Azo-containing phosphine complexes of palladium(II) and platinum(II) and their effectiveness in the Heck reaction: crystal and molecular structure of [PdCl$_2${PPh$_2${1-(4-MeC$_6$H$_4$N$_2$)-2-OC(O)Me–C$_{10}$H$_5$}}]·2EtOH

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Abstract

Reaction of Na[MCl$_4$] (M = Pd or Pd) with the azo-containing phosphines Ph$_2$P{1-(4-RC$_6$H$_4$N$_2$)-2-OR′-C$_{10}$H$_5$} {R = Me (**I**), NMe$_2$ (**II**); R′ = C(O)Me} affords the complexes [MCl$_2$L$_2$] (**1–4**) in good yield. Complexes **1–4** have all been fully characterised by elemental analysis, ^{1}H-, ^{13}C{^{1}H}-, and ^{31}P{^{1}H}-NMR spectroscopy and UV–visible spectroscopy. The use of **1** in the Heck reaction has been investigated and shown to effect up to 1000 turnovers. © 1999 Elsevier Science S.A. All rights reserved.

1. Introduction

The use of palladium-based compounds to effect, catalytically, organic transformations is widespread [1]. In particular, the vinylation of aryl halides by the so-named Heck reaction [2] is currently subject to much interest [3]. Recent studies reported in this area by various groups have shown that TONs (turnover numbers) close to and exceeding 1 000 000 have been achieved by palladium complexes that contain chelating ligands. For example, Herrmann et al. have shown that complexes based upon cyclometallated tri*o*-tolylphosphine afford a TON of up to 40 000 for aryl chlorides [4]; Shaw et al. have similarly shown that cyclometallated 1-naphthyl phosphine complexes effect TON up to 1 000 000 [5]; additionally Shaw and Perera have shown that palladium complexes containing chelating phosphines are equally effective [6], contrary to previous reports to the contrary; furthermore Bedford and co-workers have shown that palladium complexes with cyclometallated phosphite ligand sets also give rise to highly effective Heck catalysts [7]. In general, however, the reactions are generally carried out with 1–5 mol% loadings in Pd, which means the reactions are not particularly cost effective [2]. We recently reported the preparation of azo-containing phosphines [8] and some coordination compounds of Group 6 metal carbonyls [9]. Herein we report the preparation of some palladium and platinum complexes and the use of the palladium complexes in the Heck reaction.

2. Results and discussion

2.1. Complex characterisation

The azo-containing phosphines **I** and **II**, Fig. 1, were prepared by the literature method [8] and reacted with Na$_2$[MCl$_4$] to give the complexes *trans*-[PdCl$_2$L$_2$] **1** and **3** and *cis*-[PtCl$_2$L$_2$] **2** and **4** in good yield. **1–4** were all characterised by elemental analysis, solvates were confirmed by repeated analysis on separate samples (see Table 1), UV–visible spectroscopy (Table 2) and ^{1}H-, ^{31}P{^{1}H}- and ^{13}C{^{1}H}-NMR (see Tables 3 and 4). Compound **1**·2EtOH was further characterised by a single-crystal X-ray diffraction study, Table 5. The results of the Heck reactions carried out using **1** as the

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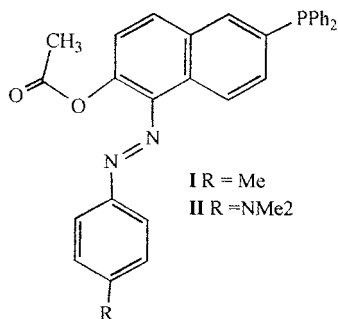*E-mail address:* k.r.flower@umist.ac.uk (K.R. Flower)

Fig. 1. The azo-containing phosphines **I** and **II**.

Table 2
UV–visible data for complexes **1–4** [a]

Complex	λ	ε
1	484.5	3167
	356.5	18083
2	488.0	3568
	351	10438
3	423	17172
4	434.5	18173

[a] Spectra recorded in $CHCl_3$, $\varepsilon = mol\ dm^{-3}\ cm^{-1}$; $\lambda_{max} = nm$.

source of the palladium catalyst are presented in Table 6. The reason for using the ester-functionalised phosphines rather than the free azohydroxyphosphines was that 1-phenylazonaphthalen-2-ols are known to complex to metal centres as O–N chelates and we did not want this to be a competing reaction [10].

The UV–visible spectra all display the expected absorptions for azo-containing species. The intensity of the absorptions by the azo chromophore is primarily responsible for the colour in these complexes. The presence of the dimethylamino group on the phenylazo ring causes the observed shift in the azo absorbance of 80 nm to longer wavelength in **3** and **4** through a conjugated interaction with the electron-accepting azochromophore [11].

The ^{1}H-NMR spectra, Table 3, all show the expected resonances for the phosphines, which are slightly perturbed on complexation and show retention of the ester moiety. The $^{31}P\{^1H\}$-NMR spectra for **1–4** all show a singlet resonance shifted downfield from the free phosphine; **2** and **4** each show a singlet resonance straddled by the expected platinum satellites, $^1J_{Pt-P}$ 3700 Hz; the magnitude of the coupling constant is indicative of a *cis* geometry. The $^{13}C\{^1H\}$-NMR spectra are all consistent with the formulation of the complexes **1** and **3** as *trans*-bisphosphine complexes; the numbering scheme for resonance assignment is illustrated in Fig. 2. All of the resonances were easily assigned using published substituent effects [12] and the presence of phosphorus coupling to the carbon nuclei, giving rise to virtual triplets for the carbon atoms in close proximity to the phosphorus nuclei [13].

2.2. Molecular structure of *1*

The molecular structure and numbering scheme for **1**·2EtOH can be found in Fig. 3; the disordered ethanol solvates are omitted for clarity, and only half the atoms are numbered as half were generated using the symmetry transformation $-x$, $y + 2$, $-z$. The solid-state structure confirms the spectroscopic data that the complex exists in the expected square planar form with the phosphines mutually *trans* to each other. All of the bond lengths in the complex are within the expected ranges with Pd–P(1) = 2.3235(19) Å, Pd–Cl(1) = 2.792(2) Å, and N(1)–N(2) = 1.241(9) Å.

2.3. The Heck reaction

Having prepared **1–4**, we carried out a preliminary investigation into the suitability of these complexes to effect the Heck vinylation of arenes. The Heck reaction is well known to be tolerant to many different functional groups [2] and we could only find one example of a coupling reaction involving precursors that contained an azo moiety and a loading of 5 mol% Pd was used in the coupling reaction [14]. The initial reaction was carried out in THF where iodotoluene was reacted with methyl acrylate in the presence of **1** in (1 mol% loading) and triethylamine as the base. The reaction was left for 17 h and after work up was shown to yield methyl cinnimate and some unreacted starting materials: the yield of pure material was 50%. We found a better yield could be obtained if a little free phosphine was added

Table 1
Physical and analytical data for compounds **1–4** [a]

Compound	Colour	Yield (%)	*m/z*	Mp (°C)	C (%)	H (%)	N (%)
1	Orange	72		236	63.5 (64.5)	4.3 (4.4)	4.5 (4.9)
2·0.5CH$_2$Cl$_2$	Orange	59	1207 [M–Cl]$^+$	222	58.2 (58.5)	4.0 (4.0)	3.9 (4.4)
3·2CH$_2$Cl$_2$	Red	56		228	57.2 (57.1)	4.4 (4.3)	5.8 (6.1)
4·CHCl$_3$	Brown	55	1265 [M–Cl]$^+$	210	55.4 (55.0)	4.0 (4.0)	6.0 (6.1)

[a] Calculated values in parentheses.

Table 3
^{1}H-NMR data [a] (δ) ppm and ^{31}P{^{1}H}-NMR data [b] (δ) ppm for compounds **1–4**

Compound	^{31}P (δ)	^{1}H (δ)
1	24.5	8.6 (d, J_{HH} 6.5, 2H, Ar–H); 8.3 (t, J_{HH} 6.0, 2H, Ar–H); 7.9–7.8 (bm, 16H, Ar–H); 7.5–7.3 (bm, 18H, Ar–H); 2.5 (s, 6H, CH_3); 2.3 (s, 6H, CH_3).
2	15.8 [$J_{Pt–P}$ 3676]	8.2 (d, J_{HH} 8.5, 2H, Ar–H); 7.8–7.6 (bm, 20H, Ar–H); 7.3–7.2 (bm, 16H, Ar–H); 5.29, (s, 1H, CH_2Cl$_2$); 2.5 (s, 6H, CH_3); 2.3 (s, 6H, CH_3).
3	24.5	8.6 (d, J_{HH} 9.3, 2H, Ar–H); 8.3 (t, J_{HH} 6.0, 2H, Ar–H); 7.9–7.8 (bm, 22H, Ar–H); 7.4 (d, J_{HH} 6.8, 4H, Ar–H); 7.3 (d, J_{HH} 8.8, 4H, Ar–H); 6.8 (d, J_{HH} 9.0, 4H, Ar–H); 5.29, (s, 4H, CH_2Cl$_2$); 3.1 (s, 12H, CH_3); 2.3 (s, 6H, CH_3).
4	15.7 [$J_{Pt–P}$ 3678]	8.2 (d, J_{HH} 9.5, 2H, Ar–H); 7.8–7.6 (bm, 18H, Ar–H); 7.3–7.2 (bm, 15H, Ar–H, CHCl$_3$); 6.8 [d, J_{HH} 8.5, 4H, Ar–H]; 3.1 [s, 12H, CH_3]; 2.3 (s, 6H, CH_3).

[a] Spectra recorded in CDCl$_3$ and referenced to CHCl$_3$; coupling constants in Hz.
[b] Spectra recorded in CDCl$_3$ and referenced to 85% H$_3$PO$_4$; coupling constants in Hz.

Table 4
^{13}C{^{1}H}-NMR [a] data (δ) for compounds **1–4**

Compound	^{13}C {^{1}H} (δ) ppm
1	169.4 [s, CO]; 151.5 [s, C(15)]; 142.4 [s, C(18)]; 138.5 [s, C(1)]; 138.3 [s, C(2)]; 135.7 [vt, J 6.5, C(5)]; 135.1 [vt, J 6.5, C(12)]; 131.9 [vt, J 6.4, C(7)]; 131.5 [s, C(4)]; 130.7 [s, C(17)]; 129.9 [s, C(14)]; 129.2 [vt, J 24.7, C(6)];128.2 [vt, J 5.8, C(13)]; 123.7 [vt, J 4.4, C(8)]; 123.3 [s, C(16)]; 122.8 [s, C(3)]; 21.5 [s, CH_3]; 20.9 [s, CH_3].
2	169.1 [s, CO], 151.4 [s, C(15)]; 142.6 [s, C(18)]; 138.9 [s, C(1)]; 137.9 [s, C(2)]; 135.9 [vt, J 5.5, C(5)]; 135.0 [vt, J 4.4, C(12)]; 132.1 [d, J 9.5, C(7)]; 131.1 [s, C(4)]; 131.0 [s, C(17)]; 130.6 [s, C(9)]; 129.8 [s, C(14)]; 129.1 [vt, J 26.9, C(6)]; 128.0 [vt, J 5.0, C(13)]; 123.6 [vt, J 5.1, C(8)]; 122.8 [s, C(16)]; 120.1 [s, C(3)]; 21.5 [s, CH_3]; 20.9 [s, CH_3].
3	169.4 [s, CO]; 152.8 [s, C(18)]; 144.6 [s, C(15)]; 139.1 [s, C(1)]; 138.2 [s, C(2)]; 136.0 [vt, J 6.5, C(5)]; 135.1 [vt, J 5.8, C(12)]; 131.4 [vt, J 9.4, C(7)]; 130.8 [s, C(9)]; 130.6 [s, C(14)]; 129.9 [s, C(4)]; 129.4 [vt, J 24.7, C(6)];128.2 [vt, J 5.1, C(13)]; 124.1 [vt, J 4.4, C(8)]; 123.4 [s, C(16)]; 121.5 [s, C(3)]; 111.4 [s, C(17)]; 40.3 [s, CH_3]; 30.0[s, CH_3].
4	169.3 [s, CO]; 152.7 [s, C(18)]; 144.6 [s, C(15)]; 138.6 [s, C(1)]; 138.5 [s, C(2)]; 136.0 [vt, J 6.5, C(5)]; 134.9 [vt, J 5.4, C(12)]; 132.0 [vt, J 9.4, C(7)]; 131.0 [s, C(14)]; 130.6 [s, C(9)]; 130.0 [vt, J 5.5, C(8)]; 129.4 [s, C(4)]; 128.0 [vt, J 5.8, C(13)]; 123.9 [s, C(16)]; 123.7 [s, C(3)]; 111.6 [s, C(17)]; 40.4 [s, CH_3]; 30.0 [s, CH_3].

[a] Spectra recorded in CDCl$_3$ at 75.5 MHz and referenced to CDCl$_3$ (77.0 ppm); coupling constants in Hz. See Fig. 2 for numbering scheme.

to the reaction mixture. To see if the yield could be improved by increasing the temperature, we chose to do the reaction in di-^{n}butyl ether; carrying out the reaction in this solvent caused complete conversion to the cinnimate, effecting a TON of 100: again a small amount of additional phosphine was added. The coupling reaction was then effected between methylacrylate and either *p*-iodotoluene *p*-bromoanisole, 6-bromo-2-methoxynaphthalene or *p*-chlorotoluene with **1** as catalyst precursor and triethylamine as the base and found the following. The reaction with *p*-chlorotoluene did not proceed to any appreciable extent, but up to 1000 turnovers could be obtained with *p*-bromoanisole. While these results are not outstanding by recent advances [3–6], they show that Pd complexes that contain azo-functionalised phosphines are capable of catalysing the Heck reaction. We are encouraged by these results to attempt to prepare azo-containing phosphines that have potential to act as P–N chelates to the metal centre, since they should display enhanced reactivity in the Heck reaction, especially when the results reported by Shaw and Perera on chelating phosphine complexes are borne in mind [6]. The problem associated with the chelating azo-phosphine approach, however, is the lack

of synthetic methodology for their preparation and it is extremely likely that the synthesis will be non-trivial: we are currently investigating a range of possible routes.

Table 5
Selected bond lengths (Å) and angles (°) for **1** [a]

Pd(1)–Cl(1)	2.279(2)	Pd(1)–P(1)	2.3235(19)
P(1)–C(24)	1.810(8)	P(1)–C(18)	1.812(8)
P(1)–C(5)	1.813(8)	O(1)–C(1)	1.392(11)
O(1)–C(30)	1.503(19)	N(1)–N(2)	1.241(9)
N(1)–C(2)	1.407(10)	N(2)–C(11)	1.433(11)
C(1)–C(8)	1.369(14)	C(1)–C(2)	1.385(13)
C(2)–C(10)	1.425(11)	C(3)–C(4)	1.348(11)
C(32)–C(33)	1.59(2)	O(2)–C(30)	1.223(19)
C(30)–C(31)	1.71(2)		
Cl(1)–Pd(1)–Cl(1) # 1	180.0	Cl(1)–Pd(1)–P(1)	92.97(7)
Cl(1) # 1–Pd(1)–P(1)	87.03(7)	Cl(1)–Pd(1)–P(1) # 1	87.03(7)
Cl(1) # 1–Pd(1)–P(1) # 1	92.97(7)	P(1)–Pd(1)–P(1) # 1	180.00(10)
C(1)–O(1)–C(30)	115.6(10)	N(2)–N(1)–C(2)	114.7(7)
N(1)–N(2)–C(11)	114.3(8)	C(8)–C(1)–C(2)	121.7(8)
C(2)–C(1)–O(1)	121.7(8)	C(1)–C(2)–N(1)	126.5(8)
C(16)–C(11)–N(2)	115.7(9)	C(12)–C(11)–N(2)	124.3(8)

[a] Symmetry transformations used to generate equivalent atoms: # 1 $-x$, $-y+2$, $-z$.

Table 6
Summary of the Heck reactions using **1** as palladium precursor

Aryl Halide	Alkene	Base	Catalyst loading	Solvent	Time (h)	Yield(%)	TON	Extra phosphine
4-Iodotoluene	Methylacrylate	Et$_3$N	1	THF	17	50 [a]	50	no
4-Iodotoluene	Methylacrylate	Et$_3$N	1	THF	17	55 [a]	55	yes
4-Iodotoluene	Methylacrylate	Et$_3$N	2	THF	17	75 [a]	38	no
4-Iodotoluene	Methylacrylate	Et$_3$N	1	Bu$_2$O	48	100 [a]	100	yes
4-Bromoanisole	Methylacrylate	Et$_3$N	1	Bu$_2$O	48	100 [a]/58 [b]	100/58	yes
4-Bromoanisole	Methylacrylate	Et$_3$N	0.1	Bu$_2$O	72	100 [a]/71 [b]	1000/710	yes
6-Bromo-2-methoxynaph-thalene	Methylacrylate	Et$_3$N	1	Bu$_2$O	48	100 [a]	100	yes
4-Chlorotoluene	Methylacrylate	Et$_3$N	1	Bu$_2$O	72	0 [a]	0	yes

[a] Yield by NMR.
[b] Isolated yield.

3. Conclusions

We have shown that a collection of palladium and platinum complexes containing azo-functionalised phosphines can be prepared and that the palladium complexes are reasonable precatalysts for the Heck reaction.

4. Experimental

4.1. General considerations

All solvents were dried by refluxing over an appropriate drying agent and distilled before use. The azophosphines **I**, **II** were prepared by the published method [8]. Na$_2$[MCl$_4$] (M = Pd, Pt) were loaned to us by Johnson Matthey; all other chemicals were purchased from commercial sources and used as received. Melting points were measured on a Griffin Melting Point Apparatus and are uncorrected. ^{1}H-NMR (200.2 MHz) and ^{31}P{^{1}H}-NMR (81.3 MHz) spectra were recorded on a Bruker DPX200 spectrometer; ^{13}C{^{1}H}-NMR (75.5 MHz) spectra were recorded on a Bruker DPX300 spectrometer; ^{1}H and ^{13}C{^{1}H} spectra were referenced to CHCl$_3$ (δ 7.26) and CHCl$_3$ (δ 77.0) and ^{31}P{^{1}H}

spectra were referenced externally to 85% H$_3$PO$_4$. Positive FAB spectra were obtained on a Kratos MS50TC spectrometer in a 3-nitrobenzyl alcohol matrix. UV–visible spectra were recorded on a Shimadzu UV20101 PC spectrometer in CHCl$_3$ (AR) from BDH. Elemental analyses were performed by the Microanalytical Service, Department of Chemistry, UMIST; solvates of crystallisation were confirmed by NMR data and repeated elemental analysis. The syntheses of the metal complexes were carried out in the open and the Heck reactions were carried out under an atmosphere of dinitrogen.

4.2. Complex preparation

4.2.1. trans-[Pd(PPh$_2${1-(4-RC$_6$H$_4$N$_2$)-2-OC[O]Me–C$_{10}$H$_5$}$)_2$Cl$_2$] 1

To Na$_2$[PdCl$_4$] (0.075 g, 0.26 mmol) dissolved in H$_2$O (1 ml) was added dropwise **I** (0.25 g, 0.51 mmol) in THF (5 ml) and the resulting solution was stirred for 2 h. An orange powder was collected by filtration, washed with water, followed by dry diethyl ether and dried to give **1** (0.22 g, 72%).

Complex **3** was prepared in an analogous manner. Recrystallisation from CH$_2$Cl$_2$–hexane yielded **3**·2CH$_2$Cl$_2$ as a brown powder (0.17 g, 59%).

4.2.2. cis-[Pt(PPh$_2${1-(4-RC$_6$H$_4$N$_2$)-2-OC[O]Me–C$_{10}$H$_5$}$)_2$Cl$_2$] 2

To Na$_2$[PtCl$_4$] (0.098 g, 0.26 mmol) dissolved in H$_2$O (1 ml) at 60°C was added dropwise **I** (0.25 g, 0.51 mmol) in THF (5 ml) and the resulting solution was stirred for 3 h at 60°C. The solution was cooled and the THF was removed under reduced pressure. CH$_2$Cl$_2$ (5 ml) was added to the resulting crude material, dried over anhydrous MgSO$_4$ and filtered. Hexane was added to the solution resulting in a brown powder which was collected by filtration and dried to give **2**·0.5CH$_2$Cl$_2$ (0.22 g, 72%).
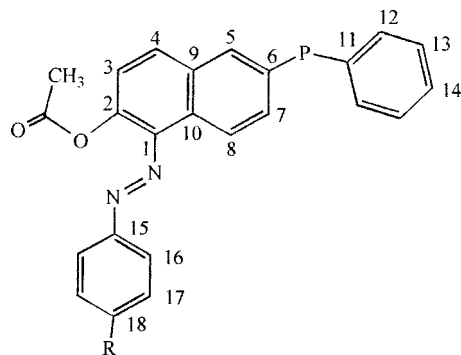

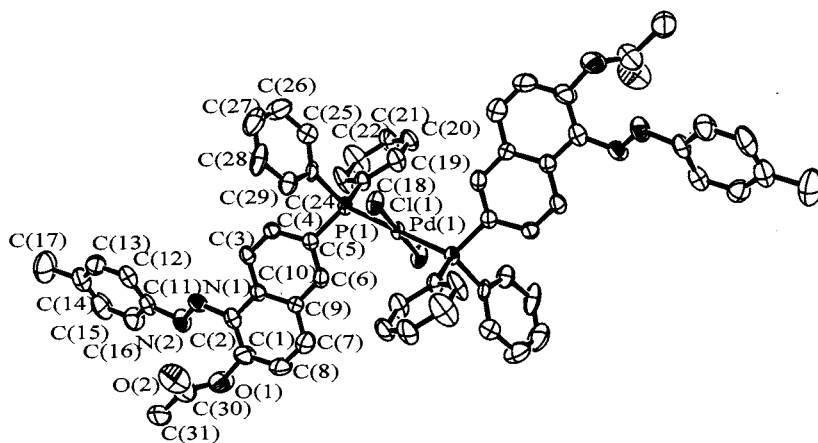Fig. 2. Numbering scheme used in assigning ^{13}C{^{1}H}-NMR spectra.

Fig. 3. ORTEP representation of **1** showing the atomic numbering scheme.

Complex **4** was prepared in an analogous manner. Recrystallisation from $CHCl_3$–hexane gave **4**·$CHCl_3$ as a brown powder (0.17 g, 55%).

4.3. Heck reactions

A typical Heck reaction was performed (for a catalyst loading of 1 mol%) as follows:

To 4-iodotoluene (0.94 g, 4.3 mmol) in di-*n*-butyl ether (20 ml) were added methyl acrylate (0.55 g, 6.5 mmol), Et_3N (0.8 ml, 5.6 mmol), **3** (0.05 g, 0.043 mmol) and **I** (0.05 g, 0.1 mmol) under an atmosphere of dinitrogen. The mixture was refluxed for 48 h and then cooled to room temperature. The solvent was removed in vacuo, the crude product extracted with diethyl ether and filtered. The diethyl ether was removed under reduced pressure affording 0.65 g of a solid, a small portion of which was dissolved in $CDCl_3$ and the ^{1}H-NMR spectrum recorded.

4.4. Crystallography

An orange tablet ($0.2 \times 0.1 \times 0.1$ mm) of **1**·2EtOH ($C_{62}H_{56}Cl_2N_4O_4P_2Pd \cdot 2C_2H_5OH$; M_w 1246.44) was mounted on a Nonius MACH 4-circle diffractometer using graphite monochromated Mo–K_α (0.71073 Å) radiation. Lattice constants, were determined from the setting angles of 25 accurately controlled reflections: Triclinic; $P\bar{1}$; $a = 10.234(4)$ Å; $b = 10.961(3)$ Å; $c = 13.291(4)$ Å; $\alpha = 76.824(19)°$; $\beta = 86.87(3)°$; $\gamma = 78.00(3)°$; $Z = 1$. The $\omega/2\theta$ scan technique was used with ω scan width of $0.9° = 0.35 \tan \theta$ to collect 5285 reflections with $2\theta \leq 50°$. The intensities were corrected for Lorenz, polarisation and absorption (0.536 mm^{-1}). The SHELX97 suite of programs [15] was used to solve the structure by direct methods and refined using full-matrix least squares based on F^2, hydrogen atoms were constrained to chemically reasonable positions: $R[I >$

$2\sigma(I)]$; R_1 0.0751, wR_2 0.1724; R (all data) $R_1 = 0.1300$, $wR_2 = 0.2024$. Selected bond lengths and angles can be found in Table 5.

5. Supplementary material

All crystallographic data have been deposited at Cambridge Crystallographic Data Centre, CCDC No. 124615. Copies of this information can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1123-336-033; e-mail: deposit@ccdc.ac.uk or www: http://www.ccdc.cam.ac.uk).

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