, CH_2CP, $^1J_{CP}$ 73.4 Hz), 59.6 (s, CH_3O), 69.9 (d, CH_3OCH_2, $^2J_{CP}$ 8.1 Hz), 128.2 (d, 4*m*-C, $^3J_{CP}$ 11.4 Hz), 130.2 (d, *ipso*-C, $^1J_{CP}$ 96.9 Hz), 130.8 (d, *ipso*-C, $^1J_{CP}$ 96.9 Hz), 132.0 (d, 4*o*-C, $^4J_{CP}$ 1.1 Hz), 132.1 (d, 2*p*-C, $^2J_{CP}$ 10.4 Hz), 152.9 (d, C=CP, $^2J_{CP}$ 1.1 Hz). ^{31}P NMR (81 MHz, $CDCl_3$): δ 34.3. HRMS *m*/*z*: 389.1418 found (calcd for $C_{22}H_{27}ClO_2P$, $(M+H)^+$ requires 389.1437).

14. The X-ray crystal structure for compound **10** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 847993. Formula: $C_{12}H_{22}ClO_2P$. Crystal system, space group Orthorhombic, *Pcab*. Unit cell parameters: a = 11.0602(2) Å, b = 13.8647(2) Å, c = 19.2508(4) Å, α = 90°, β = 90°, γ = 90°. V = 2952.04(9) Å^3; T = 193(2) K; Z = 8; ρ_{calc} = 1.191 g cm^{-3}; μ = 0.354 mm^{-1} (for MoKα, λ = 0.71073 Å); F(000) = 1136; full-matrix least-squares on F^2; parameters = 145; restraints = 0; R(all) = 0.083; wR(all) = 0.341; GooF(all) = 1.889. *Key intramolecular bond lengths, Å*: C(1)–C(2) 1.332(2); C(2)–C(3) 1.524(2); C(3)–C(4) 1.568(2); C(4)–C(1) 1.515(2); C(1)–Cl(5) 1.7232(13); C(2)–C(6) 1.496(2); P(10)–C(13) 1.7943(15); P(10)–C(12) 1.794(2); P(10)–O(11) 1.4911(10). *Key intramolecular bond angles*: Cl(5)–C(1)–C(2) 134.99(11)°; C(1)–C(2)–C(3) 91.65(10)°; C(2)–C(3)–C(4) 87.57(9)°; C(3)–C(4)–C(1) 83.50(9)°; C(1)–C(2)–C(6) 138.59(13)°.