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Expression of the prohelicity of bis-cyclomanganated 2,3-diphenylquinoxaline through reactions with diaryldiazomethanes†

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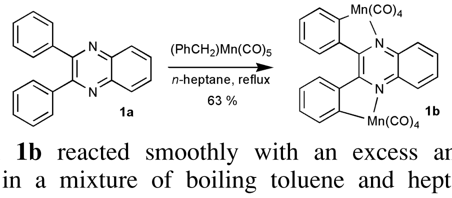
The reactions of bis-cyclomanganated 2,3-diphenylquinoxaline with diazodiphenylmethane and 9-diazofluorene allowed the formation of a new oligomeric and dinuclear manganospiralene and the ready preparation of a pentacyclic helix comprising two (η^5-fluorenyl)Mn(CO)$_3$ fragments, whose helicity can be locked upon one-dimensional linear coordination to silver cation.

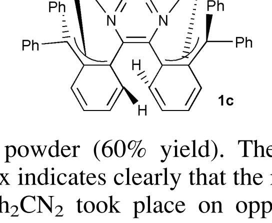
The conformational stability of helicenes depends mostly on the number of fused rings[1] whose geometrical features contribute in defining the overall 'chirality'.[2] Bis-cyclometallated 2,3-diphenyl-substituted quinoxalines and pyrazines such as those studied by Steel and Caygill[3] [M = Pd(II)]] can be considered as dipallada-analogs of pentahelicenes as they possess the structural features of pentahelicenes, *i.e.* a low barrier to conformational change[4] and the rich reactivity of the chelated metal centers.[5] Helicity in the solid state stems from the steric repulsion existing between the two metallated phenyl groups connected at the 2- and 3-positions of the diaza-benzene ring. Such a chiral helical system is fluxional in solution and can be qualified as being 'prohelical' rather than strictly helical. We were interested in studying the stereochemical features of reactions occurring in the coordination sphere of each chelated metal in a such dinuclear substrate and in evaluating to what extent this intrinsic 'prohelicity' could be advantageously used in the stereoselective synthesis of polynuclear manganospiralenes.[6]

The reaction of 2,3-diphenylquinoxaline **1a**[7] with (Ph$_2$CH$_2$)Mn(CO)$_5$ afforded the dinuclear complex **1b** [eqn. (1)].†



(1)

Complex **1b** reacted smoothly with an excess amount of Ph$_2$CN$_2$ in a mixture of boiling toluene and heptane. The reaction product, **1c**, which was purified by conventional flash chromatography and recrystallised, was recovered as an air-stable dark-blue powder (60% yield). The structure of this binuclear complex indicates clearly that the reaction of the two equivalents of Ph$_2$CN$_2$ took place on opposite faces of the substrate **1b**, in an expected *anti*-fashion with respect to the mean plane of the chelate (Fig. 1).‡ Two successive *anti* insertions of Ph$_2$CN$_2$ in a C$_{Ar}$–Mn bond result in an increase of the torsion angle between the two phenyl groups and the heterocycle, thus yielding a much less sterically congested product **1c** (Scheme 1). In complex **1c**, the heterocycle is embedded between the two *endo* phenyl rings (Fig. 1). The stacking of the aromatic rings is characterised by interplanar angles of *ca.* 20° and distances between centroids of vicinal rings of *ca.* 3.4 Å. The phenylene rings are twisted by a value of *ca.* 50° with respect to the central heterocycle, and are mutually involved in CH–π interactions[8] through the hydrogen atoms located at C21 and C50 respectively.



Complex **1b** reacted smoothly with 9-diazofluorene in refluxing toluene to yield a new, stable bimetallic product **1d** (79% yield) containing three 1,2-disubstituted aromatics and

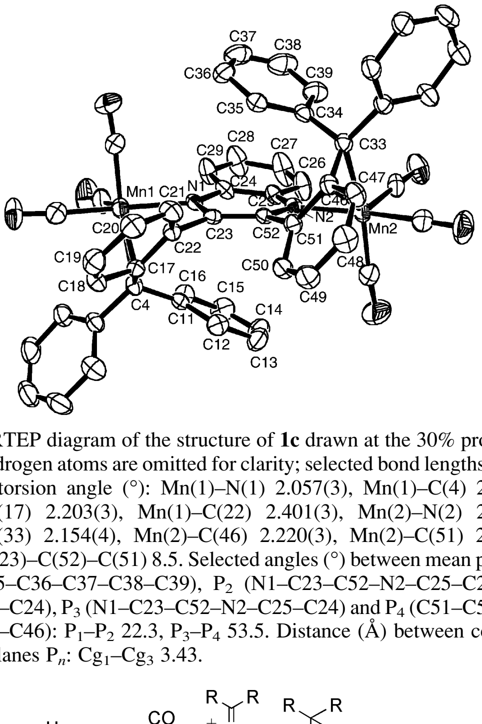
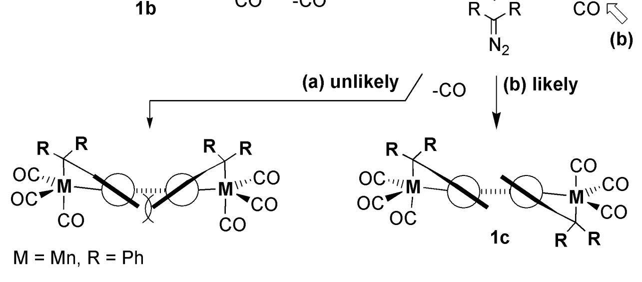


Fig. 1 ORTEP diagram of the structure of **1c** drawn at the 30% probability level. Hydrogen atoms are omitted for clarity; selected bond lengths (Å) and absolute torsion angle (°): Mn(1)–N(1) 2.057(3), Mn(1)–C(4) 2.161(4), Mn(1)–C(17) 2.203(3), Mn(1)–C(22) 2.401(3), Mn(2)–N(2) 2.043(3), Mn(2)–C(33) 2.154(4), Mn(2)–C(46) 2.220(3), Mn(2)–C(51) 2.388(3); C(22)–C(23)–C(52)–C(51) 8.5. Selected angles (°) between mean planes P$_1$ (C34–C35–C36–C37–C38–C39), P$_2$ (N1–C23–C52–N2–C25–C26–C27–C28–C29–C24), P$_3$ (N1–C23–C52–N2–C25–C24) and P$_4$ (C51–C50–C49–C48–C47–C46): P$_1$–P$_2$ 22.3, P$_3$–P$_4$ 53.5. Distance (Å) between centroids, Cg$_n$, of planes P$_n$: Cg$_1$–Cg$_3$ 3.43.



Scheme 1 Two pathways in the sequential addition of Ph$_2$CN$_2$ to **1b**.

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† Electronic supplementary information (ESI) available: preparation procedure and spectroscopic data for **1b–d**, crystal data for polymer **1e**. See http://www.rsc.org/suppdata/cc/b1/b111570g

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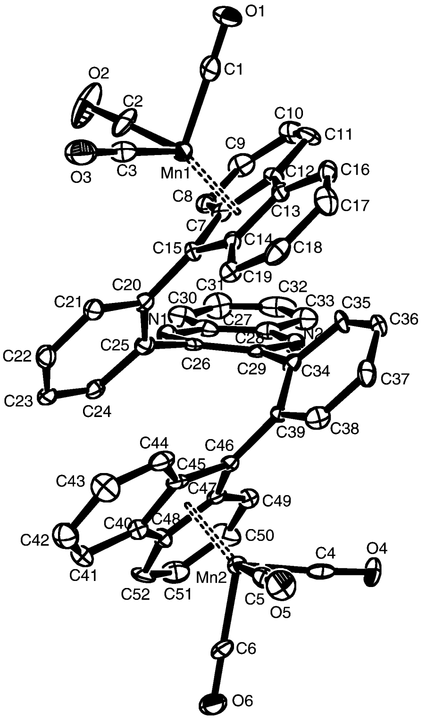
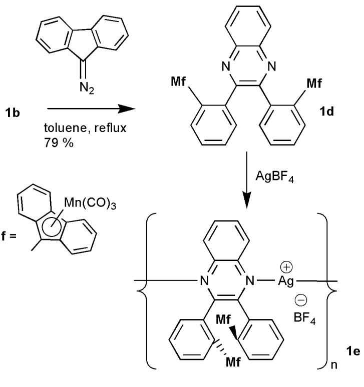


Fig. 2 ORTEP diagram of the structure of **1d** drawn at the 40% probability level. Hydrogen atoms and solvated CH_2Cl_2 are omitted for clarity; selected bond lengths (Å) and angles (°): Mn(1)–C(15) 2.147(8), Mn(1)–C(7) 2.190(7), Mn(1)–C(14) 2.201(7), Mn(1)–C(13) 2.207(7), Mn(1)–C(12) 2.233(7); C(14)–C(15)–C(7) 105.5(6), C(15)–C(14)–C(13) 110.5(6), C(14)–C(13)–C(12) 106.8(7), C(13)–C(12)–C(7) 107.9(6). Angle (°) between mean planes P_1 (C12–C13–C14–C15–C7) and P_2 (C34–C35–C36–C37–C38–C39): 12.7(4). Distance (Å) between centroids, Cg_n, of planes P_n: Cg_1–Cg_2 3.70.

two terminal (η^5-fluorenyl)Mn$(CO)_3$ fragments.† In agreement with analogous observations made for the reaction of XRe$(CO)_3L_3$ with $C_5H_4N_2$,[9] complex **1d** likely results from the formal insertion of a fluorenylidene moiety into the C_{Ar}–Mn bond and a succession of subsequent haptotropic shifts that end by forming the final appended bis(η^5-fluorenyl)Mn$(CO)_3$ complex (Scheme 2). The structure of **1d** is helical in shape as a result of the compact arrangement of the three central 1,2-disubstituted aromatics (Fig. 2). The two Mn$(CO)_3$ moieties point outwards to minimize steric interactions and allow stabilising intramolecular π–π stacking.

The reaction of **1d** with stoichiometric amounts of $AgBF_4$ in acetone cleanly afforded a new bright red linear hybrid inorganic/organometallic polymer[10] **1e** (Scheme 2).† Slow recrystallisation of a crude sample of **1e** from a THF–MeOH solution by diffusion in n-heptane afforded red crystals. X-Ray diffraction analysis showed that polymer **1e**, spontaneously crystallises as a conglomerate in the non-centrosymmetric space group $P2_12_12_1$. Similarly to **1d**, the pentacyclic ligand of the polymer **1e** adopts a helical shape.



Scheme 2 Reaction of **1b** with 9-diazofluorene and reactivity of the product **1d** towards coordination to Ag^+.

This study shows that bis-cyclomanganated 2,3-diphenyl-1,4-diazabenzene compounds, through exaltation of their intrinsic prohelicity, are convenient substrates for the stereoselective elaboration of helical molecules.

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Notes and references

‡ For compounds **1c–e**, the intrinsic low quality of the analysed crystals yielded structures with poor resolution. *Crystal data* for **1c**: $C_{52}H_{32}Mn_2N_2O_6$, M = 890.72, monoclinic, $P2_1/n$, a = 15.6887(7), b = 16.7698(9), c = 15.9857(7) Å, β = 93.588(5)°, V = 4197.5(3) Å^3, Z = 4, D_c = 1.41 g cm^{-3}, μ = 0.657 mm^{-1}, $F(000)$ = 1824, λ(MoKα) = 0.71073 Å, T = 294 K, dark blue, dimensions 0.20 × 0.14 × 0.10 mm. A total of 16 708 reflections were collected with $2.5 < \theta(°) < 27.51$. R = 0.035, R_w = 0.040, GOF = 1.040, maximum residual electron density 0.289 e Å^{-3}. 3947 unique reflections had intensities $I > 3\sigma(I)$. CCDC reference number 176859.

For **1d**: $C_{52}H_{28}Mn_2N_2O_6 \cdot CH_2Cl_2$, M = 971.62, orthorhombic, $Pbca$, a = 14.8379(2), b = 35.4532(3), c = 16.3322(5) Å, V = 8591.6(3) Å^3, Z = 8, D_c = 1.50 g cm^{-3}, μ = 0.769 mm^{-1}, $F(000)$ = 3952, λ(MoKα) = 0.71073 Å, T = 173 K, yellow, dimensions 0.16 × 0.13 × 0.10 mm. A total of 19 157 reflections were collected with $2.5 < \theta(°) < 27.48$. R = 0.051, R_w = 0.082, GOF = 1.415, maximum residual electron density 0.589 e Å^{-3}. 3614 unique reflections had intensities $I > 3\sigma(I)$. CCDC reference number 176860.

For **1e**: $C_{53}H_{31}AgMn_2N_2O_6 \cdot BF_4 \cdot 2CH_3OH$, M = 1176.48, orthorhombic, $P2_12_12_1$, a = 13.6186(5), b = 15.1375(7), c = 25.032(1) Å, V = 5160.5(4) Å^3, Z = 4, D_c = 1.51 g cm^{-3}, μ = 0.930 mm^{-1}, $F(000)$ = 2372, λ(MoKα) = 0.71073 Å, T = 173 K, red, dimensions 0.12 × 0.10 × 0.08 mm. A total of 11 811 reflections were collected with $2.5 < \theta(°) < 27.48$. R = 0.058, R_w = 0.080, GOF = 1.513, maximum residual electron density 0.959 e Å^{-3}. 3656 unique reflections had intensities $I > 3\sigma(I)$. CCDC reference number 176861.

See http://www.rsc.org/suppdata/cc/b1/b111570g/ for crystallographic data in CIF or other electronic format.

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