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Synthesis and properties of a new class of nitrogen-rich multinuclear[m.n] ferrocenophanes†

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The synthesis of the first tetraaza[3,3]ferrocenophane, from the previously unreported 1,1′-bis(triphenylphosphoranylidenamino)ferrocene and its conversion into a nitrogen-rich [2,2]bis-[3,3]ferrocenophane is described. The electronic behaviour of these multinuclear ferrocenophanes indicates a strong electronic coupling between the iron centers.

In recent years, transition-metal mixed-valence (MV) compounds have played an important role in the study of intramolecular electron transfer.[1] The physical properties of rigid-rod π-conjugated molecules such as biferrocenes and [m.n]ferrocenophanes linked by π-bridges are determined predominantly by the extent of delocalization and by electronic interactions between the iron centers.[2] Within this wide area of research, compounds containing a bridging sp-carbon chain (oligoynes or cumulenes) between ferrocenyl moieties have received considerable attention,[3] but despite of this rich chemistry no multinuclear [m.n]ferrocenophanes bridged by cumulenic or heterocumulenic chains have been reported previously.[4]

We wish to report here the synthesis of the first [3.3.]ferrocenophane in which the ferrocenyl termini are directly attached by carbodiimide functions and its easy derivatization to an extremely nitrogen-rich bisferrocenophane with an unprecedented topology.

The aza-Wittig protocol is the method of choice for building up the carbodiimide moieties so that a reliable procedure for the synthesis of the previously unreported bis(iminophosphorane) **2** was needed.

The bis(iminophosphorane) **2** is readily prepared by the Staudinger reaction between triphenylphosphine and 1,1′-diazidoferrocene **1**, which has been prepared from ferrocene by using 2,4,6-triisopropylbenzenesulfonyl azide (trisylazide) as a strong azide-transfer reagent. Thus, reaction of 1,1′-dilithioferrocene with trisylazide at 0 °C afforded directly **1**, which was used without further purification for the next step in the Staudinger reaction with triphenylphosphine. This procedure allows the one-flask conversion of ferrocene into the bis(iminophosphorane) **2** in an overall yield of 59%.

Interestingly, the aza-Wittig reaction between the bis(iminophosphorane) **2** and carbon dioxide gave the bis(carbodiimide) **3** directly, with an unprecedented tetraaza[3,3]-ferrocenophane framework, in 65% yield, but it has not been possible to date to separate it completely from the oligomers that also form. In order to obtain **3** in better yield, 1,1′-bis(isocyanato)ferrocene[5] was used and gave compound **3** as the only reaction product in 88% yield.

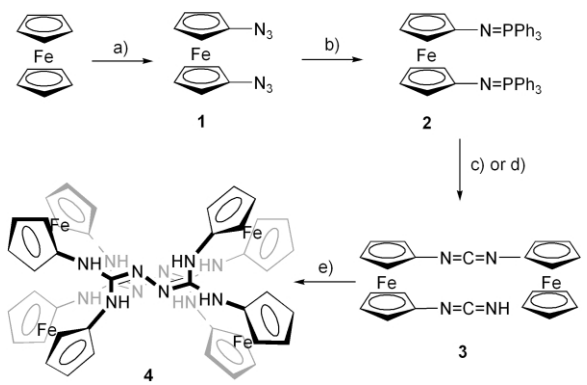
In spite of the fact that **3** is a crystalline compound, several attempts to obtain single crystals failed. To rationalize the properties of **3**, we decided to perform calculations at the DFT[6] level of theory. The resulting optimized geometry for the lower potential energy and higher symmetry isomer $\mathbf{3}_{D2}$ has a helical-chiral conformation belonging to the D_2 symmetry group, both ferrocene subunits being nearly orthogonal relative to each other ("twist" form). The other local minimum $\mathbf{3}_{C2}$ consists of a *syn* arrangement of the ferrocenes around both carbodiimide moieties with axial chirality having overall C_2 symmetry. The thermodynamically more stable $\mathbf{3}_{C1}$ isomer, with a distance between the two iron atoms of 6.755 Å, is derived from any of the other ground states through just only one carbodiimide N-inversion process.

Reaction of [3,3]ferrocenophane **3** with hydrazine in dichloromethane yielded the 2:2 adduct **4** in 64% yield. This extremely nitrogen-rich, 12 nitrogen atom, ferrocene derivative could be considered as a new class of ferrocenophane namely a [2.2]bis-[3.3]ferrocenophane in which the organometallic fragments are linked by four guanidine moieties. HR-FAB$^+$ mass spectrum of **4** displays an intense isotopic cluster peaking at *m/z* 961.099 assignable to the molecular ion. The relative abundance of the isotopic cluster is in good agreement with the simulated spectrum. The ^{1}H-NMR spectrum exhibits in the ferrocene region six signals in 1:1:1:2:1:2 ratio, showing the pairwise magnetic equivalence of the ferrocene units.

Due to the large number of heavy atoms, thus precluding DFT investigation, the structure of the tetrakisguanidino-ferrocenephane **4** has been calculated only at the semi-empirical PM3(d) level. The four Fe atoms are arranged almost co-planar in a rectangular fashion with Fe···Fe distances of 4.216 and 8.355 Å for the short and large sides, respectively.

The redox potential of **2**, determined by cyclic voltammetry (CV), at $E_{1/2} = -0.84$ V *vs* ferrocene/ferrocenium (Fe/Fe$^+$) couple is the most negative shift in redox potential observed for a ferrocene derivative. This large cathodic shift is due to the high degree of electron donation from the iminophosphorane groups and is higher than those observed in 1,1′-diaminoferrocene ($E_{1/2} = -0.60$ V *vs* Fe/Fe$^+$),[7] 1,1′-bis(dimethylamino)ferrocene ($E_{1/2} = -0.63$ V *vs* Fe/Fe$^+$),[8] decamethylferrocene ($E_{1/2} = -0.63$ V *vs* Fe/Fe$^+$),[9] and 1,1′-bis(trimethylsilylamino)ferrocene ($E_{1/2} = -0.51$ V *vs* Fe/Fe$^+$).[10]

The cyclic voltammogram of **3**, in dichloromethane (Fig. 2a), displays two reversible one-electron oxidation waves at a formal potential of +0.09 and +0.29 V *vs* Fe/Fe$^+$, indicating that the first



Scheme 1 Synthesis of **3** and **4**.‡ Reagents: a) n-BuLi, TMEDA, diethyl ether, rt, then 0 °C and trisylazide; b) Ph_3P, CH_2Cl_2, rt; c) 1,1′-bis(isocyanato)ferrocene, THF, rt, 88%; d) CO_2, THF, rt, 65%; e) N_2H_4; CH_2Cl_2, rt.

† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b3/b313797j/

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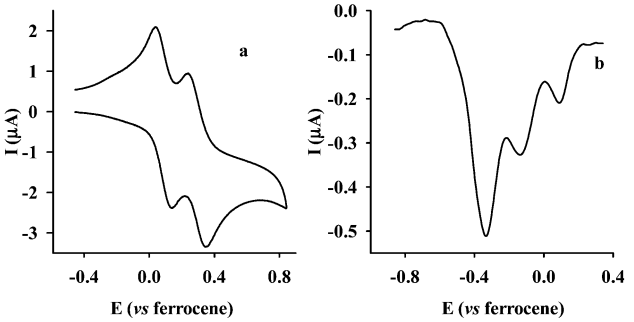

Fig. 2 a) Cyclic voltammogram of compound **3** (1 mM) in CH_2Cl_2/Bu_4NClO_4 scanned at 0.2 V s^{-1}. b) Differential pulsed voltammetry of compound **4** (0.5 mM) in DMF/Bu_4NClO_4; 50 mV, pulse amplitude; 50 ms. pulse width; 1 s, pulse period; 4 mV s^{-1} scan rate.

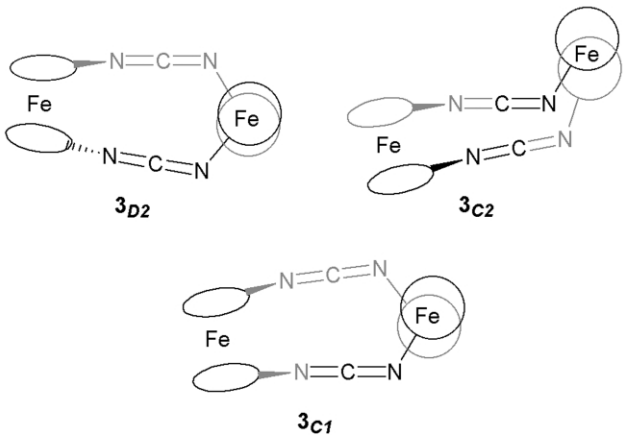

Fig. 1 Schematic representation of the three stereoisomers.

oxidation yields a mixed-valence compound stabilised by delocalization over both ferrocene groups. The separation between the waves of $\Delta E_{1/2}$ = 200 mV, which indicates that the mixed-valence compound is thermodynamically stabilised towards disproportionation to give **3** and $\mathbf{3}^{2+}$ by the comproportionation constant of $K_c = 2.4 \times 10^3$ which suggests that **3** is a Class II derivative.[11]

The chemical reversibility of the oxidation process and the value of the comproportionation constant obtained for **3** indicated that the mixed-valence complex $\mathbf{3}^+$ constituted an accessible synthetic target. Thus, by addition of 0.5 equivalents of silver trifluoromethanesulfonate to a toluene solution of **3**, an analytically pure sample of $\mathbf{3}^+$ was obtained and studied by Mössbauer and IR spectroscopies.

The ^{57}Fe Mössbauer spectra at both 80 and 298 K show two doublets, one with a quadrupole splitting (ΔE_Q) of ~ 2.3 mms^{-1} (Fe^{II} metallocene) and the other with ΔE_Q ~ 0.5 mms^{-1} (Fe^{III} metallocene). This pattern of two doublets is what is expected for a mixed-valence biferrocenium cation which is valence trapped on the time scale of the Mössbauer technique (electron-transfer rate < 10^7 s^{-1}). The isomer shift of the doublets are typical of substituted ferrocenes.

Previous IR studies on mixed-valence biferrocenes indicated that a localized mixed-valence biferrocenium cation should exhibit one C–H bending band for the Fe^{II} ferrocenyl moiety and another one for the Fe^{III} ferrocenium moiety,[12] while only one averaged band is expected for delocalized mixed-valence species. In our case, the IR spectrum of the neutral form **3** displays a C–H bending vibration band at 810 cm^{-1}, while in the mixed-valence biferrocenium cation $\mathbf{3}^+$ two bands appear at 819 and 830 cm^{-1}, consistent with a localized system.

The differential pulse voltammetry (DPV) of **4**, in DMF, shows three well-resolved peaks in the ratio 2:1:1 (Fig. 2b). The first process with a potential defined as $E^o_{1,2}$ at −0.31 V *vs* Fe/Fe^+ couple, is actually two closely overlapping one-electron transfer processes centered at the non-adjacent ferrocenes. The smaller peaks at E^o_3 = −0.09 and E^o_4 = +0.14 V *vs* Fe/Fe^+ respectively consist of remaining ferrocene-centered redox processes. Interestingly, the separation between the first and second peaks ($\Delta E_{1/2}$ = 220 mV) is almost the same as the separation between the second and third ($\Delta E_{1/2}$ = 230 mV). These data indicate for the first time that an effective electronic coupling exists between the iron centers, which is mediated by the guanidino bridges; in the absence of any interaction one would expect one peak corresponding to the only ferrocene environment present.

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Notes and references

‡ All new compounds were fully characterized by elemental analysis, IR, MS, ^{1}H- and ^{13}C-NMR and HMQC experiments.

1 (*a*) R. D. Cannon and R. P. White, *Prog. Inorg. Chem.*, 1988, **36**, 195–298; (*b*) I. Manners, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1620–1621; (*c*) B. Groβman, J. Heinze, E. Herdtweg, F. H. Kohler, H. Nöth, H. Schwenk, M. Spiegler, W. Wachter and B. Weber, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 387–389; (*d*) M. Hissler, A. Elgharyoury, A. Harriman and R. Ziessel, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 1717–1720; (*e*) K. D. Demadis, C. M. Hartshorn and T. J. Meyer, *Chem. Rev.*, 2001, **101**, 2655–2685.

2 Review article: S. Barlow and D. O'Hare, *Chem. Rev.*, 1997, **97**, 637–639.

3 (*a*) C. Levanda and D. O. Cowan, *J. Am. Chem. Soc.*, 1974, **96**, 6728–6789; (*b*) M. Rosenblum, N. M. Brawn, J. Papenmeier and M. Applebaum, *J. Organomet. Chem.*, 1966, **6**, 173–180; (*c*) K. Schlögl and H. Egger, *Monatsh. Chem.*, 1963, **94**, 376–392; (*d*) Z. Yuan, G. Stringer, R. Jobe, D. Kreller, K. Scott, L. Koch, N. J. Taylor and T. B. Marder, *J. Organomet. Chem.*, 1993, **452**, 115–120.

4 For perferrocenylated cumulenes see: B. Bildstein, *Coord. Chem. Rev.*, 2000, **206–207**, 369–394. For diferrocenyl carbodiimide see: K. Schlögl and H. Mechtler, *Angew. Chem., Int. Ed. Engl.*, 1996, **5**, 596.

5 P. M. Petrovitch, *Double Liaison*, 1996, **133**, 1093; P. M. Petrovitch, *Chem. Abstr.*, 1968, **68**, 29843s.

6 (*a*) E. J. Baerends, D. E. Ellis and P. Ros, *Chem. Phys.*, 1973, **2**, 41–51; (*b*) W. Kohn, A. D. Becke and R. G. Parr, *J. Phys. Chem.*, 1996, **100**, 12974–12980.

7 A. Shafir, M. P. Power, G. D. Whitener and J. Arnold, *Organometallics*, 2000, **19**, 3978–3982.

8 K.-P. Stahl, G. Boche and W. Massa, *J. Organomet. Chem.*, 1984, **277**, 113–125.

9 M. F. Ryan, D. E. Richarson, D. L. Lichtenberger and N. E. Gruhn, *Organometallics*, 1994, **13**, 1190–1199.

10 A. Shafir, M. P. Power, G. D. Whitener and J. Arnold, *Organometallics*, 2001, **20**, 1365–1369.

11 (*a*) M. Robin and P. Day, *Adv. Inorg. Radiochem.*, 1967, **10**, 247–427; (*b*) C. Creutz, *Prog. Inorg. Chem.*, 1983, **30**, 1–71.Mixed-valence compounds are classified in three categories. Class I: the redox centers are completely localized and behave as separated entities. Class II: intermediate coupling between the mixed-valence centers exits. Class III: the system is completely delocalized and the redox centers show intermediate valence states.

12 (*a*) T.-Y. Dong, C.-K. Chang, S.-H. Lee, L.-L. Lai, M. Y.-N. Chiang and K.-J. Lin, *Organometallics*, 1997, **16**, 5816–5825; (*b*) T.-Y. Dong, D. N. Hendrickson, K. Iwai, M. J. Cohn, A. L. Rheingold, H. Sano and S. Motoyama, *J. Am. Chem. Soc*, 1985, **107**, 7996–8008.