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Syntheses and molecular structures of $Ru_3(\mu\text{-}H)(\mu_3\text{-}CPh_2CCC{\equiv}CPh)(CO)_9$ and $Ru_3\{\mu_3\text{-}CPhCHCC(=CPh_2)CH=CPh\}(\mu\text{-}CO)(CO)_8$

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Abstract

The reaction between $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2CPh_2(OH)\}(CO)_9$ and HC≡CPh, carried out in the presence of $HBF_4 \cdot Me_2O$, afforded the cluster complexes $Ru_3(\mu\text{-}H)(\mu_3\text{-}CPh_2CCC{\equiv}CPh)(CO)_9$ (**5**) and $Ru_3\{\mu_3\text{-}CPhCHCC(=CPh_2)CH=CPh\}(\mu\text{-}CO)(CO)_8$ (**6**), both of which were characterised by single-crystal X-ray studies.

Keywords: Ruthenium; Clusters; Reactions with alkynes; Allenylidene

1. Introduction

Ruthenium carbonyl cluster complexes containing allenylidene ligands have been known for over 20 years [1], although improved syntheses were described only recently [2,3]. A common precursor of the allenylidene clusters is the alkyne complex $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2CPh_2(OH)\}(CO)_9$ (**1**) which, with $HBF_4 \cdot OMe_2$ rearranges by migration of OH to the cluster to give allenylidene **2** (Scheme 1). Since then, several accounts of their reactivity have appeared [4–6], including studies of their reactions with alkynes [7–9]. Two major types of product were obtained upon reaction of **2** with alkynes, containing either one (**3**) or two alkyne molecules (**4**) [8]. The products are formed by formal insertion of the alkyne into one of the Ru–C σ bonds in **2**. In all cases, the original allenylidene ligand remains attached to the Ru_3 cluster via Ru–C σ or π bonds. While in **3**, the cluster-bonded hydroxy group originally present in **2** is retained, formation of the other product types occurs with concomitant dehydration. This reaction probably involves the terminal H atom from one of the alkynes. In an attempt to simplify the reaction conditions, we have examined the direct reaction between the precursor cluster **1** and the terminal alkyne HC≡CPh in the presence of $HBF_4 \cdot Me_2O$.

2. Results and discussion

The reaction between $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C_2CPh_2(OH)\}(CO)_9$ and HC≡CPh was carried out in dichloromethane by adding $HBF_4 \cdot Me_2O$ to the mixture. A rapid change in colour from pale yellow to dark red ensued. After 5 min, separation of the products by preparative t.l.c. on silica gel gave two fractions. Further work-up gave two complexes identified as $Ru_3(\mu\text{-}H)(\mu_3\text{-}CPh_2CCC{\equiv}CPh)(CO)_9$ (**5**) and $Ru_3\{\mu_3\text{-}CPhCHCC(=CPh_2)CH=CPh\}(\mu\text{-}CO)(CO)_8$ (**6**) by single-crystal X-ray studies (Scheme 2). These complexes were obtained in 13% and 9% yields only, which we could not improve. The nature of other products formed in this reaction remains unknown, a multitude of thin bands being only partially separated on the t.l.c. plate.

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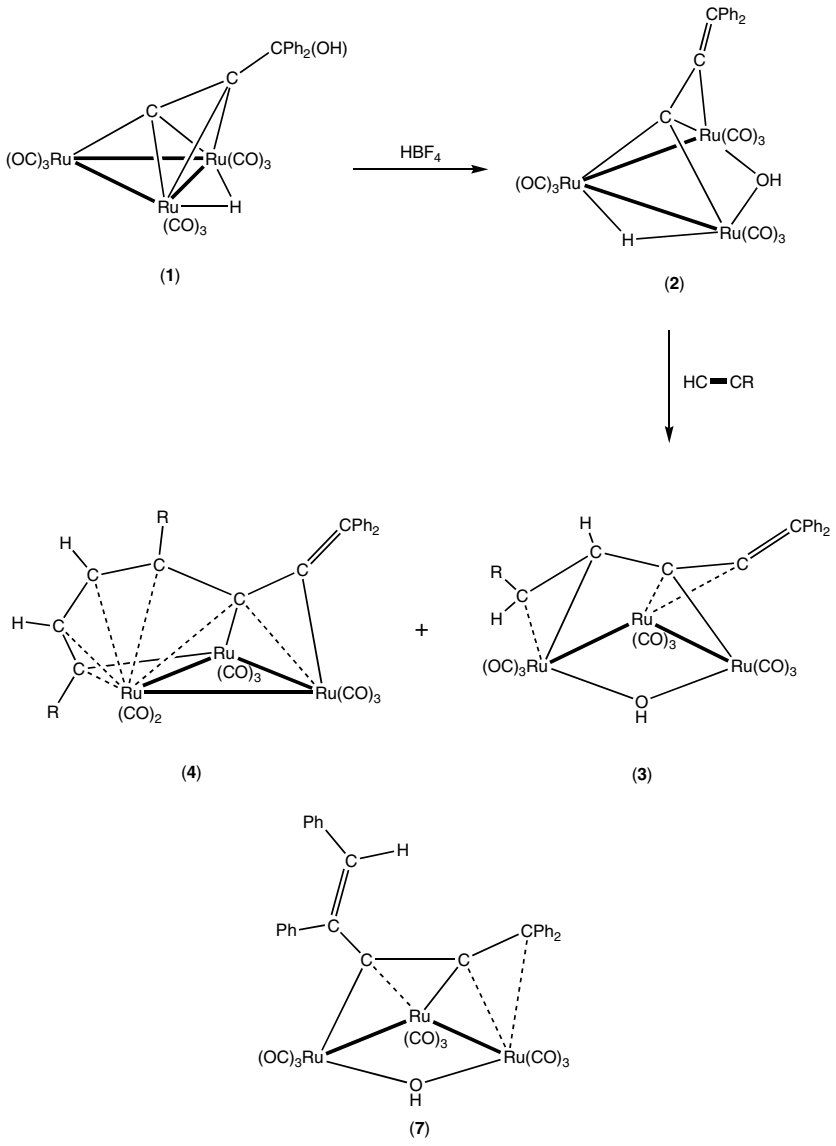


Scheme 1.

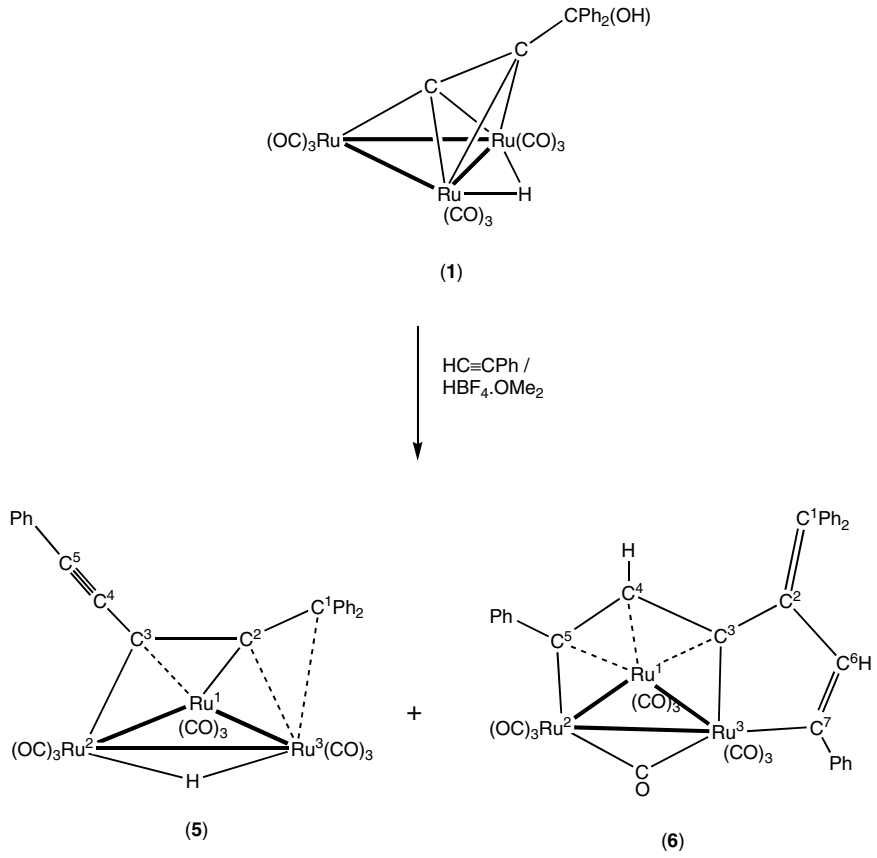
2.1. Molecular structures

Figs. 1 and 2 depict projections of molecules of **5** and **6** oblique to the plane of the closed triangular Ru_3 cluster found in both complexes. Significant bond distances and angles are collected in Table 1.

The cluster-bonded propargyl alcohol of the precursor has undergone loss of water and subsequently added one (**5**) or two (**6**) molecules of phenylacetylene to give the organic ligands found in these two complexes. In **5**, a cluster-bound hydride ligand is present, whereas in **6**, its position is taken by a bridging CO group, the Ru–Ru bonds being the longest in the two Ru_3 units [2.9775(4) Å in **5**, 2.8919(4) Å in **6**].

The organic ligand in **5** formally comprises a phenylethynyl group as a substituent to a μ_3-1,1-diphenylallenyl ligand, namely $CPh_2{=}C{=}C{-}C{\equiv}CPh$. This is attached to the cluster only by the allenyl system, with C(1)–C(2) and C(2)–C(3) being π-bonded to Ru(3) and Ru(1), respectively, while C(3) is also σ-bonded to Ru(2) [C(3)–Ru(2) 2.056(3) Å]. The C(1)–C(2) and C(2)–C(3) distances are 1.384(4) and 1.410(3) Å, respectively, as expected for C=C double bonds coordinated to the Ru atoms. The dimensions of the phenylethynyl substituent are normal, with distances along the C(3)–C(4)–C(5)–C(51) fragment being 1.424(4), 1.197(5) and 1.438(5) Å, respectively. This sequence of atoms is essentially linear with angles at C(4) and C(5) being 176.1(3) and 178.3(3)°.

In **6**, two PhC_2 units have added to the CPh_2CC unit to give a branched chain, which is attached to the Ru_3 cluster by σ bonds from C(5) to Ru(2) [2.113(3) Å] and from C(3) and C(7) to Ru(3) [2.059, 2.133(3) Å], and by a π-allylic interaction of C(3)–C(4)–C(5) with Ru(1)



Scheme 2.

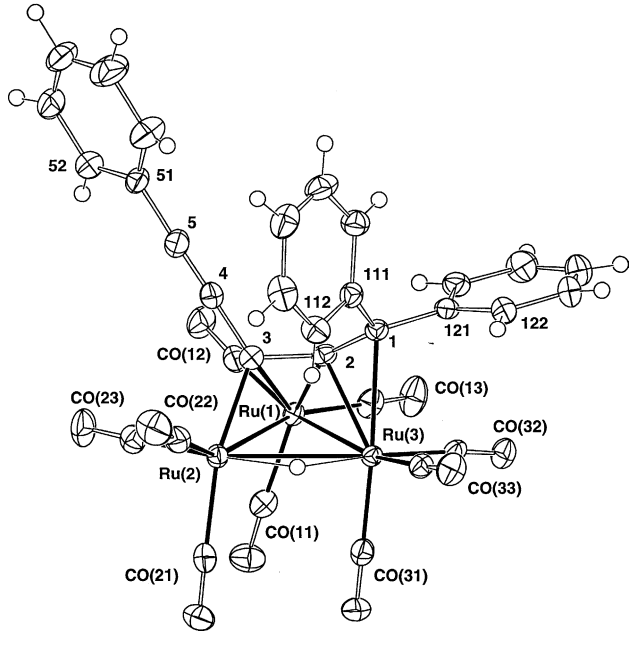


Fig. 1. Plot of a molecule of $Ru_3(\mu\text{-}H)(\mu_3\text{-}CPh_2CCC{\equiv}CPh)(CO)_9$ (**5**).

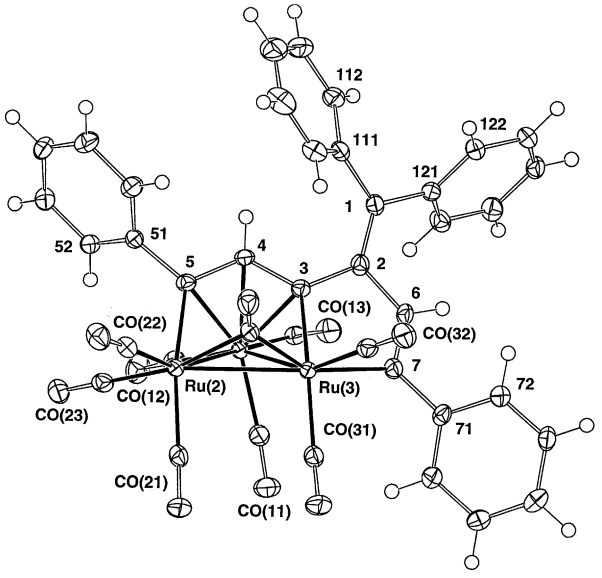


Fig. 2. Plot of a molecule of $Ru_3\{\mu_3\text{-}CPhCHCC(=CPh_2)CH=CPh\}(\mu\text{-}CO)(CO)_8$ (**6**).

[2.274–2.312(4) Å]. Atom C(2) carries the exocyclic diphenylmethylene group [C(1)–C(2) 1.370(5) Å], while there is also a double bond between C(6) and C(7) [1.353(5) Å]. In fact, the Ru(1–3)–C(3–5) fragment is similar to that found in many other complexes, for example, $Ru_3(\mu\text{-}H)(\mu_3\text{-}CHCHCMe)(CO)_9$ [10]. In contrast

Table 1
Selected bond parameters for **5** and **6**

	5	**6**
Bond lengths (Å)		
Ru(1)–Ru(2)	2.7784(4)	2.7616(4)
Ru(1)–Ru(3)	2.7951(3)	2.8019(5)
Ru(2)–Ru(3)	2.9775(4)	2.8919(4)
Ru(1)–C(2)	2.097(3)	
Ru(1)–C(3)	2.232(3)	2.284(4)
Ru(1)–C(4)		2.274(4)
Ru(1)–C(5)		2.312(4)
Ru(2)–C(3)	2.056(3)	
Ru(2)–C(5)		2.113(3)
Ru(3)–C(1)	2.444(3)	
Ru(3)–C(2)	2.222(3)	
Ru(3)–C(3)		2.059(3)
Ru(3)–C(7)		2.133(3)
C(1)–C(2)	1.384(4)	1.370(5)
C(1)–C(111)	1.515(5)	1.483(5)
C(1)–C(121)	1.500(3)	1.496(5)
C(2)–C(3)	1.410(3)	1.492(4)
C(2)–C(6)		1.458(5)
C(3)–C(4)	1.424(4)	1.421(4)
C(4)–C(5)	1.197(5)	1.416(4)
C(5)–C(51)	1.438(5)	1.495(4)
C(6)–C(7)		1.353(5)
C(7)–C(71)		1.468(5)
Bond angles (°)		
C(2)–C(1)–C(111)	114.5(2)	124.4(3)
C(2)–C(1)–C(121)	124.0(2)	118.9(3)
C(111)–C(1)–C(121)	116.2(3)	116.7(3)
C(1)–C(2)–C(3)	134.0(3)	127.4(3)
C(1)–C(2)–C(6)		122.3(6)
C(2)–C(3)–C(4)	120.3(3)	121.4(3)
C(3)–C(2)–C(6)		110.1(3)
C(3)–C(4)–C(5)	176.1(3)	123.7(3)
C(4)–C(5)–C(51)	178.3(3)	113.3(3)

Other data for **6**: Ru(2,3)–C(33) 2.246, 2.025(4) Å; Ru(2,3)–C(33)–O(33) 132.2(2), 142.6(3); C(2)–C(6)–C(7) 119.5(3), C(6)–C(7)–C(71) 121.1(3), C(4)–C(5)–Ru(2) 122.5(2), C(2,4)–C(3)–Ru(3) 114.4, 124.2(2); C(6)–C(7)–Ru(3) 113.4(2), C(3)–Ru(3)–C(7) 78.9(1)°.

to the latter, the additional C(2)–C(6)–C(7) chain which links C(3) to Ru(3) results in replacement of the μ-H ligand by an asymmetric bridging CO group [Ru(2,3)–C(33) 2.246, 2.025(4)] Å.

In the absence of $HBF_4 \cdot Me_2O$, no reaction occurs at r.t. Even with added acid, low yields of products obtained precluded NMR spectroscopic study and consistent elemental analyses were not obtained. The IR spectrum of **5** contained only terminal *v*(CO) bands between 1987 and 2093 cm^{-1}, whereas that of **6** contained both terminal (between 1973 and 2087 cm^{-1}) and a bridging *v*(CO) absorption (at 1872 cm^{-1}). Their negative ion electrospray mass spectra, obtained using NaOMe as an aid to ionisation [11], contained $[M + OMe]^-$ ions, together with fragment ions derived by loss of CO ligands from the molecular ion.

In both cases, the formation of these complexes can be envisaged as an addition of one or two phenylacetylene molecules to a diphenylallenylidene ligand formed by loss of OH from the precursor, probably as water by combination with the cluster-bound H atom. This dehydration is a long-established route to allenylidene complexes, although in the present case we are unable to determine whether this occurs before or after addition of the alkyne. In the case of **5**, direct C–C bond formation has formally occurred, perhaps from an intermediate alkynyl; the resulting structure is similar to one of the isomers (**7**) of the product formed from non-terminal alkynes, such as C_2Ph_2, and **2**, which retains the hydroxy group and has added a proton to the C≡C triple bond. The organic ligand in **6** is derived by unusual insertion of one molecule of phenylethyne into each of the Ru–C(2) and –C(3) bonds to the allenylidene ligand, the resulting $Ph_2C{=}C(CH{=}CPh)CCHCPh$ ligand being attached by an Ru(3)–C(7) σ bond and the more familiar $2\eta^1, \eta^3$ arrangement of the C(3-5) fragment.

3. Conclusions

Generation of an allenylidene ruthenium carbonyl cluster in the presence of an alkyne has given two complexes containing organic ligands formed by combination of the allenylidene with one or two molecules of alkyne. However, only low yields were obtained and our initial objective, to improve the yields of allenylidene-alkyne complexes, has not been achieved. Comparison of the molecular structures of these products with those of other alkyne adducts obtained directly from the allenylidene clusters shows that whereas complexes of type **3**, containing one molecule of alkyne, retain the cluster-bound OH group which bridges a non-bonded Ru···Ru vector, the similar product from the present reaction does not contain any OH ligand, formal replacement by a hydride and closing of the cluster occurring. In the case of the bis(alkyne) adduct, the organic ligand is isomeric with that found in **4**, where linking between the two molecules of alkyne has occurred. Instead, each of the atoms C(2) and C(3) of the original allenylidene ligand are attached to a molecule of the alkyne to give a μ_3-$CPhCHC(=CPh_2)CH{=}CPh$ ligand.

4. Experimental

4.1. General experimental conditions

All reactions were carried out under dry, high purity argon using standard Schlenk techniques. Common solvents were dried, distilled under argon and degassed before use.

4.2. Instrumentation

Infrared spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Spectra in cyclohexane were obtained using a solution cell of 0.5 mm path-length with NaCl windows. ES mass spectra: VG Platform 2. Solutions in MeOH, containing NaOMe as an aid to ionisation [11], were directly infused into the instrument.

4.3. Reagents

The complex $Ru_3(\mu\text{-H})\{\mu_3\text{-}C_2CPh_2(OH)\}(CO)_9$ (**1**) was prepared as previously described [2].

4.4. Reaction of $Ru_3(\mu\text{-H})\{\mu_3\text{-}C_2CPh_2(OH)\}(CO)_9$ with $HC{\equiv}CPh$ and $HBF_4 \cdot Me_2O$

Three drops of $HBF_4 \cdot Me_2O$ were added to a pale yellow solution of $Ru_3(\mu\text{-H})\{\mu_3\text{-}C_2CPh_2(OH)\}(CO)_9$ (103 mg, 0.135 mmol) and $HC{\equiv}CPh$ (28 mg, 0.27 mmol) in CH_2Cl_2 (5 ml), whereupon the colour changed immediately to red. After stirring at r.t. for 5 min, solvent was removed and the residue separated by preparative t.l.c. (silica gel, hexane eluant) into two bands. The first yellow band (R_f 0.60) contained $Ru_3(\mu\text{-H})(\mu_3\text{-}CPh_2CCC{\equiv}CPh)(CO)_9$ (**5**) (15 mg, 13%), obtained as yellow crystals from pentane. Anal. Calcd. ($C_{32}H_6O_9Ru_3$): M, 849. IR: ν(CO) 2093m, 2070m, 2045s, 2027m, 2024m, 2011m, 2003w, 1993m, 1987w cm^{-1}. ES MS (MeOH + NaOMe, negative ion, m/z): 880, $[M + OMe]^-$; 820–652, $[M - H - nCO]^-$ ($n = 1$–7). The second, red band (R_f 0.55) contained $Ru_3\{\mu_3\text{-}CPhCHCC(=CPh_2)CH=CPh\}(\mu\text{-CO})(CO)_8$ (**6**) (11 mg, 9%) which formed red crystals (MeOH). Anal. Calcd. ($C_{40}H_{22}O_9Ru_3$): M, 951. IR: ν(CO) 2087m, 2053m, 2044s, 2027m, 2021w, 2007m, 1996w, 1973w (br), 1872m (br) cm^{-1}. ES MS (MeOH + NaOMe), negative ion, m/z): 982, $[M + OMe]^-$; 895–755, $[M - nCO]^-$ ($n = 2$–7); 681, 653, 625, $[M - nCO - HC_2Ph]^-$ ($n = 6$–8).

4.5. Structure determinations

Full spheres of diffraction data to $2\theta_{max} = 58°$ were measured at ca. 153 K using a Bruker AXS CCD area-detector instrument. N_{tot} reflections were merged to N unique (R_{int} quoted) after "empirical"/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being used in the full matrix least squares refinement. All data were measured using monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å. Anisotropic thermal parameter forms were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ were refined for **5** and constrained at estimated values in **6**. Conventional residuals R, R_w on $|F|$ are given [weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$]. Neutral atom complex scattering factors were used; computation used the XTAL 3.7 program system [12]. Pertinent results are given in the figures (which show non-hydrogen atoms with 50% probability amplitude displacement ellipsoids and hydrogen atoms with arbitrary radii of 0.1 Å) and tables.

(**5**). $Ru_3(\mu\text{-H})(\mu_3\text{-}CPh_2CCC{\equiv}CPh)(CO)_9{\equiv}C_{32}H_{16}O_9Ru_3$, $M = 847.68$. Monoclinic, space group $P2_1/n$, $a = 19.078(3)$, $b = 9.018(1)$, $c = 19.782(3)$ Å, $\beta = 117.792(2)°$, $V = 3011$ Å^3, $Z = 4$. $D_c = 1.87_0$ g cm^{-3}, μ(Mo-Kα) = 15.4 cm^{-1}, $T_{min/max} = 0.78$. Crystal size $0.15 \times 0.15 \times 0.12$ mm. $N_{tot} = 35138$, $N = 7646$ ($R_{int} = 0.030$), $N_o = 6398$. $R = 0.029$, $R_w = 0.034$.

(**6**). $Ru_3\{\mu_3\text{-}CPhCHCC(=CPh_2)CH=CPh\}(\mu\text{-CO})(CO)_8{\equiv}C_{40}H_{22}O_9Ru_3$, $M = 949.82$. Triclinic, space group $P\bar{1}$, $a = 10.294(1)$, $b = 10.899(1)$, $c = 15.929(2)$ Å, $\alpha = 96.544(1)$, $\beta = 90.397(1)$, $\gamma = 102.524(1)°$, $V = 1732$ Å^3, $Z = 2$. $D_c = 1.82_1$ g cm^{-3}, μ(Mo-Kα) = 13.5 cm^{-1}, $T_{min/max} = 0.88$. Crystal size $0.15 \times 0.15 \times 0.12$ mm. $N_{tot} = 20544$, $N = 8569$ ($R_{int} = 0.025$), $N_o = 6697$. $R = 0.035$, $R_w = 0.037$.

5. Supplementary material

Full details of the structure determination (except structure factors) for **5** and **6** have been deposited with the Cambridge Crystallographic Data Centre as CCDC 220159 and 220160, 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 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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