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Note

An unusual norbornadiene coupling product: synthesis, characterization, and structure of the ruthenocene $(C_5Me_5)Ru(\eta^5\text{-}C_5H_4C_9H_{11})$

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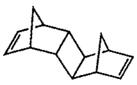
Abstract

Treatment of $(C_5Me_5)_2Ru_2Cl_4$ with excess norbornadiene (NBD) in refluxing ethanol yields the substituted ruthenocene complex $(C_5Me_5)Ru(\eta^5\text{-}C_5H_4C_9H_{11})$, which possesses a cyclopentadienyl (Cp) ring bearing a tricyclo[4.2.1.0^{2,5}]-non-7-en-3-yl substituent. This compound has been characterized by NMR spectroscopy and X-ray crystallography. The substituted Cp ring is formed by coupling of two NBD units, C–C bond cleavage, migration of one hydrogen atom from one carbon atom to another, and loss of a hydrogen atom (presumably as HCl). Crystal data: monoclinic, space group $P2_1/n$, with $a = 10.0285(5)$, $b = 9.1801(5)$, $c = 21.249(1)$ Å, $\beta = 95.327(1)°$, $V = 1947.9(2)$ Å^3, $Z = 4$, $wR_2 = 0.0580$ for 4611 data and 291 parameters. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Group 8; Ruthenocene; Norbornadiene; Ring-opening metathesis polymerization

1. Introduction

Several classes of transition metal complexes catalyze the dimerization or trimerization of norbornadiene (NBD) [1]. For example, both thermal and photochemical activation of $Ni(CO)_4$ gives catalysts for the dimerization of NBD [2]. The products obtained by thermal activation have structures **1** and **2**, whereas the products obtained by photolytic activation have structures **3** and **4**. The rhodium complex $RhCl(PPh_3)_3$ also catalyzes the formation of linked NBD dimers, the principal products being **4**–**6** [3]. The highly symmetric heptacyclic dimer **7** can also be obtained, especially if the *exo* faces of NBD are blocked [4,5]. Interestingly, the cyclooctatetrene complex Ru(COD)(COT) catalyzes the dimerization of NBD to the unusual pentacyclic dimer **8** [1].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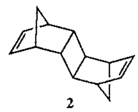
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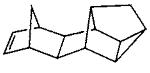
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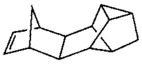
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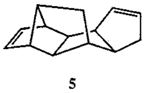
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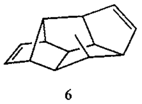
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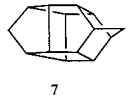
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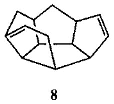
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In some cases, organometallic compounds can be isolated which contain metal-bound NBD dimers. Treating $[Ir(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) with excess NBD, followed by addition of 2,4-pentanedione and Na_2CO_3, yields a compound with the formula $Ir(NBD)_3(acac)$ (acac = acetylacetonate). An X-ray crystal structure of this product showed that one NBD ligand was bound to iridium in the typical η^2:η^2 fashion, but that the other two NBD ligands had coupled to form an iridacyclopentane ring (structure **9**) [6]. The two NBD units in this metallacycle are linked in an *exo*–*trans*–*exo* fashion. A nickel compound, $Ni(C_{14}H_{16})(bipy)$, is known that contains two NBD molecules linked in an *exo*–*trans*–*endo* geometry

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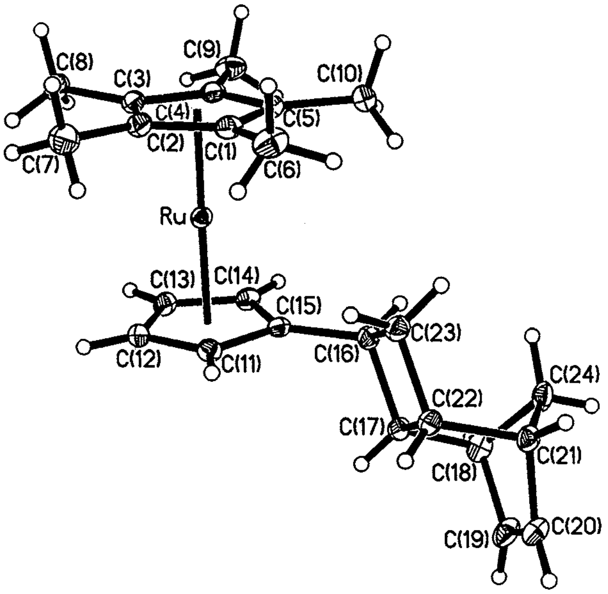


Fig. 1. Molecular structure of $(C_5Me_5)Ru(\eta^5\text{-}C_5H_4C_9H_{11})$ (**1**) with ellipsoids shown at 30% probability density. Hydrogen atoms are shown as arbitrarily sized spheres.

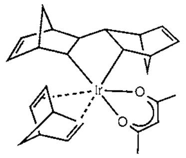
Table 1
Crystal data for $(C_5Me_5)Ru(\eta^5\text{-}C_5H_4C_9H_{11})$ (**1**)

Formula	$C_{24}H_{30}Ru$
Formula weight	419.55
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Collection method	Area detector
Diffractometer	Siemens smart system
Crystal size (mm)	0.20 × 0.18 × 0.16
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	10.0285(5)
b (Å)	9.1801(5)
c (Å)	21.249(1)
β (°)	95.327(1)
V (Å^3)	1947.9(2)
Z	4
D_{calc} (g cm^{-3})	1.431
μ (mm^{-1})	0.808
θ Range (°)	1.93–28.27
Index ranges	$-12 \le h \le 12$, $-6 \le k \le 11$, $-28 \le l \le 27$
Refinement	Full-matrix on F^2
Measured reflections	12 311
Independent reflections	4611
Reflections with $I > 2\sigma(I)$	3441
Parameters	291
Restraints	0
Goodness-of-fit on F^2	1.017
Absorption correction	ψ-Scan
Max./min. transmission	0.276/0.245
Extinction coefficient	None
wR_2 (observed data)	0.0540
wR_2 (all data)	0.0580
$\Delta\rho$ (max./min., e Å^{-3})	0.36/−0.39

Table 2
Selected bond lengths (Å) and angles (°) for $(C_5Me_5)Ru(\eta^5\text{-}C_5H_4C_9H_{11})$ (**1**)

Bond lengths			
Ru–C(11)	2.192(2)	C(17)–C(22)	1.559(3)
Ru–C(12)	2.200(2)	C(18)–C(19)	1.517(4)
Ru–C(13)	2.193(2)	C(18)–C(24)	1.524(4)
Ru–C(14)	2.179(2)	C(19)–C(20)	1.325(3)
Ru–C(15)	2.195(2)	C(20)–C(21)	1.520(3)
C(15)–C(16)	1.500(3)	C(21)–C(24)	1.536(3)
C(16)–C(23)	1.551(3)	C(21)–C(22)	1.552(3)
C(16)–C(17)	1.564(3)	C(22)–C(23)	1.541(3)
C(17)–C(18)	1.555(3)		
Bond angles			
C(15)–C(16)–C(23)	116.4(2)	C(19)–C(20)–C(21)	107.1(2)
C(15)–C(16)–C(17)	114.3(2)	C(20)–C(21)–C(24)	99.8(2)
C(23)–C(16)–C(17)	89.1(2)	C(20)–C(21)–C(22)	104.3(2)
C(18)–C(17)–C(22)	102.6(2)	C(24)–C(21)–C(22)	101.3(2)
C(18)–C(17)–C(16)	117.7(2)	C(23)–C(22)–C(21)	117.7(2)
C(22)–C(17)–C(16)	90.0(2)	C(23)–C(22)–C(17)	89.7(2)
C(19)–C(18)–C(24)	99.4(2)	C(21)–C(22)–C(17)	103.0(2)
C(19)–C(18)–C(17)	104.6(2)	C(22)–C(23)–C(16)	91.2(2)
C(24)–C(18)–C(17)	101.6(2)	C(18)–C(24)–C(21)	94.5(2)
C(20)–C(19)–C(18)	108.3(2)		

(structure **10**) [7]. Finally, a compound with the formula $RuCl(NBD)(C_{14}H_{17})$, which contains two NBD molecules (and a proton) linked in an *endo–endo* fashion as shown in structure **11**, was formed when $[Ru(NBD)Cl_2]_n$ was reduced with zinc in the presence of NBD [8].



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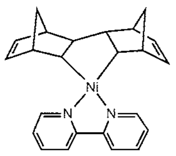

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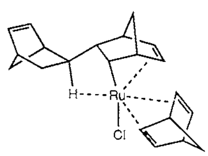

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Herein we report a new kind of norbornadiene coupling reaction.

2. Results and discussion

We have recently reported that $(C_5Me_5)_2Os_2Br_4$ and related complexes are precatalysts for ring-opening metathesis polymerization reactions [9]. During our polymerization experiments, we found that treating the dinuclear ruthenium compound $(C_5Me_5)_2Ru_2Cl_4$ [10,11] with 1000 equivalents of NBD in refluxing ethanol afforded a single organometallic product (as judged by ^{1}H-NMR spectroscopy) in addition to a small amount of polynorbornadiene.

When this reaction was performed on a larger scale, a product with the formula $(C_5Me_5)Ru(C_{14}H_{15})$ (**1**) was isolated as a white solid in 38% yield. This compound gave the same ^{1}H-NMR spectrum as that obtained

Table 3
^{1}H- and ^{1}H COSY-NMR data for $(C_5Me_5)Ru(\eta^5\text{-}C_5H_4C_9H_{11})$ (**1**)

Label	^{1}H [a]		^{1}H COSY [b]
a	5.96	d of AB quartet ($J_{HH} = 2.8$)	b, h, (g)
b	5.93	d of AB quartet ($J_{HH} = 2.8$)	a, g, (h)
c	4.16	dt ($J_{HH} = 2.1$, 1.1)	d, e, f
d	4.13	Overlapping and 2nd order	c, e, f
e	4.12	Overlapping and 2nd order	c, d, f
f	4.11	Overlapping and 2nd order	c, d, or e
g	2.67	Broad d ($J_{HH} = 1.2$)	b, n, p, l/m, (a)
h	2.57	Broad d ($J_{HH} = 1.2$)	a, n, p, (b)
I	2.23	ddd ($J_{HH} = 9.7$, 5.7, 3.6)	o, l/m
j	1.95	Overlaps with k	p, (l/m)
k	1.92	s	–
l	1.91	Overlaps with k	(g), (n), (m), (p)
m	1.88	Overlaps with k	(p), (o), (i), (l), (j)
n	1.71	d ($J_{HH} = 9.1$)	p, g, h, (l/m)
o	1.62	ddd ($J_{HH} = 12.7$, 9.1, 3.8)	m, i
p	1.38	dt ($J_{HH} = 9.0$, 1.5)	n, h, g, l

[a] All chemical shifts are reported in ppm; all coupling constants are reported in Hz.

[b] Parentheses indicate weak coupling, solidus indicates alternative assignments.

from the polymerization reaction, and the molecular formula was confirmed by field desorption (FD) MS.

Colorless crystals of **1** were grown from ether by evaporation, and the structure obtained from X-ray crystallography is shown in Fig. 1. Crystal data are summarized in Table 1, and selected bond distances and angles are given in Table 2. As the structure indicates, **1** is actually a substituted ruthenocene complex, and the formula of **1** is better written as $(C_5Me_5)Ru(\eta^5\text{-}C_5H_4C_9H_{11})$. The cyclopentadienyl (Cp) ring has a pendant tricyclo[4.2.1.0^{2,5}]-non-7-en-3-yl substituent; the $\eta^3\text{-}C_5H_4C_9H_{11}$ ligand can be viewed as the 2 + 2 addition product of NBD with a vinylcyclopentadienyl ring that is itself formed from NBD in several steps.

The ^{1}H-, ^{13}C-, ^{1}H COSY-, and HETCOR-NMR spectra of this compound are summarized in Tables 3 and 4. In the ^{1}H-NMR spectrum, the four protons attached directly to the monosubstituted Cp ring give closely spaced resonances at δ 4.16, 4.13, 4.12, and 4.11; three of these resonances show second-order coupling, and all four are coupled to each other. In the $^{13}C\{^1H\}$-NMR spectrum, the chemical shift of the four Cp carbons are also very similar at δ 72.53, 72.46, 72.4, and 70.8, whereas the substituted quaternary carbon of the Cp ring gives a signal at δ 84.9. The other proton and carbon assignments (Fig. 2) were made by analyzing the couplings seen in the ^{1}H COSY, HETCOR, and HMBC spectra. For example, the methylene hydrogen p shows long-range coupling to carbons M and I, indicating that p is the hydrogen atom that is related to these carbons by three σ bonds in an anti-conformation [12].

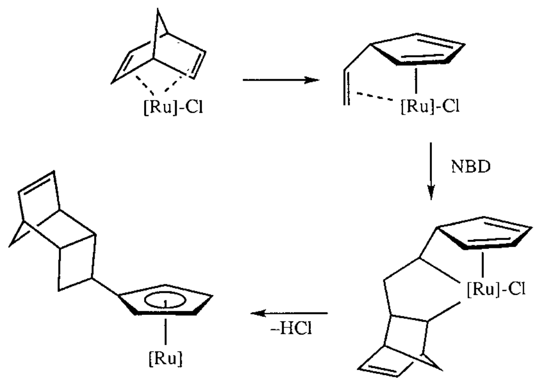
To form the substituted Cp ring from two NBD molecules involves at least four chemical steps: (1) a C–C bond coupling step, (2) loss of a hydrogen atom (probably as HCl), (3) hydrogen atom transfer, and (4) cleavage of a carbon–carbon bond.

A possible mechanism for this reaction is shown in Scheme 1. The sequence begins with the rearrangement of a coordinated NBD ligand to a vinylcyclopentadiene

Table 4
^{13}C-, HETCOR-, and HMBC-NMR data for $(C_5Me_5)Ru(\eta^5\text{-}C_5H_4C_9H_{11})$ (**1**)

Label	^{13}C [a]		Assignment	HETCOR	HMBC
A	135.8	d ($J_{CH} = 144$)	CH=CH	a	–
B	135.3	d ($J_{CH} = 140$)	CH=CH	b	–
C	97.2	d ($J_{CH} = 4.5$)	C	–	2 of c, d, e, or f
D	84.9	s	$\mathit{C}_5\mathrm{Me}_5$	–	–
E	72.53	dquin ($J_{CH} = 170$, 6.7)	$\mathit{C}_5\mathrm{H}_4\mathrm{R}$	f	–
F	72.46	dquin ($J_{CH} = 170$, 6.7)	$\mathit{C}_5\mathrm{H}_4\mathrm{R}$	e	–
G	71.4	dquin ($J_{CH} = 176$, 7.0)	$\mathit{C}_5\mathrm{H}_4\mathrm{R}$	d	–
H	70.8	dquin ($J_{CH} = 176$, 6.0)	$\mathit{C}_5\mathrm{H}_4\mathrm{R}$	c	–
I	46.0	d ($J_{CH} = 150$)	CH	l	p
J	44.8	d ($J_{CH} = 150$)	CH	g	–
K	44.6	d ($J_{CH} = 150$)	CH	h	–
L	40.8	t ($J_{CH} = 133$)	CH$_2$	n, p	–
M	33.8	d ($J_{CH} = 150$)	CH	j	p
N	33.0	d ($J_{CH} = 142$)	CH	i	–
O	28.7	t ($J_{CH} = 134$)	CH$_2$	m, o	–
P	12.4	q ($J_{CH} = 126$)	$\mathrm{C}_5\mathit{Me}_5$	k	–

[a] All chemical shifts are reported in ppm; all coupling constants are reported in Hz.



Scheme 1. Proposed mechanism for the formation of $(C_5Me_5)Ru(\eta^5\text{-}C_5H_4C_9H_{11})$ (**1**); [Ru] = $(C_5Me_5)Ru$.

group. Similar rearrangements have been reported, although the mechanism by which the C–C bond is cleaved remains obscure [13,14]. The coordinated vinyl group could react with a second equivalent of NBD to give a metallacyclopentane, in a step that is well precedented. Subsequent reductive elimination to form a C–C bond and close the four-membered ring, and elimination of HCl to aromatize the cyclopentadiene group, completes the reaction sequence.

As far as we know, this reaction to form a substituted metallocene is unprecedented. The only similar rearrangement that has been described previously is the synthesis of ruthenocenes by the rearrangement of vinylcyclopentenes [15].

3. Experimental

All experiments were performed under argon or vacuum by using standard Schlenk techniques unless otherwise specified. Solvents were distilled under nitrogen from magnesium (ethanol), calcium hydride (acetonitrile), or sodium benzophenone (pentane, diethyl ether). NBD (Aldrich) was distilled from sodium before use. The starting material $(C_5Me_5)_2Ru_2Cl_4$ was prepared by following literature procedures [10,11].

The IR spectrum was obtained on a Nicolet Impact 410 instrument as a Nujol mull between KBr plates. All NMR spectra were obtained on a General Electric GN500 spectrometer at 500 MHz (^1H) and 125 MHz (^{13}C). Chemical shifts are reported in parts per million (δ) relative to $SiMe_4$; positive chemical shifts correspond to resonance frequencies higher than that of the reference. FD mass spectra were obtained on a Finnigan-MAT 731 mass spectrometer; the samples were loaded as pentane solutions. The shapes of all peak envelopes correspond with those calculated from the natural abundance isotopic distributions. Melting points were measured on a Thomas-Hoover Unimelt apparatus in sealed capillaries under argon. Microanalyses were performed by the staff of the Microanalytical Laboratory of the School of Chemical Sciences.

3.1. *(Pentamethylcyclopentadienyl){(tricyclo[4.2.1.0^{2,5}]-non-7-en-3-yl)cyclopentadienyl}-ruthenium(II),* $(C_5Me_5)Ru(\eta^5\text{-}C_5H_4C_9H_{11})$

To a solution of $(C_5Me_5)_2Ru_2Cl_4$ (0.882 g, 1.44 mmol) in ethanol (70 ml) was added NBD (10.0 ml, 92.7 mmol). The solution was refluxed for 18 h and the brownish orange solution became yellow–orange. A small amount of white precipitate formed. The ethanol was removed under vacuum, and the residue was extracted with pentane (2 × 20 ml). The combined extracts were filtered through Celite. The pentane was removed under vacuum, and the resulting residue was dissolved in acetonitrile (20 ml) and concentrated to 10 ml. The solution was stored at $-20°C$ for 3 weeks and a white solid precipitated from an insoluble oil. The acetonitrile supernatant was removed, and the white solid was sublimed at 65°C over 3 days at 10^{-3} Torr. Yield: 1.21 g (38%). MS (FD): *m/z* 420 [M^+]. M.p. (dec.): 74°C. Anal. Calc. for $C_{24}H_{30}Ru$: C, 68.7; H,

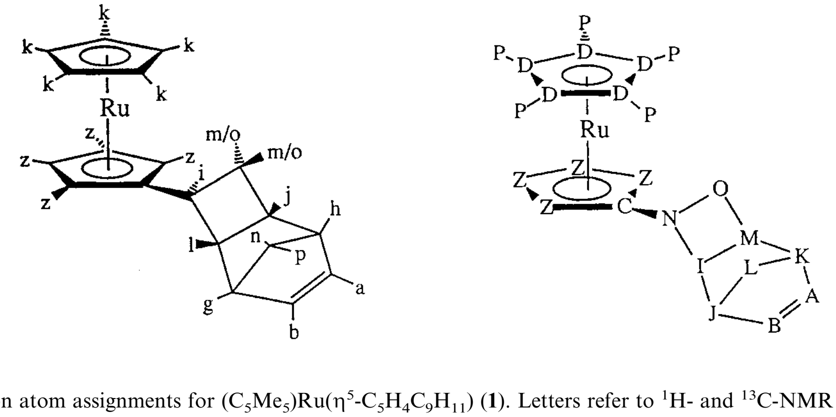


Fig. 2. Hydrogen and carbon atom assignments for $(C_5Me_5)Ru(\eta^5\text{-}C_5H_4C_9H_{11})$ (**1**). Letters refer to ^1H- and ^{13}C-NMR resonances listed in Tables 3 and 4: z = hydrogen atoms c, d, e, or f, and Z = carbon atoms E, F, G, or H.

7.12. Found: C, 68.7; H, 7.25%. IR (cm^{-1}): 3094 (m), 3057 (s), 2726 (w), 2664 (w), 1328 (m), 1292 (w), 1279 (w), 1252 (w), 1238 (w), 1221 (w), 1206 (w), 1157 (w), 1090 (w), 1072 (w), 1043 (m), 1031 (s), 995 (w), 926 (w), 895 (w), 859 (w), 846 (m), 805 (s), 790 (w), 749 (w), 727 (w), 703 (s), 671 (w), 586 (s), 515 (w), 486 (w), 469 (w), 440 (m), 416 (m).

3.2. *Crystallographic study of* $(C_5Me_5)Ru(\eta^5\text{-}C_5H_4C_9H_{11})$ *[16]*

Single crystals of $(C_5Me_5)Ru(\eta^5\text{-}C_5H_4C_9H_{11})$, grown from diethyl ether, were mounted on glass fibers with Crytox and immediately cooled to −75°C in a cold nitrogen gas stream on the diffractometer. Standard peak search and least-squares refinement using 5938 reflections yielded the cell dimensions.

Data were collected with an area detector. Systematic absences for $0k0$ ($k \neq 2n$) and $h0l$ ($h+l \neq 2n$) were only consistent with space group $P2_1/n$. The measured intensities were reduced to structure factor amplitudes and their estimated S.D. values by correction for background and Lorentz and polarization effects. Although corrections for crystal decay were unnecessary, a ellipsoidal ψ-scan absorption correction was applied. Systematically absent reflections were deleted and symmetry equivalent reflections were averaged to yield the set of unique data. All 4611 data were used in the least-squares refinement.

The structure was solved using direct methods (SHELXTL). The correct position for the ruthenium atom was deduced from an E-map. Subsequent least-squares refinement and difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. The quantity minimized by the least-squares program was $\Sigma w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.0200P)^2\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both real and imaginary components of anomalous dispersion. In the final cycle of least-squares, independent anisotropic displacement factors were refined for the nonhydrogen atoms and the methyl hydrogen atoms were fixed in 'idealized' positions with C–H = 0.99 Å. The isotropic displacement factors for the methyl hydrogen atoms were set equal to 1.5 times U_{eq} of the attached carbon atom. The remaining hydrogen atoms were located in the difference Fourier map and their locations were independently refined with individual isotropic displacement factors. Correction for secondary extinction was unnecessary. Successful convergence was indicated by the maximum shift/error of 0.003 for the last cycle. The largest peak in the final Fourier difference map (0.36 e $Å^{-3}$) was located in the center of the C1–C5 bond, 0.718 from C1 and 0.722 Å from C5. A final analysis of variance between observed and calculated structure factors showed no apparent errors.

4. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC 118915 for compound **1**.

Acknowledgements

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