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Reactions of Ru(Cp*) complexes with P(*o*-tolyl)$_3$

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Abstract

Reaction of [Ru(Cp*)(CH$_3$CN)$_3$](PF$_6$) with P(*o*-tolyl)$_3$ affords [Ru(Cp*){(η^6-*o*-tolyl)P(*o*-tolyl)$_2$}](PF$_6$) (**4**) in which the P-atom is not coordinated to the metal. The solid-state structure of **4** has been determined. A related reaction with P(*p*-tolyl)$_3$ reveals a small quantity [Ru(Cp*){(η^6-*p*-tolyl)P(*o*-tolyl)$_2$}](PF$_6$), in solution, but mostly the expected bis-phosphine complex. Reaction of the Ru(IV) dication, [Ru(Cp*)(η^3-PhCHCHCH$_2$)(DMF)$_2$](PF$_6$)$_2$, with P(*o*-tolyl)$_3$ gives a mixture of the phosphonium salt, C$_6$H$_5$CH=CHCH$_2$P(*o*-tolyl)$_3$ (**9**) and the dication [Ru(Cp*)(η^6-C$_6$H$_5$CH=CHCH$_2$P(*o*-tolyl)$_3$)](PF$_6$)$_2$ (**10**). Salt **9** forms via attack of the P-atom on the allyl ligand. The latter product results from complexation of **9** via the phenyl group of the former allyl ligand. It would seem that the sterically demanding P(*o*-tolyl)$_3$ ligand is not readily compatible with the Ru(Cp*) fragment, in either the +2 or +4 oxidation state. Detailed NMR studies are reported.

Keywords: Ru(η^6-*o*-tolyl)P(*o*-tolyl)$_2$; NMR; X-ray; P-allylation

1. Introduction

A variety of complexes of ruthenium continue to attract interest both for their organometallic and catalytic chemistry [1–14]. The now readily available Ru(II) salts, [Ru(Cp or Cp*)(CH$_3$CN)$_3$](PF$_6$) [4e], have been widely employed as starting materials in the synthesis, study and catalytic reactions of an increasing number of half sandwich complexes. Equally popular are the Ru–η^6-arene complexes [15–17] and/or complexes that contain tertiary phosphine ligands [1,2,5,6,8,14–17].

The ease with which [Ru(Cp or Cp*)(CH$_3$CN)$_3$](PF$_6$) forms coordinatively unsaturated complexes, and subsequently reacts with organic arenes, has led to the observation of a relatively large number of cationic [Ru(Cp or Cp*)(η^6-arene)](anion) complex salts, where the arene might be a solvent molecule or an organic reagent [18a,18b,18e]. For reactions involving EAr$_3$ ligands, with E = As, Sb or Bi, an aryl moiety on the E-atom can compete with the electron pair on the E-atom for the ruthenium center [19]. In a rare example (not involving a Cp ring), one aromatic ring of Binap has been shown to be capable of an η^6 bonding mode [18c]. Normally, such arene complexes of Ru(II) do not readily dissociate the arene, although there are indications in the literature that this reaction is likely in acetonitrile solution [18b]. There are not many reports on Ru(II) arene complexes where the η^6-arene contains strongly electron withdrawing groups [18d], supporting the idea that the relative stability of such complexes may depend markedly on the arene and/or the remaining ligands.

We report here some unexpected coordination behavior involving the Ru(Cp*) fragment and, primarily, the tris *o*, *m* and *p*-tolyl phosphine compounds, **1**–**3**, respectively.

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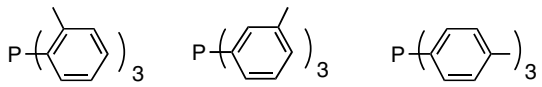
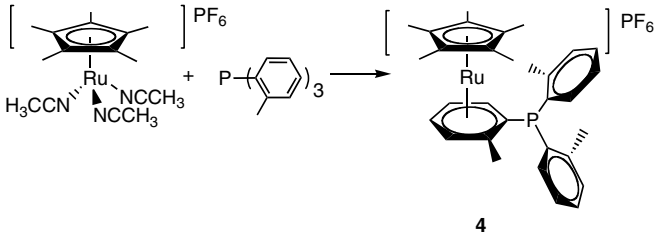


1 2 3

2. Results and discussion

Monitoring the reaction of $[Ru(Cp^*)(CH_3CN)_3](PF_6)$ with 2 equiv. of *o*-tolyl phosphine, **1**, via NMR suggested that $[Ru(Cp^*)\{(\eta^6\text{-}o\text{-tolyl})P(o\text{-tolyl})_2\}](PF_6)$ (**4**) was formed, in addition to ca. 1 equiv. of unreacted phosphine. Complex **4** could be isolated in good yield (see Eq. (1)) from the reaction mixture as a yellow powder.



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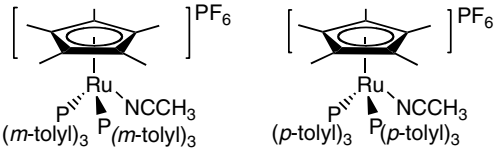
(1)

The ^{31}P NMR spectrum reveals a singlet at $\delta = -36.7$. This chemical shift appears at an unusually low frequency, and provides an indication of the formation of the unexpected product. Fig. 1 shows this signal (as an inset) as well as the four well-resolved proton resonances of the complexed *o*-tolyl group ($\delta = 5.40$, 5.69, 5.74 and 5.84). Fig. 2 shows sections of the one-bond (left) and ^{13}C, ^{1}H long-range (right) correlations, from which one can assign the four ^{13}CH and the two fully substituted carbon signals of the complexed arene moiety at $\delta > 100$ ppm. These ^{1}H and ^{13}C absorptions are all shifted to relatively low frequency, in keeping with the literature [20]. There are three non-equivalent methyl resonances in both the ^{1}H and ^{13}C spectra and these can be assigned using Overhauser methods.

Crystals suitable for X-ray diffraction have been obtained and Fig. 3 shows two views of the cation. A selection of bond lengths and bond angles is given in the caption to the figure. The immediate coordination sphere of the metal contains the Cp^* and one η^6-*o*-tolyl group. One of the remaining two *o*-tolyl groups is situated away from the metal, below the plane of the complexed arene moiety thereby minimizing possible steric effects between the $P(o\text{-tolyl})_2$ group and the Cp^*. As expected the Ru–C(η^6-*o*-tolyl) separations for C11, C12 and C16 are somewhat longer than for C13–C15, presumably due to the steric effects associated with the $P(o\text{-tolyl})_2$ group. These Ru–C bond lengths are in the region expected for Ru–arene complexes [21–31]. The five Ru–C(Cp^*) separations are all normal and not significantly different.

The analogous reaction with 2 equiv. of the *meta* tolyl phosphine, **2**, gave the expected bis-phosphine product, **5**, $\delta\ ^{31}P = 42.7$. A related reaction with the *p*-tolyl phosphine, **3**, gave mostly **6**, $\delta\ ^{31}P = 41.2$ as expected.



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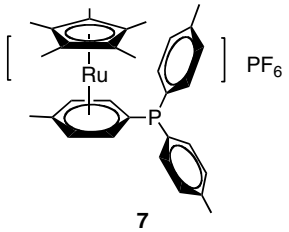

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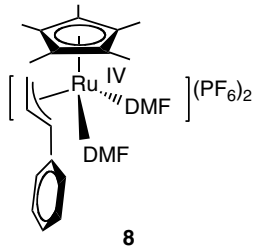
However, a small amount (ca. 4%) of the (η^6-*p*-tolyl), salt, **7**, $\delta\ ^{31}P = 25.9$ could be observed in solution. Support for this structure comes from both the ^{1}H (see Fig. 4) and ^{13}C NMR spectra from which the characteristic low frequency chemical shifts of the complexed arene, **7** are readily measured. The similarity in parts of the ^{1}H spectrum of **4** and **7** is coincidental.[1] Obviously, the difference in stability between **6** and **7** is not so large as to prevent the formation of a readily detectable amount of the somewhat surprising arene complex, **7**.



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We have recently prepared the Ru(IV) dicationic allyl complex **8** [32]. This salt is an interesting catalytic precursor in a Friedel-Crafts type coupling reaction [32]. Given the ease with which the DMF molecules can be replaced, the salt **8** was allowed to react with 2 equiv. of $P(o\text{-tolyl})_3$ in acetone solution at room temperature. The crude isolated solid product, which was washed with ether to remove excess unreacted phosphine, proved to be a mixture of two components, **9** and **10**, in a ratio of ca. two to one (see Scheme 1). The two phosphorus chemical

[1] The spin system for the four protons of the coordinated *p*-tolyl ring is AA′M, M′X ($X = {}^{31}P$), so that it will never be first order, and the appearance of a triplet and a doublet for **7** is somewhat deceptive. The four protons of the coordinated *o*-tolyl ring can afford a first order spectrum.

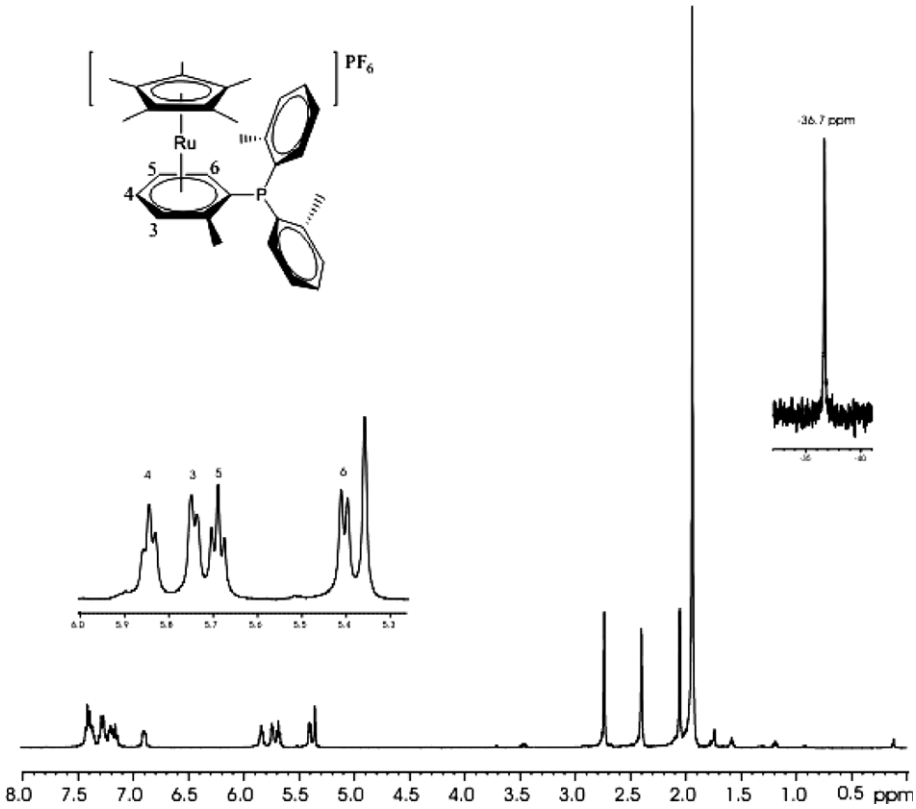


Fig. 1. The complete ^{1}H NMR spectrum for **4** (bottom trace) showing the non-equivalent *o*-tolyl methyl groups and (top left) the expansion of the region containing the arene protons 3–6, plus (top right) the ^{31}P signal. Once the arene ring is complexed, the ^{31}P spin–spin coupling to the ring protons is reduced in magnitude and often not resolved (CD_2Cl_2, 500 MHz).

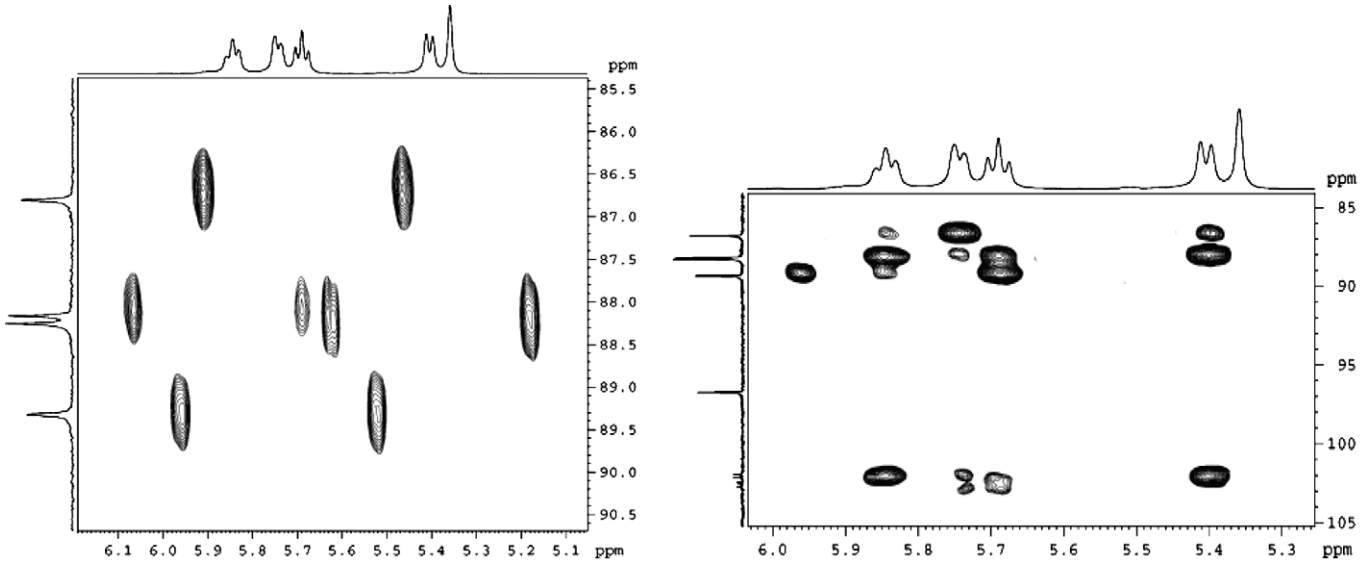
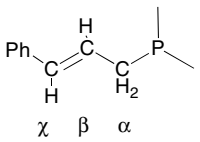


Fig. 2. One-bond correlation (left) showing the four ^{13}C chemical shifts for the CH resonances in the complexed arene and long-range correlation (right) indicating the positions of the two arene *ipso*-carbons for salt **4**, close to 102 ppm (CD_2Cl_2, 125 MHz).

shifts are found at $\delta = 26.1$ and $\delta = 24.2$ (see Fig. 5) for the major and minor components, respectively. In the ^{1}H NMR spectrum of the major species, the four protons of the allyl fragment appear as three resonances at (a) $\delta = 7.05$ (Ph─C*H*═) with $^{3}J_{HH} = 15.4$ Hz and $^{3}J_{PH} = 4.3$ Hz, (b) $\delta = 6.02$ ppm (═C*H*CH_2, as a complex multiplet strongly overlapped with the complexed arene resonances of **10**) and (c) $\delta = 4.77$ (PCH_2) with $^{2}J_{PH} = 14.0$ Hz and $^{3}J_{HH} = 7.5$ Hz. The first two chemical shifts plus the 15.4 Hz $^{3}J_{HH}$ coupling are in agreement

with a *trans* olefin fragment. The presence of the 14 Hz ^{31}P coupling to the α-carbon was proven by a ^{31}P, ^{1}H correlation.



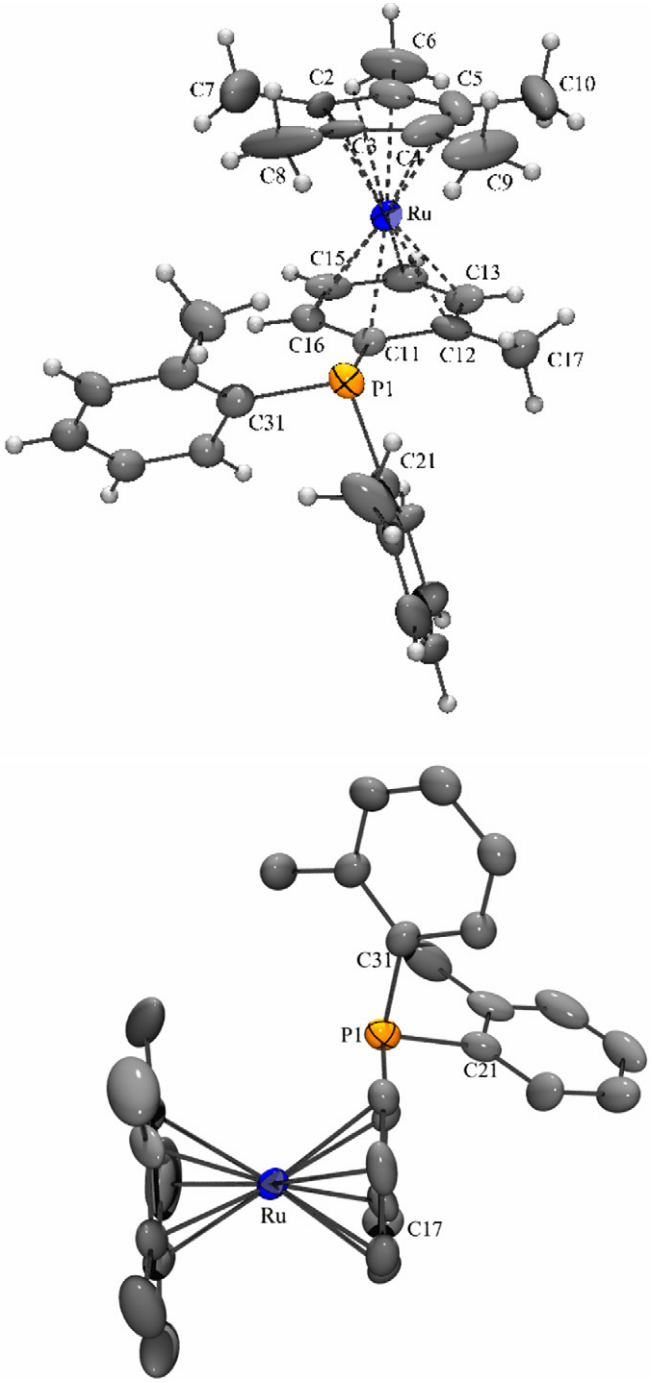


Fig. 3. ORTEP views of the cation of salt **4** showing 50% probability ellipsoids. Ru–C(1), 2.172(6), Ru–C(2), 2.188(5), Ru–C(3), 2.180(6), Ru–C(4), 2.174(6), Ru–C(5), 2.184(7), Ru–C(11), 2.254(5), Ru–C(12), 2.222(6), Ru–C(13), 2.207(5), Ru–C(14), 2.204(6), Ru–C(15), 2.199(6), Ru–C(16), 2.216(6), Ru-center of the cp*,1.819(6), Ru-center of the complexed arene, 1.705(6), P(1)–C(11), 1.846(5) P(1)–C(21), 1.825(6), P(1)–C(31), 1.844(7), C(21)–P(1)–C(31), 99.2(3) C(21)–P(1)–C(11), 101.5(3), C(31)–P(1)–C(11), 101.9(3).

The analogous proton allyl signals for the minor product, **10**, were found at (a) $\delta = 6.92$ (Ph—C*H*= $^{3}J_{HH} = 14.9$ Hz and $^{4}J_{PH} = 4.0$ Hz), (b) $\delta = 6.30$ (=C*H*CH_2 $^{3}J_{HH} = 14.9$, $^{3}J_{HH} = 7.3$ and $^{3}J_{PH} = 4.0$ Hz) and (c) $\delta = 4.92$ (PCH_2 $^{3}J_{PH} = 14.1$ Hz and $^{3}J_{HH} = 7.3$ Hz). Once again the presence of ^{31}P coupling was shown by a ^{31}P, ^{1}H correlation, and the two relatively high frequency proton chemical shifts plus the 14.9 Hz $^{3}J_{HH}$ coupling are in agreement with a *trans* olefin fragment.

In **10** one finds a rather strongly second order group of multiplets between 5.6 ppm and 5.9 ppm, which are assigned as the complexed arene proton signals, whereas the Ph protons of the allyl fragment in **9** are found at routine positions.

The PCH_2 proton resonances in both **9** and **10** can be correlated to *aliphatic* $^{13}CH_2$ signals at $\delta = 29.3$ and $\delta = 29.2$, for the major and minor products, respectively. Both ^{13}C resonances show relatively large $^{1}J_{P,C}$ values of ca. 52 Hz which are typical for sp^3 hybridized carbons attached to a quaternary P-atom [33]. We note that $^{1}J_{P,C}$ in the known phosphonium salt, $Ph_3PCH_2CH{=}CH_2$, at 49.7 Hz and $^{2}J_{PH}$ at 14.9 Hz [33b] are in excellent agreement with our measured values.

Strong evidence in support of the (η^6-C_6H_5) ligand in **10** comes from the ^{13}C NMR results. One finds three ^{13}C NMR CH signals for the complexed arene of **10** at the expected low frequencies: $\delta = 85.1$ (*ortho*) $\delta = 87.3$ (*meta*) and at $\delta = 87.12$ (*para*) in the ratio 2:2:1 respectively. The olefinic carbons of the *trans* double bonds in both **9** and **10** are found in a typical region for such sp^2 carbons.

For both **9** and **10** one observes 3 equiv. methyl resonances in both the ^{1}H and ^{13}C spectra, thereby completing the solution structure proof. We note that there is a report of a complexed ammonium ion, $CH_2{=}CHCH_2{-}NEt_3^+$, derived from the attack of triethylamine, as a nucleophile, on a Ru(IV) allyl complex [34].

To investigate whether other bulky PR_3 donors might also chose to avoid P-complexation, we studied related reactions using the phosphite ligands, **11** and **12**. Reaction of $[Ru(Cp^*)(CH_3CN)_3](PF_6)$ with 2.1 equiv. of tris *ortho* xenyl phosphite, **11**, leads to predominantly the mono-phosphite product. However, a series of weak signals in the ^{1}H spectrum in the region between 5.4 ppm and 6.2 ppm suggest the presence of a small proportion, less than 5%, of arene complexed species. Reaction of $[Ru(Cp^*)(CH_3CN)_3](PF_6)$ with 1.1 equiv. of the phosphite **12** resulted in the mono-phosphite complex, $Ru(Cp^*)$-(**12**)$(CH_3CN)_2](PF_6)$ (**14**) with *no trace* of arene complexed species observable in the ^{1}H NMR spectrum. Product **13**, $Ru(Cp^*)$ (**11**)$(CH_3CN)_2](PF_6)$, could be isolated by layer-

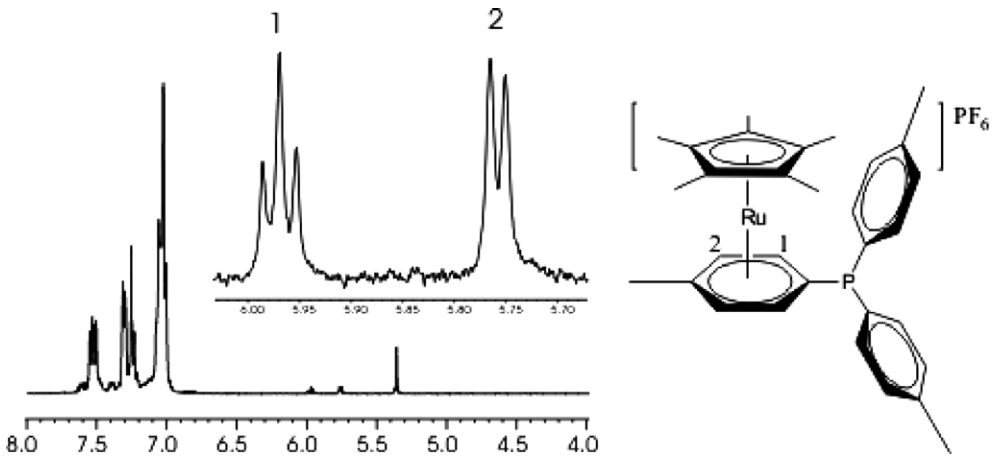
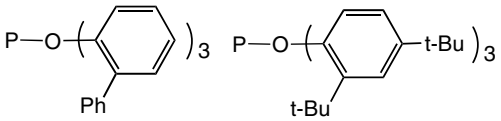


Fig. 4. Expansion of the region of the ^{1}H spectrum between 5.7 ppm and 6 ppm showing the arene resonances for the small quantity of the η^6-complex arising from the *p*-tolyl phosphine (CD_2Cl_2, 500 MHz).

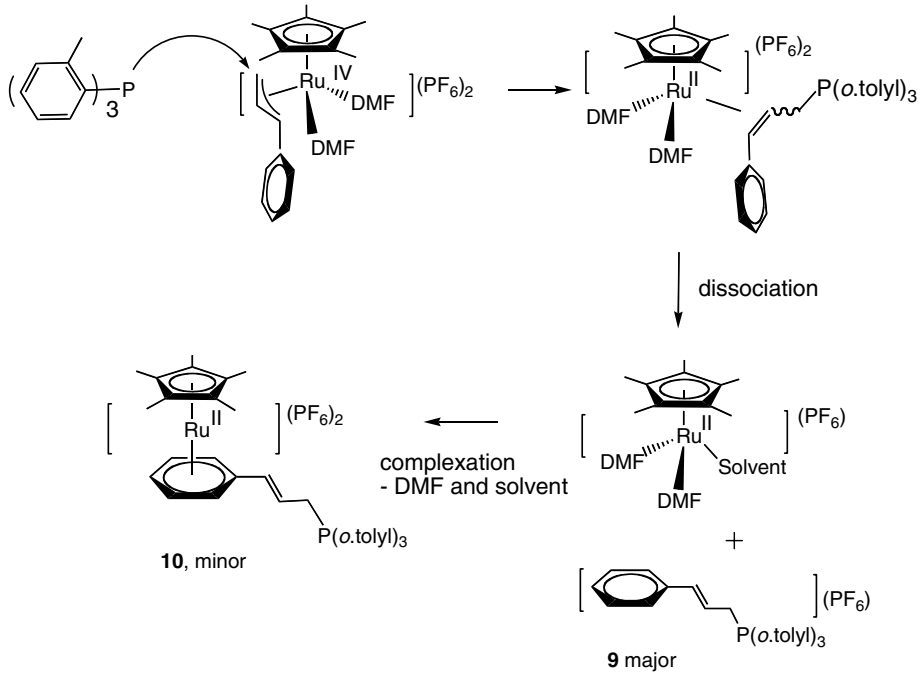
ing an acetone solution of the crude product with diethyl ether and cooling to −40 °C. Presumably the oxygen atoms of these phosphite ligands provide enough flexibility such that the three P-substituents can be comfortably placed in a position remote from the Cp^* ring.



It is interesting that the most intense set of peaks in the MALDI mass spectra of **13** and **14** correspond to Ru(Cp^*) (**11**), $m/z = 775$, and Ru(Cp^*) (**12**), $m/z = 883.5$, respectively, i.e., the loss of the two acetonitrile molecules. For **14**, these are more or less the only signals between *m*/*e* 600–900. Moreover, the strongest signals in the mass spectra of the isomeric bis-phosphine salts **5** and **6**, correspond to the cation of **7**, i.e., "Ru(Cp^*)(phosphine)". Although these mass spectra do not prove structure, it seems likely that these are the 18e η^6-arene cations. All of the NMR and mass spectral observations support the idea that P-coordination will not always result in the most stable species.

3. Conclusions

The solution NMR data for **9** and **10** support the view that the reaction of the bulky phosphine **1** with the Ru(IV) allyl, **8** does not lead to a stable routine P-coordinated



Scheme 1.

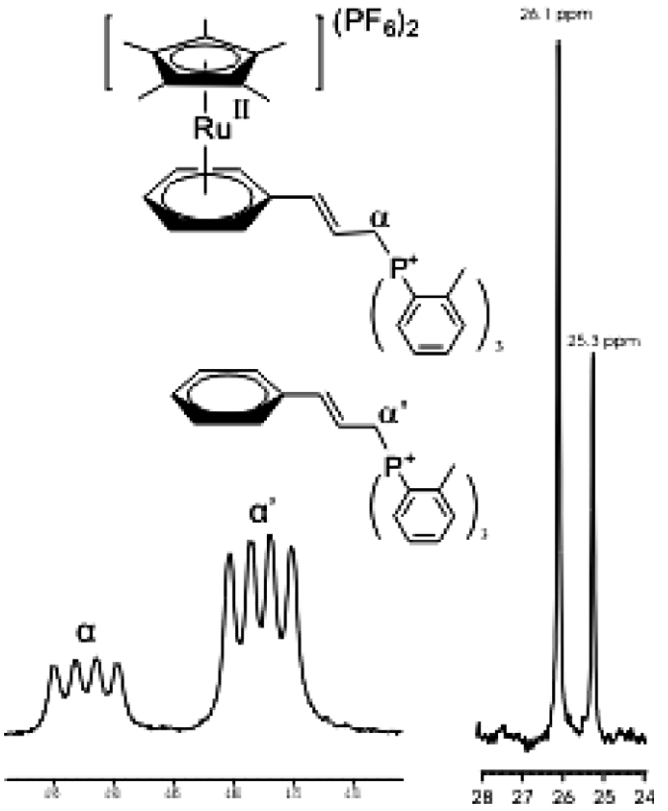


Fig. 5. A section of the ^{1}H NMR spectrum showing the two aliphatic PCH_2 resonances for **9** and **10** (left) (acetone-d_6, 400 MHz) plus the two ^{31}P resonances (right) (CD_2Cl_2, 202 MHz). The observed doublet of doublets stems from $^3J(^{31}P,^1H)$ and $^3J(^1H,^1H)$.

phosphine complex. Whether inter- or intra-molecular, the P-atom prefers to attack the Ru(IV) allyl complex at a terminal allyl carbon center, with subsequent reductive elimination to afford a Ru(II) species. The phosphonium salt, **9**, which forms, is relatively stable, but then so is the Ru(II) η^6-$C_6H_5CH{=}CHCH_2P(o\text{-tolyl})_3$ arene complex, **10**. It would seem that, just as found for the reaction leading to **4**, the sterically demanding ligand **1**, is not readily compatible with the Ru(Cp*) fragment, in either the +2 or +4 oxidation state. The bulky phosphite ligands **11** and **12**, behave in a conventional manner to form **13** and **14**, although there is a hint that some very modest quantities of arene complexes may be present using **11**.

4. Experimental

All reactions and manipulations were performed under an N_2 atmosphere using standard Schlenk techniques. The solvents and reagents were dried and distilled using standard procedures and stored under nitrogen. NMR spectra were recorded with Bruker DPX-300, 400, and 500 MHz spectrometers. For salts **4**–**7**, **9** and **10**, the spectra were measured at 273 K to avoid decomposition. Chemical shifts are given in ppm; coupling constants (J) in Hertz. Elemental analyses and mass spectroscopic studies [35] were performed at ETHZ.

The ^{31}P resonance for the PF_6 anion, although not noted in the preparative sections, was found for each salt, at $\delta = -144.4$ as a sharp septet.

Crystallography. Air stable, yellow crystals of **4**, suitable for X-ray diffraction were obtained by crystallization from dichloromethane/diethyl ether solution. A crystal of **4** was mounted on a Bruker APEX diffractometer, equipped with a CCD detector, and cooled, using a cold nitrogen stream, to 150(2) K for the data collection. The space group was determined from the systematic absences, while the cell constants were refined, at the end of the data collection, with the data reduction software SAINT [36]. The experimental conditions for the data collections, crystallographic and other relevant data are listed in Table 1 and in Supplementary Material (as a cif file).

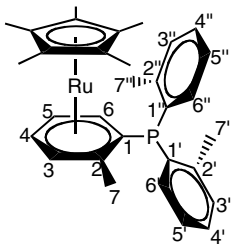
The collected intensities were corrected for Lorentz and polarization factors [36], and empirically for absorption using the SADABS program [37]. The structure was solved by direct and Fourier methods and refined by full matrix least squares [38], minimizing the function $[\sum w(F_o^2 - (1/k)F_c^2)^2]$ and using anisotropic displacement parameters for all atoms, except the hydrogens. The contribution of the hydrogen atoms, in their calculated position was included in the refinement using a riding model ($B(H) = aB(C_{bonded})$ (Å^2), where $a = 1.4$ for the hydrogen atoms of the methyl groups and $a = 1.2$ for the others). No extinction correction was deemed necessary. Upon convergence the final Fourier difference map showed no significant peaks. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were

Table 1
X-ray crystallographic data for compound **4**

Molecular formula	$C_{31}H_{36}F_6P_2Ru$
Molecular weight	685.61
T (K)	150 (2)
Diffractometer	Bruker APEX CCD
Crystal system	Orthorhombic
Space group (no.)	$P2_12_12_1(19)$
a (Å)	11.390 (2)
b (Å)	12.149 (2)
c (Å)	21.631 (3)
V (Å^3)	2993.4 (7)
Z	4
$d_{(calc)}$ (g cm^{-3})	1.521
μ (cm^{-1})	6.88
Transmission	0.79915–1.00000
Radiation	Mo Kα (graphite monochromated)
λ (Å)	0.71073
θ Range (°)	$1.92 < \theta < 24.49$
Data collected	19728
Unique data	4954
Data observed (n_o) $[\lvert F_o\rvert^2 > 2.0\sigma(\lvert F\rvert^2)]$	4593
Parameters refined (n_v)	361
R_{int}	0.0321
R (observed reflections)	0.0437
R_w^2 (observed reflections)	0.0931
GoF	1.142
Flack's parameter	0.06(5)

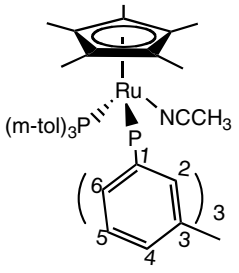
$R = \sum(|F_o - (1/k)F_c|)/\sum|F_o|$ $R_w^2 = [\sum w(F_o^2 - (1/k)F_c^2)^2/\sum w|F_o^2|^2]$.
$\mathrm{GOF} = [\sum_w(F_o^2 - (1/k)F_c^2)^2/(n_o - n_v)]^{1/2}$.

taken from the literature [39]. The handedness of the structure was confirmed by refining the Flack's parameter [40]. All calculations were carried out by using the PC version of the programs: WINGX [41], SHELX-97 [38] and ORTEP [42].

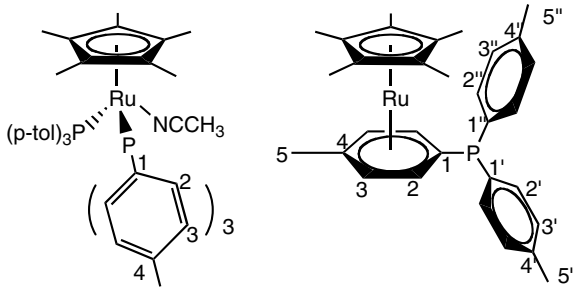


[RuCp(η⁶-o-tol)P(o-tol)₂]PF₆ (**4**)*. A solution of P(*o*-tol)$_3$ (157.3 mg, 0.517 mmol) in 3 mL acetone was added to a solution of [RuCp*(CH$_3$CN)$_3$]PF$_6$ (108.6 mg, 0.215 mmol) in 3 mL acetone. The yellow reaction mixture was stirred for 2 h at room temperature after which time the solvent was removed under vacuum. The resulting crude product was washed with diethyl ether to afford a pale yellow solid. Yield 125.6 mg (85%). Crystals suitable for diffraction were obtained by layering a dichloromethane solution of the crude product with diethyl ether.

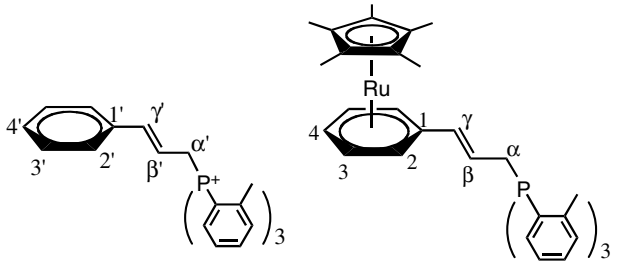
^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 0 °C) δ (ppm): 1.95 (s, 15H, C$_5$Me$_5$), 2.10 (s, 3H, Me7), 2.39 (s, 3H, Me7′), 2.74 (s, 3H, Me7″) 5.40 (d, $J = 5.8$ Hz, 1H, H6), 5.69 (t, $J = 5.8$ Hz, 1H, H5), 5.74 (d, $J = 5.4$ Hz, 1H, H3), 5.84 (t, $J = 5.4$. Hz, 1H, H4), 6.90 (dd, $J = 7.23$, 3.65 Hz, 1H, H6′), 7.16 (m, 1H, H5′), 7.21 (m, 1H, H3′), 7.26 (m, 1H, H6″), 7.29 (m, 1H, H4′), 7.38 (m, 1H, H4″), 7.41 (m, 1H, H3″), 7.42 (m, 1H, H5″). ^{13}C{^{1}H}NMR (125 MHz, CD$_2$Cl$_2$, 0 °C) δ (ppm): 10.6 (C$_5$*Me*$_5$), 18.8 (Me7), 21.4 (Me7′), 22.2 (Me7″), 86.8 (C5), 88.2 (C3), 88.3 (C6), 89.3 (C4), 96.7 (*C*$_5$Me$_5$), 102.0 (C2), 102.6 (C1), 126.9 (C3′), 127.4 (C6″), 129.9 (C4′), 130.0 (C2″), 131.2 (C5′), 131.5 (C3″), 137.8 (C4″), 142.3 (C1′), 148.0 (C1″). ^{31}P{^{1}H}NMR (202 MHz, CD$_2$Cl$_2$, 0 °C) δ (ppm): −36.7. Elemental Anal. Calc. for C$_{31}$H$_{36}$F$_6$P$_2$Ru: C, 54.31; H, 5.29. Found: C, 53.55; H, 5.34%. Mass spectrometry: *m*/*z*: 541.1 [*M*$^+$].



[RuCp(P(m-tol)$_3$)$_2$CH$_3$CN]PF$_6$ (**5**)*. A solution of P(*m*-tol)$_3$ (97.0 mg, 0.319 mmol) in 2 mL acetone was added to a solution of [RuCp*(CH$_3$CN)$_3$]PF$_6$ (80.0 mg, 0.159 mmol) in 3 mL acetone. The yellow reaction mixture was stirred for 2 h at room temperature after which time the solvent was removed under vacuum. The resulting crude product was washed with diethyl ether to afford a yellow solid. Yield: 76.5 mg (47%). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 0 °C) δ (ppm): 1.16 (s, 15H, C$_5$Me$_5$), 2.20 (s, 18H, 6Me), 2.72 (s, 3H, MeCN), 6.99 (m, 6H, H2), 7.03 (m, 6H, H6), 7.11 (m, 6H, H5), 7.14 (m, 6H, H4). ^{13}C{^{1}H}NMR (125 MHz, CD$_2$Cl$_2$, 0 °C) δ (ppm): 5.7 (*Me*CN), 9.8 (C$_5$*Me*$_5$), 21.9 (6Me), 93.4 (*C*$_5$Me$_5$), 128.0 (C5), 129.8 (Me*C*N), 130.8 (C4), 131.3 (C6), 134.5 (C2), 135.2 (C1), 137.8 (C3). ^{31}P{^{1}H}NMR (202 MHz, CD$_2$Cl$_2$, 0 °C) δ (ppm): 42.7.



[RuCp(P(p-tol)$_3$)$_2$CH$_3$CN]PF$_6$ (**6**) and [RuCp*(η⁶-p-tol)P(p-tol)$_2$]PF$_6$ (**7**)*. A solution of P(*p*-tol)$_3$ (114.8 mg, 0.377 mmol) in 3 mL acetone was added to a solution of [RuCp*(CH$_3$CN)$_3$]PF$_6$ (90.6 mg, 0.179 mmol) in 3 mL acetone. The yellow reaction mixture was stirred for 2 h at room temperature after which time the solvent was removed under vacuum. The resulting crude product was washed with diethyl ether to afford a yellow solid that was found to be a mixture of **6** and **7**. Yield: 151.2 mg. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 0 °C) δ (ppm): 1.15 (s, 15H, C$_5$Me$_5$, **6**), 1.92 (s, 15H, C$_5$Me$_5$, **7**), 2.30 (s, 3H, H7, **7**), 2.37 (s, 18H, 6Me, **6**), 2.64 (s, 3H, MeCN, **6**), 5.76 (d, $J = 6.4$ Hz, 2H, H3, **7**), 5.97 (dd, $J_{PH} = 6.7$ Hz, $J = 6.4$ Hz, 2H, H2, **7**), 7.02 (m, 12H, H3, **6**), 7.06 (m, 12H, H2, **6**). ^{13}C{^{1}H}NMR (125 MHz, CD$_2$Cl$_2$, 0 °C) δ (ppm): 5.6 (*Me*CN, **6**), 9.6 (C$_5$*Me*$_5$, **6**), 10.9 (C$_5$*Me*$_5$, **7**), 18.4 (Me, C5, **7**), 21.3 (6Me, **6**), 87.9 (C2, **7**), 88.3 (C3, **7**), 92.8 (*C*$_5$Me$_5$), 102.0 (C4, **7**), 128.8 (C3, **6**), 129.5 (Me*C*N, **6**), 132.3 (C1, **6**), 134.1 (C2, **6**), 140.6 (C4, **6**). ^{31}P{^{1}H}NMR(202 MHz, CD$_2$Cl$_2$, 0 °C) δ (ppm): 41.2 (**6**), 25.9 (**7**). Elemental Anal. Calc. for 96% C$_{54}$H$_{60}$NF$_6$P$_3$Ru and 4% C$_{31}$H$_{36}$F$_6$P$_2$Ru: C, 62.58; H, 5.83. Found: C, 61.94; H, 6.06%. Mass spectrometry: *m*/*z*: 305 P(*p*-tol)$_3$, 541 [*M*$^+$−CH$_3$CN–P(*p*-tol)$_3$] **6** and [*M*$^+$] **7**, 845 [*M*$^+$−CH$_3$CN] **6**.



*[Ph–CH=CH–CH$_2$-P(o-tol)$_3$]PF$_6$ (**9**) and [RuCp*η^6-C$_5$H$_5$–CH=CH–CH$_2$P (o-tol)$_3$](PF$_6$)$_2$ (**10**)*. A solution of P(*o*-tol)$_3$ (34.9 mg, 0.115 mmol) in 1 mL acetone was added to a solution of [RuCp*(DMF)$_2$(η^3-phenylallyl)](PF$_6$)$_2$ (52.5 mg, 0.057 mmol) in 1 mL acetone. The reaction mixture was stirred for 2 h at room temperature after which time the solution was concentrated under vacuum to precipitate a dark yellow powder. The solid was collected and washed with diethyl ether. It was found to be a mixture of **9** and **10**. Yield: 53.5 mg. ^{1}H NMR (400 MHz, acetone-d_6, 0 °C) δ (ppm): 1.94 (s, C$_5$*Me*$_5$), 2.39 (s, tolyl Me), 4.77 (dd, $J_{PH} = 14.1$, $J = 7.5$ Hz, Hα′), 4.92 (dd, $J_{PH} = 14.1$, $J = 7.3$ Hz, Hα), 6.02 (m, Hβ′), 6.30 (ddd, $J = 14.9$, 7.3, $J_{PH} = 4.0$ Hz, Hβ) 6.92 (dd, $J = 14.9$, $J_{PH} = 4.0$ Hz, Hχ), 7.05 (dd, $J = 15.4$, 4.3 Hz, Hχ′). ^{1}H NMR (500 MHz, CD_2Cl_2, 0 °C) δ (ppm): 5.64 (m, H3), 5.74 (m, H4), 5.83 (m, H2), 7.18 (m, H2′), 7.30 (m, H4′). ^{13}C{^{1}H}NMR (125 MHz, CD_2Cl_2, 0 °C) δ (ppm): 10.7 (C$_5$*Me*$_5$), 23.1 (d, $J_{PC} = 17.2$ Hz, tolyl methyl groups, **10**), 23.2 (d, $J_{PC} = 16.2$ Hz, tolyl methyl groups, **9**), 29.2 (d, $J_{PC} = 52.5$ Hz, Cα), 29.3 (d, $J_{PC} = 52.5$ Hz, Cβ), 85.1 (C2), 87.2 (C4), 87.3 (C3), 97.1 (C1), 97.7 (*C*$_5$Me$_5$). ^{31}P{^{1}H}NMR (202 MHz, CD_2Cl_2, 0 °C) δ (ppm): 25.3 **10**, 26.1 **9**. Mass spectrometry: *m/z*: 421 [M^+] **9**, 541 [RuCp*P(*o*-tol)$_3$]$^+$, 657 [RuCp*(P(*p*-tol)$_3$)(CH$_2$–CH–CH–Ph)]$^+$, 803 [RuCp*η^6-C$_5$H$_5$–CH=CH–CH$_2$P(*o*-tol)$_3$](PF$_6$)$^+$.

[RuCp(tris ortho xenyl phosphite)(CH$_3$CN)$_2$]PF$_6$ (**13**)*. A solution of tris *ortho* xenyl phosphite (233.2 mg, 0.433 mmol) in 3 mL acetone was added to a solution of [RuCp*(CH$_3$CN)$_3$]PF$_6$ (104.0 mg, 0.206 mmol) in 4 mL acetone. The yellow reaction mixture was stirred for 2 h at room temperature after which time the solvent was removed under vacuum. The resulting crude product was washed with diethyl ether to afford 124.6 mg of a yellow solid. Crystals of the pure monosubstituted phosphite complex were obtained by dissolving 50 mg of the yellow solid in acetone, layering with diethyl ether and cooling to −40 °C (%). ^{1}H NMR (250 MHz, acetone-d_6, room temperature) δ (ppm): 1.21 (d, $J_{PC} = 2.3$ Hz, 15H, C$_5$Me$_5$), 2.38 (s, 6H, 2MeCN), 7.07–7.70 (m, 27H, tris *ortho* xenyl phosphite protons). ^{31}P{^{1}H}NMR (101 MHz, acetone-d_6, room temperature) δ (ppm): 136.4. Elemental Anal. Calc. for C$_{50}$H$_{48}$N$_2$O$_3$F$_6$P$_2$Ru: C, 59.94; H, 4.83; N, 2.80. Found: C, 60.13; H, 5.00; N, 2.53%. Mass spectrometry: *m/z*: 775 [M^+−2CH$_3$CN], 857 [M^+], 1313 [M^+−2CH$_3$CN + tris *ortho* xenyl phosphite].

[RuCp(tris(2,4-di-tert-butylphenyl)phosphite) (CH$_3$CN)$_2$]PF$_6$ (**14**)*. A solution of tris(2,4-di-*tert*-butylphenyl)phosphite (149.5 mg, 0.231 mmol) in 3 mL acetone was added to a solution of [RuCp*(CH$_3$CN)$_3$]PF$_6$ (106.0 mg, 0.210 mmol) in 3 mL acetone. The yellow reaction mixture was stirred for 2 h at room temperature after which time the solvent was removed under vacuum. The crude product was washed with hexane and dried under vacuum to yield the yellow monosubstituted phosphite complex. Yield: 50.0 mg (21%). ^{1}H NMR (300 MHz, acetone-d_6, room temperature) δ (ppm): 1.28 (s, 27H, ^{t}Bu), 1.40 (s, 27H, ^{t}Bu), 1.63 (d, $J_{PC} = 2.7$ Hz, 15H, C$_5$Me$_5$), 2.45 (s, 6H, 2MeCN), 7.16 (dd, $J = 8.7$, 2.4 Hz, 3H), 7.47 (d, $J = 2.1$ Hz, 3H), 7.64 (dd, $J = 8.7$, 1.7 Hz, 3H). ^{31}P{^{1}H}NMR (121 MHz, acetone-d_6, room temperature) δ (ppm): 133.6. Elemental Anal. Calc. for C$_{56}$H$_{84}$N$_2$O$_3$F$_6$P$_2$Ru: C, 60.58; H, 7.63; N, 2.52. Found: C, 60.47; H, 7.57; N, 2.52%. Mass spectrometry: *m/z*: 883.5 [M^+−2CH$_3$CN].

5. Supplementary materials

CCDC 645293 contains the supplementary crystallographic data for **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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