Template controlled synthesis of a coordinated [11]ane-P_2C^{NHC} macrocycle†

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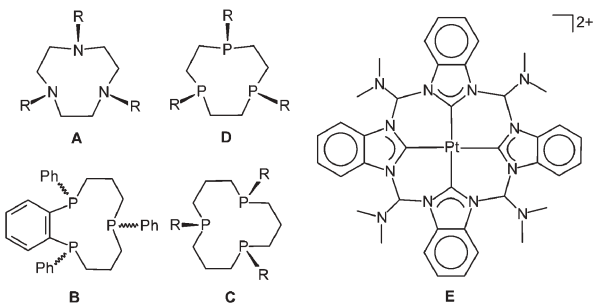
Rhenium complex [5]Cl with the coordinated [11]ane-P_2C^{NHC} macrocycle was obtained by a metal template controlled ring formation reaction; in this reaction a coordinated NH,NH-stabilised imidazolidin-2-ylidene ligand was connected *via* the nitrogen atoms to two phenyl substituents of a 2-fluorophenyl substituted diphosphine ligand.

Tridentate macrocycles such as tacn **A** (Scheme 1, tacn = triazacyclononane[1]) coordinate in a *facial* manner in octahedral complexes with the remaining coordination sites in *cis* positions to each other and *trans* to the donor atoms of the macrocycle. Compared to complexes with acyclic and/or monodentate ligands, complexes with macrocyclic ligands having the same donor set gain additional stability from the macrocyclic effects.[2] Besides **A** featuring amine donor groups more recently the synthesis and coordination chemistry of triphosphorus macrocycles has been investigated. Complexes containing 9-,[3] 10-,[4] 11-[5] and 12-[6] membered macrocyclic P_3 ligands are known. Gladysz and co-workers reported the synthesis of a complex with a 45-membered P_3 macrocycle by ring closing metathesis at a tungsten template.[7]

Only triphosphines of type **B**[8] (mixture of all possible diastereoisomers) and **C**[9] obtained by alkylation of the triphosphine ligand in $[(CO)_3Mo([12]ane\text{-}P_3H_3)]$[6e] followed by oxidative decomplexation (Scheme 1) have been isolated as free ligands. Macrocycles of type **D** have so far only been obtained as triphosphine oxides[3a] while some derivatives of type **C** have been liberated by reductive methods from their Fe^{II} complexes.[6a]



Scheme 1 Macrocycles with triamine, triphosphine and NHC-donor set.

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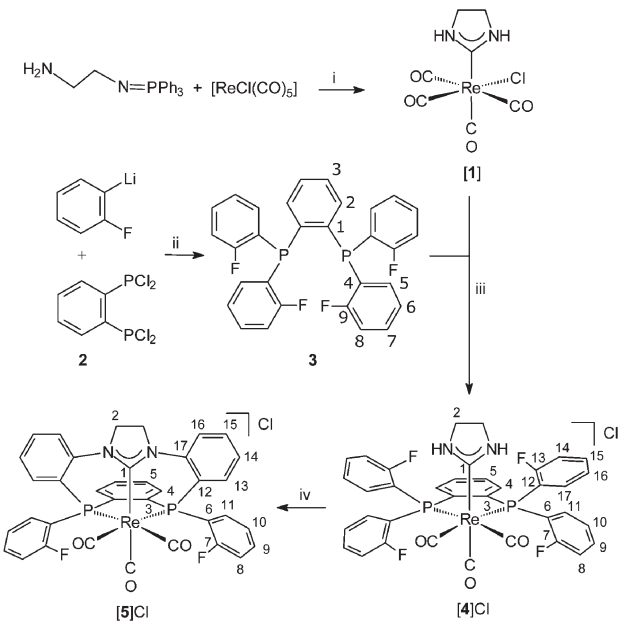
† Electronic supplementary information (ESI) available: Preparation of **[1]**, **2**, **3**, **[4]**Cl and **[5]**Cl, molecular plots of **[1]** and **3** and details of the crystal structure solutions for compounds **[1]**, **3**, **[4]**Cl·3THF and **[5]**Cl·3H_2O. See DOI: 10.1039/b617033a

Macrocycles containing N-heterocyclic carbenes (NHCs) are almost unknown.[10] The complex dication with a cyclic tetra-carbene ligand **E** (Scheme 1) was obtained by a template controlled cyclisation of *β*-functionalised phenylisocyanide[11] followed by bridging alkylation of the NH,NH-stabilised carbene ligands at a Pt^{II} centre.[12] In addition, ligands derived from cyclophanes containing two NHC donors are known[13] but by definition they are not considered macrocycles.[2]

The similarities in the donor properties of phosphines and NHCs makes the preparation of ligands with a mixed phosphine/NHC donor set an interesting preparative target. While pincer complexes with mixed R_3P/NHC ligands have been described,[14] we report here on the template controlled synthesis of the rhenium(I) complex **[5]**Cl with the novel macrocyclic PPC-ligand [11]ane-P_2C^{NHC} (Scheme 2).

The macrocycle [11]ane-P_2C^{NHC} in complex **[5]**Cl was synthesised by a template controlled cyclisation reaction. Initially, an easy to functionalise NH,NH-stabilised carbene ligand was generated at the rhenium(I) template (complex **[1]**) followed by the introduction of diphosphine **3** to give complex **[4]**Cl. Subsequently the coordinated diphosphine and the NH,NH-stabilised carbene ligand were connected *via* two new N–C bonds leading to the complex with the macrocyclic ligand.



Scheme 2 *Reagents and conditions*: (i) as described,[17] THF, 25 °C, 12 h; (ii) 1. Et_2O, −78 °C 4 h, 2. 25 °C, 12 h; (iii) CH_3CN, reflux, 6 h; (iv) THF, KO*t*-Bu, 25 °C, 5 d.

Complexes containing NH,NH-stabilised benzimidazolin-2-ylidenes[11,12,15] and imidazolidin-2-ylidenes[16] are accessible from complexes with β-functionalised isocyanides. The NH,NH-substituted carbene ligands are easily N,N′-alkylated.[11,12,16] Alternatively, complex [**1**] bearing an NH,NH-stabilised carbene ligand was prepared by reaction of β-aminoethylphosphinimine and $[ReCl(CO)_5]$ following a procedure described by Liu *et al.*[17] (Scheme 2). We assume that this reaction proceeds by formation of triphenylphosphine oxide and coordinated β-aminoethyl isocyanide by deoxygenation of a carbonyl ligand. Subsequently the β-aminoethyl isocyanide ligand reacts under intramolecular cyclisation to give the complex with the NH,NH-stabilised carbene ligand.[16]

Surprisingly, the IR spectrum of [**1**] shows two N–H stretching frequencies at ν = 3429 and 3265 cm^{-1}. ‡ This observation is due to an intermolecular hydrogen bond between a NH-proton and a chloro ligand from an adjacent molecule. The crystal structure analysis of [**1**]§ (see ESI†) confirms the existence of such an intermolecular hydrogen bond (NH···Cl distance 2.386 Å). Similar carbene-NH···Cl interactions have been described.[18]

The chelating diphosphine **3**[19] was prepared from 1,2-bis(dichlorophosphino)benzene[20] and *ortho*-lithiated fluorobenzene. The molecular structure of **3**§ is described in the ESI.† Reaction of [**1**] with **3** in refluxing acetonitrile leads to the substitution of the chloro ligand as well as of one CO ligand in nearly quantitative yield (98%) and formation of [**4**]Cl (Scheme 2). Complex [**4**]Cl has been characterised by spectroscopy‡ and X-ray crystallography.§

The IR spectrum of [**4**]Cl exhibits only one weak N–H absorption at ν = 3460 cm^{-1}. The $^{13}C\{^1H\}$ NMR spectrum shows the resonance of the carbene carbon atom at δ 189.8. This signal is split into a triplet ($^2J_{CP}$ = 9.8 Hz) by coupling with both phosphorus atoms in the *cis* positions. The resonance of the carbonyl carbon atom *trans* to the carbene ligand is observed at δ 190.0 as a broad multiplet. The remaining CO ligands give rise to a signal at δ 191.0 which is observed as a doublet of doublets due to the coupling with the phosphorus atoms ($^2J_{CP\text{-}trans}$ = 52 Hz, $^2J_{CP\text{-}cis}$ = 8 Hz) of the diphosphine ligand. Inversion of the phosphorus atoms is prevented by coordination of the diphosphine resulting in two chemical inequivalent phenyl rings and thereby generating two chemical inequivalent fluorine atoms. Consequently, the ^{19}F NMR spectrum exhibits two resonances at δ −100 and −98.

The X-ray diffraction analysis of [**4**]Cl·3THF (Fig. 1)§ confirms the expected *facial* arrangement of the ligands in a distorted octahedral complex. Bond length and angles in the cation $[\mathbf{4}]^+$ fall in the expected range. The plane of the carbene ligand is orientated between P1/P2 and C4/C6 in a manner which allows a minimal interaction with the coordinated diphosphine.

Addition of KO*t*-Bu to a suspension of [**4**]Cl in THF leads within five days to a clear solution from which the light yellow complex $[Re(CO)_3([11]ane\text{-}P_2C^{NHC})]Cl$ [**5**]Cl precipitates in 90% yield (Scheme 2). The imidazolidin-2-ylidene in $[\mathbf{5}]^+$ is no longer able to rotate around the Re–C bond after formation of the macrocycle. Hence, the diastereotopic CH_2–CH_2 protons of the backbone give rise to two resonances at δ 4.61 and 3.15, which appear as multiplets by geminal und ^3J coupling (AA′BB′ spin system).‡ NOE experiments confirm that the downfield resonance at δ 4.61 can be assigned to the protons interacting with the anisotropy cone of the central bridging phenyl ring.

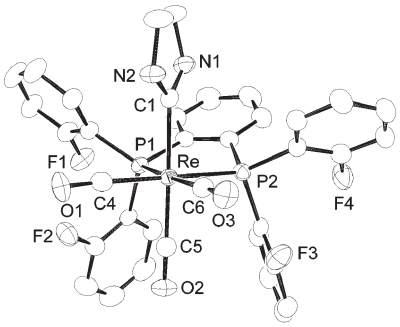


Fig. 1 Molecular structure of complex cation $[\mathbf{4}]^+$ in [**4**]Cl·3THF. Selected bond lengths (Å) and angles (°): Re–P1 2.428(2), Re–P2 2.420(2), Re–C1 2.188(5), Re–C4 1.971(5), Re–C5 1.950(5), Re–C6 1.975(6); P1–Re–P2 80.11(5), P1–Re–C1 90.60(13), P1–Re–C4 93.54(14), P1–Re–C5 90.50(15), P1–Re–C6 173.31(14), P2–Re–C1 90.43(13), P2–Re–C4 173.60(14), P2–Re–C5 91.53(15), P2–Re–C6 93.21(15).

The X-ray diffraction analysis with crystals of [**5**]Cl·3H_2O§ (Fig. 2) confirms the formation of the coordinated macrocycle $[11]ane\text{-}P_2C^{NHC}$. All bond distances in $[\mathbf{5}]^+$ are shortened in comparison to equivalent bonds in $[\mathbf{4}]^+$. This is most noticeable for the Re–C1 and Re–P bonds. The bond angles in the cation $[\mathbf{5}]^+$ deviate more strongly from octahedral geometry than those found for the cation $[\mathbf{4}]^+$. This effect is most pronounced for those angles involving donor groups of the macrocycle. For example, the P–Re–C1 bond angles in the cation $[\mathbf{4}]^+$ (P1–Re–C1 90.60(13)°, P2–Re–C1 90.43(13)°) are nearly orthogonal whereas significant smaller values for the equivalent angles were found in the cation $[\mathbf{5}]^+$ (P1–Re–C1 77.96(10)°, P2–Re–C1 79.12(10)°).

We have shown that the coordinated PPC macrocycle $[11]ane\text{-}P_2C^{NHC}$ can be obtained in a template controlled reaction of a tricarbonylrhenium(I) complex containing a NH,NH-stabilised carbene ligand and a 2-fluorophenyl substituted diphosphine ligand. The novel PPC macrocycle should have similar useful properties as its NNN and PPP analogues. Encouraging preliminary results indicate, that the macrocycle synthesis can be transferred to other template metals. Further experiments regarding the liberation of the macrocyclic ligand from the metal centre as well as the generation of this and similar hetero-donor phosphine/carbene macrocycles on catalytically active metal centres are in progress.

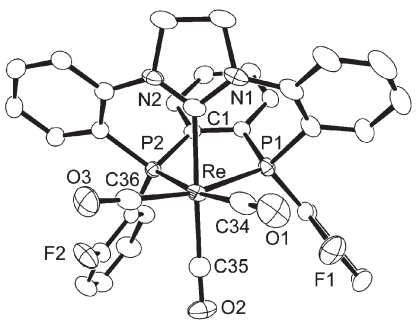


Fig. 2 Molecular structure of complex cation $[\mathbf{5}]^+$ in [**5**]Cl·3H_2O. Selected bond lengths (Å) and angles (°): Re–P1 2.3957(13), Re–P2 2.3895(14), Re–C1 2.172(4), Re–C34 1.966(4), Re–C35 1.950(4), Re–C36 1.966(4); P1–Re–P2 81.58(5), P1–Re–C1 77.96(10), P1–Re–C34 91.72(13), P1–Re–C35 97.93(12), P1–Re–C36 167.33(12), P2–Re–C1 79.12(10), P2–Re–C34 170.73(13), P2–Re–C35 96.60(11), P2–Re–C36 91.15(13).

Notes and references

‡ *Spectroscopic data* for [**1**], **2**, **3**, [**4**]Cl and [**5**]Cl. [**1**]: NMR: ^{1}H (400.1 MHz, $CDCl_3$): δ 6.90 (s, br, 2H, N*H*), 3.72 (s, 4H, NCH_2CH_2N); ^{13}C{^{1}H} (100.6 MHz, $CDCl_3$): δ 193.6 (NCN), 186.8 (CO), 184.9 (CO), 184.7 (CO), 44.2 (N*C*H$_2$*C*H$_2$N); IR (KBr): ν 3429 (s, NH), 3265 (s, br, NH), 2107 (s, CO), 2016 (s, CO), 1993 (s, br, CO), 1924 cm^{-1} (s, br, CO); ES-MS+: *m*/*z* (%): 426.9455 (100) (calc. $[C_7H_6N_2ClO_4Re + Na]^+$ 426.9457). **2**: NMR: ^{13}C{^{1}H} (100.6 MHz, $CDCl_3$): δ 144.6 (d, $^{1}J_{PC}$ = 13 Hz, Ar–C$_{ipso}$), 133.8 (Ar–C$_{meta}$), 131.1 (d, $^{2}J_{PC}$ = 9 Hz, Ar–C$_{ortho}$); ^{31}P{^{1}H} (162.0 MHz, $CDCl_3$): δ 151. **3**: NMR: ^{1}H (400.1 MHz, $CDCl_3$, assignment, see Scheme 2): δ 7.33 (m, 2H, Ar–H3), 7.31 (m, 4H, Ar–H7), 7.14 (m, 2H, Ar–H2), 7.04 (m, 4H, Ar–H6), 7.00 (m, 4H, Ar–H8), 6.92 (m, 4H, Ar–H5); ^{13}C{^{1}H} (100.6 MHz, $CDCl_3$, assignment, see Scheme 2): δ 164.1 (d, $^{1}J_{CF}$ = 264 Hz, Ar–C9), 140.7 (m, Ar–C1), 134.7 (m, Ar–C5), 133.9 (m, Ar–C2), 131.1 (d, $^{3}J_{CF}$ = 8.3 Hz, Ar–C7), 129.9 (Ar–C3), 124.4 (d, $^{3}J_{CP}$ = 2.7 Hz, Ar–C6), 122.7 (m, Ar–C4), 115.2 (d, $^{2}J_{CF}$ = 23.2 Hz, Ar–C8); ^{31}P{^{1}H} (162.0 MHz, $CDCl_3$): δ −36 (m); ^{19}F (376.5 MHz, $CDCl_3$): δ −103 (m); ES-MS+: *m*/*z* (%): 541.0872 (100) (calc. $[C_{30}H_{20}F_4P_2 + Na]^+$ 541.0869), 519.1062 (18) (calc. $[C_{30}H_{20}F_4P_2 + H]^+$ 519.1055). [**4**]Cl: NMR: ^{1}H (400.1 MHz, CD_3CN, assignment, see Scheme 2): δ 8.02 (m, 2H, Ar–H4), 7.88 (m, 2H, Ar–H5), 7.67 (m, 2H, Ar–H9), 7.44 (m, 2H, Ar–H15), 7.39 (m, 2H, Ar–H10), 7.32 (m, 2H, Ar–H11), 7.27 (m, 2H, Ar–H8), 7.16 (m, 2H, Ar–H16), 7.10 (m, 2H, Ar–H14), 6.92 (m, 2H, Ar–H17), 6.56 (s, 2H, NH), 3.21 (s, 4H, NCH_2CH_2N); ^{13}C{^{1}H} (100.6 MHz, CD_3CN, assignment, see Scheme 2): δ 191.0 (dd, $^{2}J_{CP\text{-}trans}$ = 50.4 Hz, $^{2}J_{CP\text{-}cis}$ = 8.2 Hz, CO$_{cis\text{-}C1}$), 190.0 (m, br, CO$_{trans\text{-}C1}$), 189.8 (t, $^{2}J_{CP}$ = 9.8 Hz, C1), 164.5 (d, $^{1}J_{CF}$ = 249 Hz, C7), 163.4 (dd, $^{1}J_{CF}$ = 247 Hz, $^{2}J_{CP}$ = 4.9 Hz, C13), 139.2 (dd, $^{1}J_{CP}$ = 48.5 Hz, $^{2}J_{CP}$ = 33.4 Hz, C3), 136.8 (dd, $^{2}J_{CP}$ = 14.0 Hz, $^{3}J_{CP}$ = 2.5 Hz, C4), 136.8 (m, C11), 136.6 (dd, $^{3}J_{CF}$ = 9.5 Hz, $^{4}J_{CP}$ = 2.0 Hz, C9), 134.9 (dd, $^{3}J_{CF}$ = 8.5 Hz, $^{4}J_{CP}$ = 1.6 Hz, C15), 134.8 (dd, $^{3}J_{CP}$ = 6.2 Hz, $^{4}J_{CP}$ = 2.2 Hz, C5), 133.0 (m, C17), 126.5 (dd, $^{3}J_{CP}$ = 11.2 Hz, $^{4}J_{CF}$ = 3.0 Hz, C10), 125.6 (dd, $^{3}J_{CP}$ = 8.3 Hz, $^{4}J_{CF}$ = 3.0 Hz, C16), 122.2 (ddd, $^{1}J_{CP}$ = 53 Hz, $^{2}J_{CF}$ = 17 Hz, $^{4}J_{CP}$ = 2.0 Hz, C12), 118.2 (dd, $^{2}J_{CF}$ = 23.8 Hz, $^{3}J_{CP}$ = 3.4 Hz, C8), 117.3 (ddd, $^{1}J_{CP}$ = 45 Hz, $^{2}J_{CF}$ = 16.4 Hz, $^{4}J_{CP}$ = 2.8 Hz, C6), 117.0 (dd, $^{2}J_{CF}$ = 23.0 Hz, $^{3}J_{CP}$ = 3.7 Hz, C14), 45.9 (C2); ^{31}P{^{1}H} (162.0 MHz, $CDCl_3$): δ 22 (d); ^{19}F (376.5 MHz, CD_3CN): δ −98, −100; IR (KBr): ν 3460 (w, NH), 2043 (s, CO), 1971 (s, CO), 1949 (s, CO); ES-MS+: *m*/*z* (%): 859.0893 (100) (calc. $[C_{36}H_{26}N_2F_4O_3P_2Re]^+$ 859.0909). [**5**]Cl: NMR: ^{1}H (400.1 MHz, CD_3CN, assignment, see Scheme 2): δ 7.83 (m, 2H, Ar–H5), 7.81 (m, 2H, Ar–H4), 7.69 (m, 2H, Ar–H13), 7.66 (m, 2H, Ar–H9), 7.63 (m, 2H, Ar–H16), 7.39 (m, 2H, Ar–H14), 7.38 (m, 2H, Ar–H15), 7.37 (m, 2H, Ar–H8), 7.25 (t, 2H, Ar–H10), 6.97 (m, 2H, Ar–H11), 4.61 (m, 2H, N–C(2)H–C(2)H–N), 3.15 (m, 2H, N–C(2)H–C(2)H–N); ^{13}C{^{1}H} (100.6 MHz, CD_3CN, assignment, see Scheme 2): δ 193.4 (br, CO$_{trans\text{-}C1}$), 192.3 (t, $^{2}J_{CP}$ = 13.8 Hz, C1), 191.1 (dm, $^{2}J_{CP\text{-}trans}$ 46.0, CO$_{cis\text{-}C1}$), 164.4 (dd, $^{1}J_{CF}$ = 249 Hz, $^{2}J_{CP}$ = 5.0 Hz, C7), 145.8 (d, $^{2}J_{CP}$ = 11.8 Hz, Ar–C17), 139.9 (m, Ar–C3), 136.6 (d, $^{3}J_{CF}$ = 9.2 Hz, Ar–C9), 136.2 (m, Ar–C4), 134.7 (d, $^{2}J_{CP}$ = 1.6 Hz, Ar–C13), 134.6 (m, Ar–C5), 134.3 (m, Ar–C11) 131.2 (d, $^{4}J_{CP}$ = 1.6 Hz, Ar–C15), 127.4 (d, $^{3}J_{CP}$ = 8.3 Hz, Ar–C14), 126.8 (m, Ar–C10), 125.6 (d, $^{3}J_{CP}$ = 6.3 Hz, Ar–C16), 123.8 (dd, $^{1}J_{CP}$ = 56.4 Hz, $^{4}J_{CF}$ = 4.9 Hz, Ar–C12), 117.8 (dd, $^{2}J_{CF}$ = 21.9 Hz, $^{3}J_{CP}$ = 4.2 Hz, Ar–C8), 115.1 (dd, $^{1}J_{CP}$ = 54.6 Hz, $^{2}J_{CF}$ = 17.7 Hz, Ar–C6), 52.4 (N*C*H$_2$*C*H$_2$N); ^{31}P{^{1}H} (162.0 MHz, CD_3CN): δ 16 (d); ^{19}F (376.5 MHz, CD_3CN): δ −97 (m); IR (KBr): ν 2031 (s, CO), 1963 (s, CO), 1937 (s, CO); ES-MS+: *m*/*z* (%): 819.0770 (100) (calc. $[C_{36}H_{24}N_2F_2O_3P_2Re]^+$: 819.0784).

§ *Crystal data* for [**4**]Cl·3THF and [[**5**]Cl·3H_2O]: $C_{48}H_{50}N_2ClF_4O_6P_2Re$ [$C_{36}H_{30}N_2ClF_2O_6P_2Re$], M = 1110.49 [908.21], triclinic [triclinic], $P\bar{1}$ [$P\bar{1}$], a = 11.201(5) [9.030(5)], b = 11.800(5) [10.898(5)], c = 20.504(5) [19.929(5)] Å, α = 92.239(5) [75.388(5)], β = 100.058(5) [82.356(5)], γ = 117.123(5) [68.013(5)]°, V = 2353.1(2) [1758.1(13)] Å^3, T = 150(2) [150(2)] K, λ = 0.71073 [0.71073] Å, Z = 2 [2], μ = 2.773 [3.682] mm^{-1}, 16653 [11370] data measured, 9183 [7588] unique data, R = 0.0415 [0.0308], wR = 0.0987 [0.0660] for 8650 [6915] data [$I \geqslant 2\sigma(I)$]. *Crystal data* for **3** and [[**1**]]: $C_{30}H_{20}F_4P_2$ [$C_7H_6N_2ClO_4Re$], M = 518.40 [403.79], monoclinic [monoclinic], $P2_1/c$ [$P2_1/c$], a = 10.966(2) [8.852(2)] , b = 14.272(3) [10.297(2)], c = 15.942(3) [12.389(3)] Å, β= 91.88(3) [107.84(3)], V = 2493.8(9) [1075.0(4)] Å^3, T = 150(2) [150(2)] K, λ = 0.71073 [0.71073] Å, Z = 4 [4], μ = 0.222 [11.547] mm^{-1}, 8965 [3540] data measured, 4630 [2315] unique data, R = 0.0457 [0.0264], wR = 0.0950 [0.0596] for 3481 [2070] data [$I \geqslant 2\sigma(I)$]. CCDC 624140 (**3**), 624141 ([**1**]), 624142 ([**4**]Cl·3THF) and 424143 ([**5**]Cl·3H_2O). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b617033a

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