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Dimethylxanthene- and dibenzofuran-diamido complexes of titanium

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Honouring the outstanding chemist and special friend Professor Michael B. Hursthouse on the occasion of his retirement.

Abstract

The new ligands 4,5-dialkyl-and-diaryl-amido-9,9-dimethylxanthene and 4,6-dialkyl-and-diaryl-amido dibenzofuran serve as rigid, pre-organised and tunable 'spectators' for group 4 metals. The structure of a titanium complex with 4,5-di-cyclohexylamido-9,9-dimethylxanthene is reported.

Keywords: Amido titanium; Crystal structure; Xanthene dibenzofuran; Catalytic amination

1. Introduction

The development of new rigid, pre-organised ligands is an active area of research. Of particular interest is their use in homogeneous catalysis, where a geometric perturbation introduced by such ligands could improve the activity or selectivity of the catalyst. Demonstrations of this concept in the catalytic aziridination, cyclopropanation, C–H/C–C activation and hydroformylation reactions appeared recently [1]. The use of rigid preorganised ligands with early transition metals is less common. In addition to certain *ansa*-cyclopentadienyls [2], recent work has focussed on amido ligands, which could offer wide scope for electronic and steric tuning and ligand design [3]. The generation of low coordination number, electronically/sterically unsaturated metal species, the suppression of β-hydrogen elimination and the modulation of the rate of insertion reactions are attractive goals, where ligand preorganisation may prove useful. Rigid xanthene and dibenzofuran bridged chelating diphosphines have successfully been used in Rh catalysed hydroformylation. In this case, the *n*-/*i*-aldehyde ratio is influenced by the bite angle of the chelating diphosphine [1d].

As part of our ongoing research aiming at the development of novel ligands for the early transition metals, we report here a facile method for the synthesis of chelating dialkyl- and diaryl-amido ligands with xanthene and dibenzofuran backbones and initial results on the synthesis of their titanium complexes. The tunable rigidity, bite-angle, N-attached bulk and donor characteristics make these ligands useful building blocks for the design of the metal coordination environment. They are complementary to the family of the tridentate diamido ligands developed by Schrock et al. [4]. Hagadorn et al. [5] has recently prepared bimetallic xanthene bis-amidinate complexes of Zr and Ti. A review on the catalytic activity of Ti complexes in C–C and C–N bond formation reactions has recently appeared [6].

2. Experimental

2.1. General methods

Elemental analyses were carried out by the University College, London, microanalytical laboratory. All manipulations were performed under nitrogen in a Braun

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glove-box or using standard Schlenk techniques, unless stated otherwise. Solvents were dried using standard methods and distilled under nitrogen prior use.

The starting materials 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene [7], 4,5-dibromo-dibenzofuran [8], Ti $(NMe_2)_2Cl_2$ [9] and $Ti(benzyl)_4$ [10] were prepared by literature methods.

NMR data were recorded on Bruker AMX-300 and DPX-400 spectrometers, operating at 300 and 400 MHz (^1H), respectively. The spectra were referenced internally using the signal from the residual protio-solvent (^1H) or the signals of the solvent (^{13}C). Mass spectra (ES^+) were run from acetonitrile solutions on a VG Biotec platform.

2.2. 4,5-(N,N′-bis-cyclohexylamino)-2,7-di-tert-butyl-9,9-dimethyl-xanthene ($L_a^{cy}H_2$)

An ampoule was charged with 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethyl-xanthene (2.80 g, 5.83 mmol), sodium *tert*-butoxide (1.70 g, 17.5 mmol), $Pd(dba)_2$ (0.10 g, 0.175 mmol), 1,3-bis-(2,6-diisopropylphenyl)imidazolinium chloride (0.15 g, 0.35 mmol) and 1,4-dioxane (40 cm^3). To the mixture was added cyclohexylamine (1.27 g, 12.83 mmol) and the ampoule was closed under reduced pressure and heated at 100 °C for 60 h. The reaction was allowed to cool and water (40 cm^3) was added. The mixture was extracted with diethyl ether (2×100 cm^3 then 50 cm^3). The combined organic extracts were filtered and dried with $MgSO_4$. Evaporation of the volatiles under reduced pressure yielded a pale yellow solid that was recrystallised from boiling petroleum (60/80) to give $L_a^{cy}H_2$ as a pale yellow solid. Yield: 2.29 g, 76%. Mass spectrometry (EI): *m*/*z*, 517 $(M+1)^+$ δ_H ($CDCl_3$): 1.20–2.15 (20H, m, cyclohexyl CH_2), 1.35 (18H, s, Bu^t), 1.62 (6H, s, CH_3), 3.40–3.50 (2H, m, cyclohexyl CH α to amino N), 4.03 (2H, d, NH), 6.62 (2H, s, aromatics), 6.77 (2H, s, aromatics). $^{13}C\{^1H\}$ ($CDCl_3$): 25.30, 26.75 (cyclohexyl CH_2s), 32.25 (methyls), 32.32 (Bu^t), 34.07 (cyclohexyl CH_2), 35.30, 35.58 (tertiary carbons), 52.04 (cyclohexyl CH α to amino N), 107.61, 110.58 (aromatic CHs), 130.12, 135.59, 137.36, 146.13 (quaternary aromatics).

2.3. 4,5-(N,N′-bis-mesitylamino)-2,7-di-tert-butyl-9,9-dimethyl-xanthene ($L_a^{mes}H_2$)

An ampoule was charged with 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethyl-xanthene (3.00 g, 6.25 mmol), sodium *tert*-butoxide (1.80 g, 18.75 mmol), $Pd(dba)_2$ (0.18 g, 0.3 mmol), 1,3-bis-(2,6-diisopropylphenyl)imidazolinium chloride (0.26 g, 0.6 mmol) and 1,4-dioxane (60 cm^3). To this was added 2,4,6-trimethylaniline (1.86 g, 13.74 mmol), the ampoule was closed under reduced pressure and heated at 105 °C for 4 days. The reaction was allowed to cool and water (40 cm^3) was added. The mixture was extracted with diethyl ether (3×100 cm^3). The combined organic extracts were filtered and dried with $MgSO_4$. Volatiles were removed in vacuo and the residue was recrystallised from boiling ethanol to yield the product as a cream coloured solid. Yield: 2.53 g, 69%. Mass spectrometry (EI): *m*/*z*, 590 $(M+1)^+$. δ_H ($CDCl_3$): 1.39 (18H, s, Bu^t), 1.89 (6H, s, xanthene CH_3), 2.38 (12H, s, mesityl CH_3), 2.44 (6H, s, mesityl CH_3), 5.73 (2H, s, NH), 6.37 (2H, s, aromatics), 7.03 (2H, s, aromatics), 7.09 (4H, s, mesityl aromatics). $^{13}C\{^1H\}$ ($CDCl_3$): 18.98, 21.55 (mesityl CH_3), 32.15 (xanthene CH_3), 32.20 (But), 35.18, 35.67 (tertiary carbons), 108.34, 111.49 (aromatic CHs), 129.86 (mesityl aromatic CHs), 130.35, 134.60, 135.43, 135.77, 136.45, 137.55, 146.11 (quaternary aromatics).

2.4. 4,6-(N,N′-bis-mesitylamino)-dibenzofuran ($L_b^{mes}H_2$)

An ampoule was charged with 4,6-dibromo-dibenzofuran (1.00 g, 3.1 mmol), sodium *tert*-butoxide (0.88 g, 9.2 mmol), $Pd(dba)_2$ (0.18 g, 0.3 mmol), 1,3-bis-(2,6-diisopropylphenyl)imidazolinium chloride (0.26 g, 0.6 mmol) and 1,4-dioxane (20 cm^3). To this was added 2,4,6-trimethylaniline (0.99 g, 7.3 mmol) and the ampoule was closed under reduced pressure and heated at 105 °C for 18 h. The reaction was allowed to cool and water (100 cm^3) was added before extracting the reaction into diethyl ether (3×100 cm^3). The organic extracts were combined, filtered and dried with $MgSO_4$. Volatiles were removed in vacuo and the residue was recrystallised from boiling ethanol to yield the product as a white solid. Yield: 0.82 g, 61%. Mass spectrometry (EI): *m*/*z*, 435 $(M+1)^+$ δ_H ($CDCl_3$): 2.28 (12H, s, mesityl methyls), 2.36 (6H, s, mesityl methyls), 5.69 (2H, s, NH), 6.28 (2H, d, aromatics), 7.01 (4H, s, mesityl aromatics), 7.09 (2H, t, aromatics), 7.33 (2H, d, aromatics). $^{13}C\{^1H\}$ ($CDCl_3$): 18.94, 21.64 (mesityl methyls), 109.86, 110.46, 124.27 (aromatic CHs), 125.85 (quaternary aromatic), 129.98 (mesityl aromatic CHs), 133.23, 135.55, 136.43, 136.79, 145.01 (quaternary aromatics).

2.5. Bis-(N,N′-mesitylamido-dibenzofuran) dilithium salt ($L_b^{mes}Li_2$)

To a stirred, cooled (−78 °C) solution of ($L_b^{mes}H_2$) (0.22 g, 0.5 mmol) in petroleum (20 cm^3), was added slowly via cannula Bu^nLi (0.4 cm^3 of 2.45 M solution in hexanes, 1.0 mmol). The mixture was stirred at −78 °C for 1 h, allowed to reach room temperature and stirred for 15 h. This gave a colourless precipitate, which was isolated by filtration and dried in vacuo. Yield: 0.190 g, 85%. δ_H (C_6D_6): 1.65 (12H, s, mesityl methyls), 2.09 (6H, s, mesityl methyls), 6.32 (2H, d, aromatics), 6.63 (4H, s, mesityl aromatics), 6.90–7.05 (4H, m, aromatics). $^{13}C\{^1H\}$ (C_6D_6): 19.70, 21.33 (mesityl methyls), 107.27, 112.15 (aromatic CHs), 126.94 (quaternary aromatics), 127.84 (aromatic CHs), 131.27 (mesityl aromatic CHs), 131.94, 132.12, 142.25, 145.49, 146.40 (quaternary aromatics). The dilithium salts of ($L_a^{cy}H_2$), and ($L_a^{mes}H_2$) were prepared in an analogous way.

2.6. $(L_b^{mes})Ti(NMe_2)_2$

To a stirred, cooled (−78 °C) solution of $(L_b^{mes}H_2)$ (0.24 g, 0.41 mmol) in diethyl ether (10 cm^3), was added slowly via cannula Bu^nLi (0.34 cm^3 of 2.45 M solution in hexanes, 0.81 mmol). The mixture was stirred at −78 °C for 1 h, allowed to reach room temperature and stirred for a further hour to give an orange solution with a colourless precipitate. The mixture was cooled to −25 °C and a cooled (−25 °C) solution of $Ti(NMe_2)_2Cl_2$ in diethyl ether (7 cm^3) was added slowly via cannula. The reaction was slowly allowed to reach room temperature and stirred for ca. 15 h to give a red solution and grey precipitate. The volatiles were removed in vacuo and the residue extracted into petroleum (20 cm^3) and filtered through Celite. Removal of the volatiles in vacuo gave $(L_b^{mes})Ti(NMe_2)_2$ as an orange/red oil. Yield: 0.157 g, 53%. δ_H (C_6D_6): 1.23 (18H, s, Bu^t), 1.74 (6H, s, xanthene methyls), 2.17 (6H, s, mesityl methyls), 2.22 (12H, s, mesityl methyls), 2.83 (12H, s, dimethylamides), 6.26 (2H, s, aromatics), 6.80–7.00 (6H, m, aromatics). $^{13}C\{^1H\}$ (C_6D_6): 19.92, 21.64 (mesityl methyls), 29.20 (xanthene methyls), 32.64 (Bu^t), 35.76, 37.38 (tertiary carbons), 45.99 (dimethylamides), 108.18, 109.01 (aromatic CHs), 129.79 (mesityl aromatic CHs), 132.04, 133.66, 134.23, 142.57, 147.73, 148.01, 149.39 (quaternary aromatics).

2.7. $(L_a^{cy})Ti(NMe_2)_2$

This was prepared as the complex described above from $L_a^{cy}H_2$ (0.18 g, 0.35 mmol) and $Ti(NMe_2)_2Cl_2$ (0.072 g, 0.35 mmol). It was isolated as orange solid from petroleum. X-ray quality crystals were obtained from concentrated diethyl ether solutions by cooling at 0 °C for one week. Yield: 0.14 g, 65%.

δ_H (C_6D_6) 1.10–2.10 (20H, m, cyclohexyl), 1.44 (18H, s, Bu^t), 1.64 (6H, s, methyls), 3.10 (12H, s, dimethylamides), 4.04 (2H, br m, cyclohexyl CH α to amido N), 6.77 (2H, s, aromatic), 7.12 (2H, s, aromatic).

2.8. $(L_a^{cy})Ti(Bz)_2$

In the absence of light an NMR tube equipped with Young's tap was charged with a C_6D_6 solution of $(L_a^{cy}H_2)$ (0.020 g, 0.039 mmol) and Ti(benzyl)$_4$ (0.016 g, 0.039 mmol) and the base of the NMR tube was covered in foil. A ^1H NMR spectrum was run after the mixing and showed only the presence of the two starting materials. The sample was left at RT for ca. 15 h before the ^1H NMR spectrum was recorded again. The spectrum now contained a small set of peaks assignable to the $(L_a^{cy})Ti(benzyl)_2$ complex and free toluene as well as the more pronounced peaks due to the two starting materials. The NMR tube was then heated at 80 °C for 3 h and appeared to show complete conversion of the starting materials to the product. The volatiles were removed in vacuo and the dark red residue redissolved in C_6D_6 to obtain the spectra of the pure product.

δH (C_6D_6): 1.10–2.65 (20H, m, cyclohexyl CH2s), 1.35 (18H, s, Bu^t), 1.57 (6H, s, methyls), 2.92 (4H, s, benzyl CH_2s), 5.78 (2H, br m, cyclohexyl CH α to amido N), 6.70–6.85 (4H, m, aromatics), 6.95–7.05 (6H, m, aromatics), 7.10–7.20 (4H, m, aromatics). $^{13}C\{^1H\}$: 27.57, 28.24, 29.86 (cyclohexyl CH_2s), 32.57 (Bu^t), 33.05 (methyls), 35.02, 35.74 (cyclohexyl CH2s), 38.56, 38.86 (tertiary carbons), 60.57 (cyclohexyl CH α to amido N), 84.53 (benzyl CH_2s), 107.85, 111.75, 123.50 (aromatic CHs), 127.94 (quaternary aromatic), 128.02, 129.16 (aromatic CHs), 142.32, 143.74, 148.52, 149.01 (quaternary aromatics).

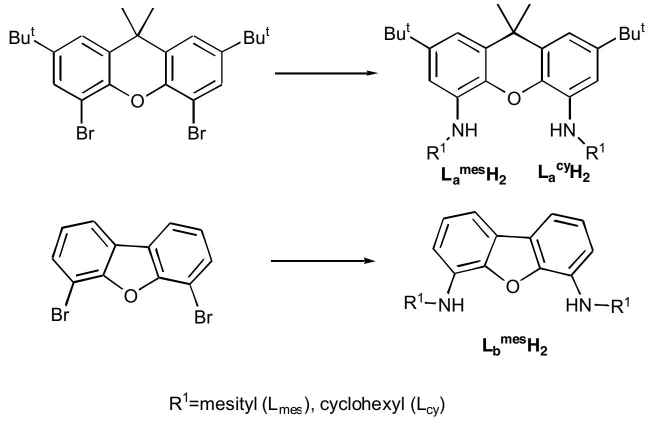
2.9. Structure determination of $(L_a^{cy})Ti(NMe_2)_2$

The data set was collected on a Bruker Nonius Kappa CCD area detector diffractometer with rotating anode FR591 and an Oxford Cryosystems low-temperature device operating in omega scanning mode with phi and omega scans to fill the Ewald sphere. The programs used for control and integration were COLLECT, SCALEPACK and DENZO [11,12]. An orange air sensitive crystal was mounted on a glass fibre with silicon grease, from Fomblin vacuum oil. Chemical formula $C_{39}H_{62}N_4OTi$. $C_4H_{10}O$; crystal system triclinic; space group $P\bar{1}$; cell dimensions $a = 10.2581(4)$ Å, $b = 12.2629(6)$ Å, $c = 18.6460(11)$ Å, $\alpha = 94.693(2)°$, $\beta = 95.234(3)°$, $\gamma = 107.671(2)°$; $Z = 2$, μ/mm^{-1} 0.230; $F(000)$ 708.0; number of data collected 23,300; number of unique data 7739; R_{int} 0.0981; final $R(|F|)$ for $I > 2\sigma(I)$ 0.0955; final $R(F^2)$ for all data 0.1547. All solutions and refinements were performed using the WINGX package [13] and all software packages within. All non-hydrogen atoms were refined using anisotropic thermal parameters and hydrogens were added using a riding model. The quality of the data was affected by the small size of the crystal and the rapid deterioration of the crystal quality during crystal selection possibly due to solvent loss. The structure contains a highly disordered molecule of diethylether and attempts to satisfactorily model this failed. As a result it was removed using the squeeze algorithm (P.v.d. Sluis, A.L. Spek, Acta Crystallogr., Sect. A 46 (1990) 194).

3. Results and discussion

The ligands $L_a^{mes}H_2$, $L_a^{cy}H_2$ and $L_b^{mes}H_2$ can be easily synthesised in multigram quantities from commercially available or easily accessible dibromo-xanthene or -dibenzofurans by Buchwald–Hartwig amination (Scheme 1).

The best conversions and selectivities are obtained with primary alkyl and aryl amines with a catalytic system comprising [1,3-bis(2,6-$Pr^i_2C_6H_3$)imidazolinium]chloride/$Pd_2(dba)_3$/Bu^tONa in dioxane [14]. Low catalyst loadings result in monoamination and dehalogenation giving rise to monoamines. The only alternative methods that have been used for the introduction of the amino (NH_2) group to xanthene ring were based on Curtius rearrangement with diphenylphosphorylazide and benzyl alcohol followed by



Scheme 1. Reagents and conditions: 2.2 equiv. R^1NH_2, 6 equiv. Bu^{t}ONa, 0.2 equiv. [1, 3-bis(2, 6-$Pr^i_2C_6H_3$)imidazolinium] chloride, 0.2 equiv. $Pd(dba)_2$, dioxane 100 °C, 12 h.

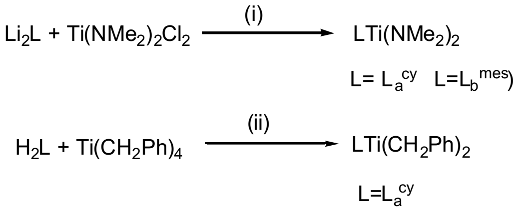
hydrogenolysis of the resulting carbamate [15]. Introduction of one dimethylamino (NMe_2) group has been accomplished by Ullman amination of the iodides under forcing conditions [16] and is of limited scope.

The new diamines were converted in almost quantitative yields to extremely air/moisture sensitive dilithium salts by reaction with Bu^{n}Li in petroleum.

The introduction of the L_a and L_b to group 4 transition metals has been successfully carried out by salt elimination from dilithium amides and metal halides or by alkane elimination from Ti tetralkyls and $L_a^{cy}H_2$ as shown in Scheme 2.

Even though the conversions are quantitative (by ^1H NMR spectroscopy) the yields of the isolated products are lower due to their high solubility in non-polar solvents. The new complexes were characterised by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. Elemental analysis data were not reproducible, possibly due to the formation of solvates (see below). The spectroscopic data support the presence of a C_s symmetric structure in solution with the plane of symmetry being perpendicular to the aromatic plane of the ligand and passing through the metal centre and the oxygen donor. The structure of $\mathbf{L_a^{cy}Ti(NMe_2)_2}$ in the solid state was determined by single crystal X-ray diffraction. A diagram of the molecule is shown in Fig. 1.

The coordination geometry around the metal can be best described as distorted square pyramidal ($\tau = 0.0186$), [17] with one dimethylamide nitrogen occupying the axial position. The diamidoxanthene ligand coordinates in the '*mer* fashion' as anticipated. The two Ti–dimethylamido bond lengths [Ti(1)–N(3) 1.888(4) Å; Ti(1)–N(2) 1.892(4) Å] are equal within the observed e.s.d.'s and shorter than the cyclohexylarylamido bonds [Ti(1)–N(1) 2.056(4) Å; Ti(1)–N(2) 2.039(4) Å]. The latter are in the range reported for less rigid 'pincer' or NON^{2-} diamido ligands [18]. All the amido groups are virtually planar. Of particular interest is the deviation of the ligand backbone from planarity due to structural constraint imposed by the linking groups (O and CMe_2). The angle defined by the two aromatic rings is ca. 15^0. In solution the structure is possibly non-rigid (idealised C_{2v}) with equivalent dimethylamido groups and methyl substituents on the 9-position.



Scheme 2. Reagents and conditions: (i) ether, −78 °C to room temperature; (ii) Me_3SiCl, toluene; (iii) toluene, 80 °C, 3 h.

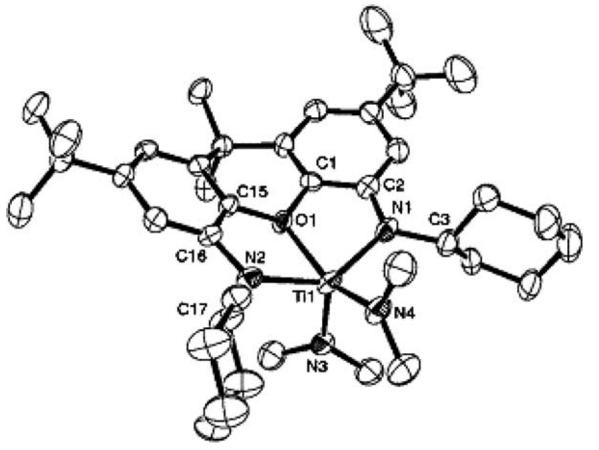


Fig. 1. ORTEP representation of the structure of $\mathbf{L_a^{cy}Ti(NMe_2)_2}$. One disordered ether molecule present in the unit cell as well as hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)–Ti(1) = 2.057(4); N(2)–Ti(1) = 2.040(4); N(3)–Ti(1) = 1.887(4); N(4)–Ti(1) = 1.893(4): O(1)–Ti(1) = 2.132(3) and N(3)–Ti(1)–N(4) = 105.15(18); N(3)–Ti(1)–N(2) = 103.92(17); N(4)–Ti(1)–N(2) = 101.64(17); N(3)–Ti(1)–N(1) = 105.55(17); N(4)–Ti(1)–N(1) = 97.36(17); N(2)–Ti(1)–N(1) = 139.08(15); N(3)–Ti(1)–O(1) = 99.97(16); N(4)–Ti(1)–O(1) = 154.80(16); N(2)–Ti(1)–O(1) = 73.73(13); N(1)–Ti(1)–O(1) = 73.72(13).

In solution, complexes $\mathbf{L_b^{mes}Ti(NMe_2)_2}$ and $\mathbf{L_a^{cy}Ti(Bz)_2}$ exhibit spectra with features similar to $\mathbf{L_a^{cy}Ti(NMe_2)_2}$ and, therefore, are expected to adopt analogous structures. We have been unable to grow crystals of $\mathbf{L_b^{mes}Ti(NMe_2)_2}$ and $\mathbf{L_a^{cy}Ti(Bz)_2}$ suitable for X-ray diffraction. The electron deficient $\mathbf{L_a^{cy}Ti(Bz)_2}$ is stable at room temperature in solution. This behaviour contrasts with the more flexible and less bulky (NON)Ti(alkyl)$_2$ which show limited stability in solution and the solid state [18b].

In summary, we have developed a general method based on Pd catalysed aromatic amination for the preparation of preorganised xanthene and dibenzofuran diamines. The diamido ligands that originate from them provide a useful tunable environment for the stabilisation of early transition metals. Extension of the scope of the catalytic amination to the synthesis of preorganised carbazole and dibenzothiophenes as well as studies of the chemistry of the new early transition metal amides as a function of ligand structural parameters is currently in progress.

4. Supplementary material

The crystallographic data for this paper have been predeposited at the Cambridge Crystallographic Database (CCDC 276930). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033).

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