[1] a) D. Braga, F. Grepioni, G. R. Desiraju, *Chem. Rev.* **1998**, *98*, 1375; b) P. F. H. Schwab, M. D. Levin, J. Michl, *Chem. Rev.* **1999**, *99*, 1863; c) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* **2000**, *100*, 853; d) T. Nakajima, A. Ishiguro, Y. Wakatsuki, *Angew. Chem.* **2001**, *113*, 1096; *Angew. Chem. Int. Ed.* **2001**, *40*, 1066.

[2] a) N. C. Norman, *Chem. Soc. Rev.* **1988**, *17*, 269–281; b) L. D. Freedman, G. O. Doak, Chem. Rev. **1982**, *82*, 15; c) N. A. Compton, R. J. Errington, N. C. Norman, *Adv. Organomet. Chem.* **1990**, *31*, 91; d) C. Silvestru, H. J. Breunig, H. Althaus, *Chem. Rev.* **1999**, *99*, 3277; e) D. F. Shriver, H. D. Kaesz, R. D. Adams, *The Chemistry of Metal Cluster Complexes*, VCH, New York, **1990**.

[3] C. Coin, T. Zevaco, E. Dunach, M. Postel, *Bull. Soc. Chim. Fr.* **1996**, *133*, 913.

[4] a) P. Majewski, *Adv. Mater.* **1994**, *6*, 460; b) R. D. Rogers, A. H. Bond, S. Aguinaga, *J. Am. Chem. Soc.* **1992**, *114*, 2960; c) S. Wang, D. B. Mitzi, G. A. Landrum, H. Genin, R. Hoffmann, *J. Am. Chem. Soc.* **1997**, *119*, 724; d) A. Ekstrand, M. Nygren, G. Westin, *J. Sol-Gel Sci. Technol.* **1997**, *8*, 697; e) F. Soares-Carvalho, P. Thomas, J. P. Mercurio, B. Frit, S. Parola, *J. Sol-Gel Sci. Technol.* **1997**, *8*, 759.

[5] K. H. Whitmire, J. C. Hutchison, A. McKnight, C. M. Jones, *J. Chem. Soc. Chem. Commun.* **1992**, 1021.

[6] J. R. Eveland, J.-Y. Saillard, K. H. Whitmire, *Inorg. Chem.* **1997**, *36*, 4387.

[7] M. Shieh, Y. Liou, B.-W. Jeng, *Organometallics* **1993**, *12*, 4926.

[8] **1**: $C_8H_9BiFeO_4$, $M_r = 433.98$, monoclinic, space group $C2$, $a = 17.347(6)$, $b = 7.152(2)$, $c = 9.523(5)$ Å, $\beta = 92.96(4)^\circ$, $V = 1179.9(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.443$ g cm^{-3}, $\mu = 16.109$ mm^{-1}, $\lambda = 0.70930$ Å, transmission range 0.54–1.00, crystal dimensions about $0.40 \times 0.50 \times 0.60$ mm^3. A total of 1134 unique reflections were collected on a Nonius (CAD-4) diffractometer at 298 K in the 2θ range 2.0–50°. Full-matrix least-squares refinement on F^2 converged to $R = 0.0628$ (all data), 0.0542 ($I > 2\sigma(I)$); $wR = 0.1763$ (all data), 0.1635 ($I > 2\sigma(I)$). All calculations were performed by using SHELXTL packages. CCDC-177971 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[9] J. E. Huheey, *Inorganic Chemistry*, 3rd ed., Harper&Row, New York, **1983**, p. 258.

[10] K. H. Whitmire, C. B. Lagrone, M. R. Churchill, J. C. Fettinger, L. V. Biondi, *Inorg. Chem.* **1984**, *23*, 4227–4232.

[11] K. H. Whitmire, M. Shieh, C. B. Lagrone, B. H. Robinson, M. R. Churchill, J. C. Fettinger, R. F. See, *Inorg. Chem.* **1987**, *26*, 2798–2807.

[12] W. Clegg, N. A. Compton, R. J. Errington, G. A. Fisher, N. C. Norman, N. Wishart, *J. Organomet. Chem.* **1990**, *399*, C21.

[13] K. H. Whitmire, M. Shieh, J. Cassidy, *Inorg. Chem.* **1989**, *28*, 3164.

[14] M. Shieh, Y. Liou, S.-M. Peng, G.-H. Lee, *Inorg. Chem.* **1993**, *32*, 2212.

[{Fe(OMe)$_2$[O$_2$CC(OH)Ph$_2$]}$_{12}$]: Synthesis and Characterization of a New Member in the Family of Molecular Ferric Wheels with the Carboxylatobis(alkoxo) Bridging Unit**

Catherine P. Raptopoulou,* Vassilis Tangoulis, and Eamon Devlin

High-nuclearity transition-metal clusters continue to attract a great deal of interest, partly because of their fascinating physical properties and partly for the architectural beauty of their structures. An interesting subarea of 3d metal cluster chemistry is the small but growing family of molecules that have circular structures. Large cyclic polymetallic clusters are valued for their ability to mimic the properties of linear coordination polymers.[1] For example, theories developed for analyzing magnetically coupled ring systems have been extensively applied to calculate the thermodynamic properties of 1D materials.[2] Furthermore, the chemistry of circular molecular clusters is also associated with supramolecular chemistry. Anion and cation recognition provide the possibility of controlling the size of clusters. A representative example of this approach is the ability to address the synthesis of molecular rings by exploiting host–guest interactions with alkali-metal cations, because alkali-metal cations are hosted by rings of different size. Thus, hexairon(III)[3–5] and hexamanganese(III)[6] complexes with cyclic M_6O_{12} cores can easily accommodate Li^+ and Na^+ ions, both in the solid state and in solution, whereas Cs^+ ions require larger rings, such as M_8O_{16}.[5]

Metal rings have excited mankind since mythological times.[7] The largest cyclic structure containing exclusively paramagnetic 3d metals is the Ni^{II}_{24} wheel reported by Winpenny and co-workers,[8] which is approximately an order of magnitude smaller that the giant wheels constructed from molybdate fragments by the Müller group;[9] a Ni^{II}_{12} wheel is also known.[10] Large, cyclic, polymetallic arrangements of other 3d metals, either unsupported or supported (by ions or molecules as guests), have been found for chromium(III),[11] manganese(III),[12] iron(II),[13] iron(III),[12,14] cobalt(II),[15] and copper(II).[16]

Restricting further discussion to the so-called ferric wheels with nuclearities equal to or higher than ten, the structurally characterized complexes that contain O-donor groups as bridging ligands are [{Fe(OMe)$_2$(O$_2$CCH$_2$Cl)}$_{10}$][14a] [{Fe(OMe)$_2$(O$_2$CMe)}$_{10}$][14b] [{Fe(OMe)$_2$L}$_{10}$][14c] where L$^-$ is

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the monoanion of 3-(4-methylbenzoyl)propionic acid, $[\{\mathrm{Fe(OMe)_2(dbm)}\}_{12}]$,[14d] where dbm$^-$ is the dibenzoylmethanato ligand, and $[\{\mathrm{Fe(OH)(XDK)Fe_2(OMe)_4(O_2CMe)_2}\}_6]$,[14e] where XDK^{2-} is the ion of *m*-xylylenediamine bis(Kemp's triacid imide). All three $\mathrm{Fe}^{\mathrm{III}}_{10}$ wheels contain chemically equivalent (μ-$\mathrm{O_2CR}$)(μ-OMe)$_2$ units, while the $\mathrm{Fe}^{\mathrm{III}}_{12}$ wheel contains chemically equivalent (μ-OMe)$_2$ units. The repeating unit in the $\mathrm{Fe}^{\mathrm{III}}_{18}$ cluster, known as the molecular 18-wheeler, comprises a (μ-hydroxo)bis(μ-carboxylato)diiron(III) moiety linked by an acetate and two methoxide ions to a third iron(III) atom; an acetate and two additional methoxide ligands on this iron center form bridges to the next trinuclear repeating unit in the cluster.[14e]

The family of ferric wheels with the (μ-$\mathrm{O_2CR}$)(μ-OR$'$)$_2$ unit is restricted to decanuclear complexes.[14a–c] We wondered whether change of the carboxylato or/and alkoxo ligands would influence the size of these wheels and permit the isolation of larger wheels. The main driving force behind our efforts was our desire to test the general belief[8] that it is not possible to generate a large 3d-metal wheel with only one type of bridging interaction. For example, while $\mathrm{Fe}^{\mathrm{III}}_{10}$ wheels can be accurately described as $[\{\mathrm{Fe(OMe)_2(O_2CR)}\}_{10}]$ (R = Me, $\mathrm{CH_2Cl}$, $\mathrm{CH_2CH_2C(O)C_6H_4Me}$) and $\mathrm{Cr}^{\mathrm{III}}_8$ wheels[11] can be described as $[\{\mathrm{CrX(O_2CR)}\}_8]$ (X = F, R = $\mathrm{CMe_3}$; X = OH, R = Ph), such a description as an oligomer of a mononuclear fragment is not accurate for larger wheels. For both the $\mathrm{Fe}^{\mathrm{III}}_{18}$ [14e] and $\mathrm{Ni}^{\mathrm{II}}_{24}$[8] wheels mentioned above, a more accurate description is as an oligomer of trinuclear building blocks. Herein we report the isolation and characterization of the unique $x = 12$ member of the $[\{\mathrm{Fe(OR')_2(O_2CR)}\}_x]$ family of ferric wheels. Since it has been recently pointed out[8, 16b] that utilization of strong interligand hydrogen bonds might be an important feature in generating large wheel-shaped clusters, we decided to employ carboxylate ligands containing suitable hydrogen-bond donor groups.

The 1:2 reaction of $\mathrm{Fe(NO_3)_3 \cdot 9\,H_2O}$ with benzilic acid, $\mathrm{Ph_2C(OH)COOH}$, in MeOH under reflux at pH ≈ 4 gave a microcrystalline solid. Diffusion of $\mathrm{Et_2O}$ into the yellow methanolic filtrate resulted in yellow crystals of $[\{\mathrm{Fe(OMe)_2[O_2CC(OH)Ph_2]}\}_{12}] \cdot 2\,\mathrm{H_2O} \cdot \mathrm{Et_2O}$ ($\mathbf{1} \cdot 2\,\mathrm{H_2O} \cdot \mathrm{Et_2O}$) formed over a period of four weeks. The initially precipitated solid was characterized as compound **1** by microanalysis and IR spectroscopy.

Single-crystal X-ray crystallography[17] showed complex **1** to be a dodecanuclear ferric wheel. The molecular structure (Figure 1) consists of a centrosymmetric ring of twelve $\mathrm{Fe^{III}}$ atoms held together by twenty-four μ_2-methoxide ligands and twelve 1,3-bridging carboxylate ligands. Each iron(III) atom has a distorted octahedral geometry and is joined to its neighbors by edge-sharing methoxide and *cis*-carboxylate bridges. The twelve iron centers are nearly coplanar, with an average deviation of ≈0.48 Å from the best least-squares plane through them. In contrast, in the cyclic dodecanuclear compound $[\{\mathrm{Fe(OMe)_2(dbm)}\}_{12}]$,[14d] which contains bis(μ-methoxo) units, the ring defined by the iron(III) atoms is not planar and the structure is best described as a twisted "ribbon".

The benzilate(−1) ion has the possibility of further interaction with the iron(III) centers through the hydroxyl oxygen atom, but, in the case of **1**, this potential is not realized and the ligand is merely bidentate, spanning metal–metal vectors in a 1,3-bridging mode.

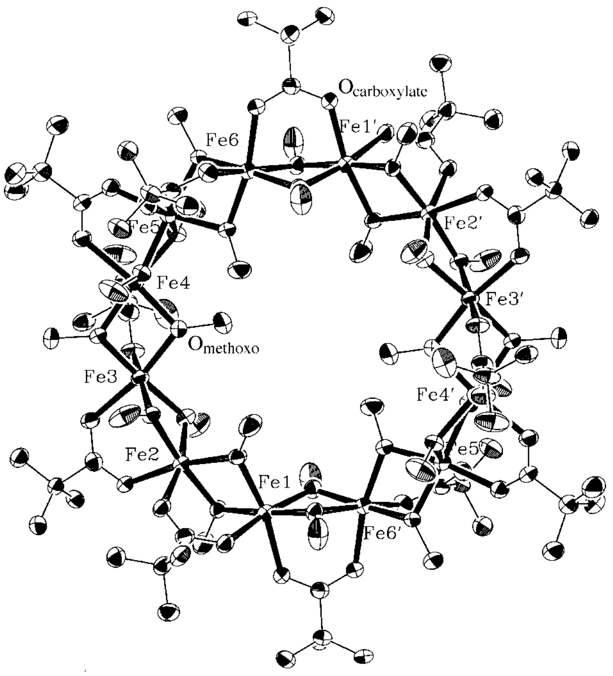

Figure 1. Molecular structure of **1**. For clarity, only the *ipso* carbon atom of each phenyl ring is shown. An inversion center relates the primed atoms to the unprimed ones. Interatomic distances [Å]: Fe ··· Fe = 3.013(1)–11.634(1), $\mathrm{Fe\text{-}O_{methoxo}}$ = 1.962(5)–1.990(5), $\mathrm{Fe\text{-}O_{carboxylate}}$ = 2.001(5)–2.100(5).

A side view of **1** is shown in Figure 2. The methoxo ligands are arranged above and below the ring defined by the iron(III) atoms. The benzilate ligands can be divided into two groups of six members each. The carboxylate moieties of the first group almost lie in the plane of the twelve metal ions (average displacement of the carboxylate oxygen atoms: 0.39 Å), while those of the second group are arranged above and below the metal ring (average displacement of the carboxylate oxygen atoms: 2.35 Å) in an alternating fashion between the carboxylate groups belonging to the first group.

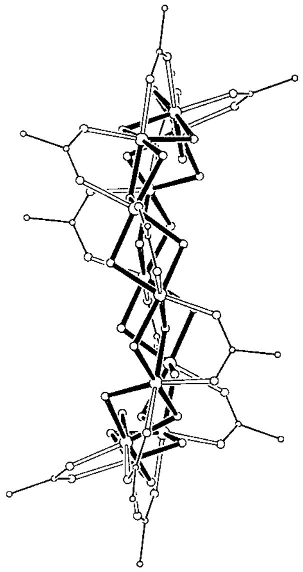

Figure 2. ORTEP diagram of a side view of **1**. Empty bonds show the arrangement of the benzilate(−1) ligands with respect to the mean plane of the iron(III) atoms (larger empty circles).

The closest Fe ··· Fe distances are almost identical in **1** ranging from 3.013 to 3.030 Å, very similar to those found in $[\{\mathrm{Fe(OMe)_2(O_2CCH_2Cl)}\}_{10}]$[14a] (average value: 3.028 Å) and shorter than the distances found[14d] in $[\{\mathrm{Fe(OMe)_2(dbm)}\}_{12}]$ (average value: 3.136 Å). The ring size in **1**, calculated by averaging the distances between iron(III) atoms on opposite sides of the ring is 11.41 Å, larger than the 9.80 and 10.34 Å values found in $[\{Fe(OMe)_2(O_2CCH_2Cl)\}_{10}]$[14a] and $[\{Fe(OMe)_2(dbm)\}_{12}]$,[14d] respectively. This difference in the ring size between the latter and **1** is a consequence of the difference in the Fe ⋯ Fe ⋯ Fe angles. These angles range from 142.6 to 146.3° in **1**, very close to the ideal 150° value required by ring-closure considerations for a planar, 12-membered ring, and from 117.3 to 136.2° in $[\{Fe(OMe)_2(dbm)\}_{12}]$[14d] (very close to the optimum value of 120° for a structure based on edge-sharing octahedra).

Complex **1** is one of the two largest cyclic ferric clusters yet reported with chemically equivalent bridging units, the other being $[\{Fe(OMe)_2(dbm)\}_{12}]$.[14d] The small family of the dodecanuclear iron clusters with exclusively O ligation also includes two $Fe^{II}_8Fe^{III}_4$ oxo/carboxylate complexes;[18a,b] these two clusters do not have cyclic structures.

The Mössbauer spectrum of a polycrystalline sample of **1** at room temperature (Figure 3) reveals a single quadrupole doublet with an isomer shift of 0.41(1) mm s^{-1} (referenced versus iron foil at room temperature) and a quadrupole splitting of 0.65(1) mm s^{-1}. The isomer-shift value is within the range expected for high-spin iron(III) centers in a non-sulfur environment.[19] The ΔE_Q value indicates a slightly unsymmetrical electric field, consistent with the variations in Fe–O bond distances revealed by the X-ray investigations.[17] The width at half height is 0.15(1) mm s^{-1}.

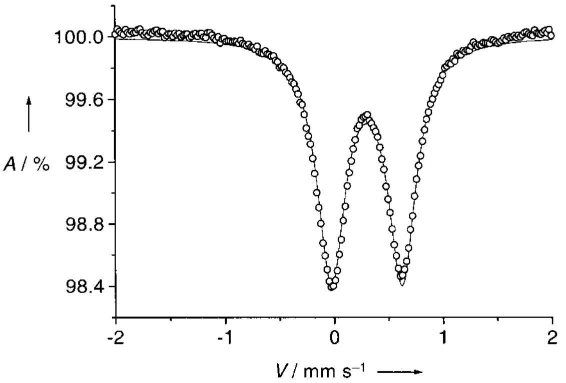

Figure 3. Mössbauer spectrum of polycrystalline **1** at room temperature. —— is the best fit to the data with the spectral parameters mentioned in the text.

The magnetic susceptibility of **1** is indicative of antiferromagnetic interactions between the high-spin iron(III) ions ($S = 5/2$). The broad maximum at 60 K in the curve (Figure 4) can be nicely fit by a Heisenberg $S = 5/2$ quantum chain model with $J = -10.9$ cm^{-1} and $g = 2.00$ ($H = J\Sigma_i S_i S_j$).[20] The departures from the calculated behavior at low temperature arise from a small percentage of paramagnetic impurity. For a ring of N ions, an energy gap $\Delta E \approx 4J/N = 3.6$ cm^{-1} is predicted between the ground state $S = 0$ and the first excited $S = 1$. The calculated J value is close to that found in other dialkoxo-bridged iron(III) complexes with similar Fe-O-Fe angles.[14a]

In conclusion, the molecular architecture of **1** underscores the ability of synthetic chemistry to enrich our world with objects of beauty.[21] The self-assembly of this complex provides further evidence for the tendency of metal ions linked by alkoxo/hydroxo ligands and *syn,syn* η^2-carboxylate bridges to form large cyclic molecules. Compound **1** is the largest cyclic ferric cluster yet reported with the carboxylatobis(alkoxo) bridging unit. It should be stressed that there are no hydrogen bonds in the structure of this cluster, which could stabilize the wheel providing an extra intramolecular force for its formation. We do not know if **1** is the largest ferric wheel containing this type of bridging interaction. Work is in progress for the preparation of other members of the family of $[\{Fe(OR')_2(O_2CR)\}_x]$ wheels by changing the nature of the R, R′ groups, while simultaneously we are trying to construct still larger wheels using the "oligomerization of high-nuclearity building blocks" design principle.[8]

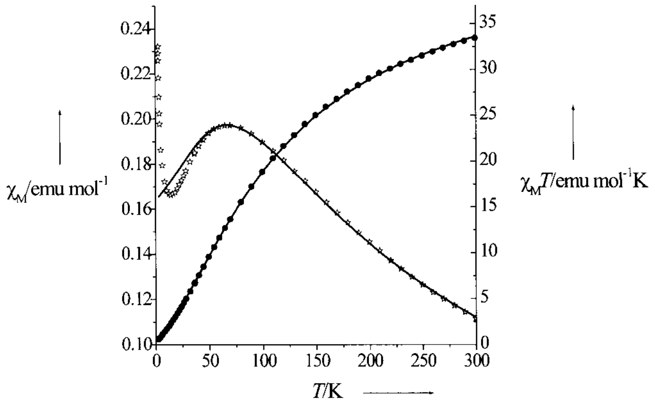

Figure 4. Magnetic susceptibility measurements of **1** in the range 2–300 K at 0.1 T applied magnetic field; (●) refer to $\chi_M T$, stars to χ_M, —— represent the best fit to the data.

Experimental Section

Solid $Ph_2C(OH)COOH$ (0.23 g, 1.0 mmol) was dissolved in a stirred solution of $Fe(NO_3)_3 \cdot 9H_2O$ (0.20 g, 0.5 mmol) in hot MeOH (20 mL). The resulting orange-red solution was heated under reflux for 10 min and then the pH value was adjusted to 4 with a solution of LiOH in MeOH. A color change to yellow occurred. The yellow solution was heated further under reflux for 1 h, during which time a yellow precipitate formed. The solid was collected by filtration, washed with cold MeOH and Et_2O (not added to the filtrate) and dried in vacuum, yield 48 %; elemental analysis calcd (%) for $C_{192}H_{204}O_{60}Fe_{12}$ (**1**): C 55.7, H 5.0; found: C 55.6, H 4.9. Yellow crystals of the product were grown by layering the methanolic filtrate with Et_2O; the formulation $\mathbf{1} \cdot 2H_2O \cdot Et_2O$ was determined crystallographically, but the analytical sample (consisting of washed and vacuum-dried crystals) was analyzed as solvent-free.

Magnetic susceptibility data were collected on microcrystalline samples of **1** with a Cryogenics S600 SQUID magnetometer with an applied field of 0.1 T and in the temperature range 2–300 K. Data were corrected with the standard procedure for the contribution of the sample holder and diamagnetism of the sample. The Mössbauer spectrum of microcrystalline **1** was measured at room temperature by a conventional constant-acceleration spectrometer equipped with a γ-ray source of ^{57}Co in Rh; isomer shifts were referenced versus a thin α-iron foil at room temperature.

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[1] L. J. De Jongh, A. R. Miedema, *Adv. Phys.* **1974**, *23*, 1.

[2] C. J. O'Connor, *Prog. Inorg. Chem.* **1982**, *29*, 203.

[3] G. L. Abbati, A. Cornia, A. C. Fabretti, W. Malavasi, L. Schenetti, A. Caneschi, D. Gatteschi, *Inorg. Chem.* **1997**, *36*, 6443.

[4] A. Caneschi, A. Cornia, A. C. Fabretti, S. Foner, D. Gatteschi, R. Grandi, L. Schenetti, *Chem. Eur. J.* **1996**, *2*, 1379.

[5] R. W. Saalfrank, I. Bernt, E. Uller, F. Hampel, *Angew. Chem.* **1997**, *109*, 2596; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2482.

[6] G. L. Abbati, A. Cornia, A. F. Fabretti, A. Caneschi, D. Gatteschi, *Inorg. Chem.* **1998**, *37*, 1430.

[7] For example, R. W. Wagner, *Das Rheingold*, Schott, Mainz, **1873**.

[8] A. L. Dearden, S. Parsons, R. E. P. Winpenny, *Angew. Chem.* **2001**, *113*, 155; *Angew. Chem. Int. Ed.* **2001**, *40*, 152.

[9] A. Müller, C. Serain, *Acc. Chem. Res.* **2000**, *33*, 2.

[10] A. J. Blake, C. M. Grant, S. Parsons, J. M. Rawson, R. E. P. Winpenny, *J. Chem. Soc. Chem. Commun.* **1994**, 2363.

[11] Representative references are: a) I. M. Atkinson, C. Benelli, M. Murrie, S. Parsons, R. E. P. Winpenny, *Chem. Commun.* **1999**, 285; b) N. V. Gerbeleu, Yu. T. Struchkov, G. A. Timco, A. S. Batsanov, K. M. Indrichan, G. A. Popovich, *Dokl. Akad. Nauk. SSSR* **1990**, *313*, 1459; c) E. J. L. McInnes, C. Anson, A. K. Powell, A. J. Thomson, S. Poussereau, R. Sessoli, *Chem. Commun.* **2001**, 89.

[12] S.-X. Liu, S. Lin, B.-Z. Lin, C.-C. Lin, J.-Q. Huang, *Angew. Chem.* **2001**, *113*, 1118; *Angew. Chem. Int. Ed.* **2001**, *40*, 1084.

[13] For example, D. Fenske, A. Fischer, *Angew. Chem.* **1995**, *107*, 340; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 307.

[14] a) K. L. Taft, C. D. Delfs, G. C. Papaefthymiou, S. Foner, D. Gatteschi, S. J. Lippard, *J. Am. Chem. Soc.* **1994**, *114*, 823; b) C. Benelli, S. Parsons, G. A. Solan, R. E. P. Winpenny, *Angew. Chem.* **1996**, *108*, 1967; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1825; c) M. Frey, S. G. Harris, J. M. Holmes, D. A. Nation, S. Parsons, P. A. Tasker, R. E. P. Winpenny, *Chem. Eur. J.* **2000**, *6*, 1407; d) A. Caneschi, A. Cornia, A. C. Fabretti, D. Gatteschi, *Angew. Chem.* **1999**, *111*, 1372; *Angew. Chem. Int. Ed.* **1999**, *38*, 1295; e) S. P. Watton, R. Fuhrmann, L. E. Pence, A. Caneschi, A. Cornia, G. L. Abbati, S. J. Lippard, *Angew. Chem.* **1997**, *109*, 2917; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2774.

[15] P. L. Jones, K. J. Byrom, J. C. Jeffery, J. A. McCleverty, M. D. Ward, *Chem.Commun.* **1997**, 1361.

[16] a) G. A. Ardizzoia, M. A. Angaroni, G. L. Monica, F. Cariati, S. Cenini, M. Moret, N. Masciocchi, *Inorg. Chem.* **1991**, *30*, 4347; b) C.-H. Chang, K. C. Hwang, C.-S. Liu, Y. Chi, A. J. Carty, L. Scoles, S.-M. Peng, G.-H. Lee, J. Reedijk, *Angew. Chem.* **2001**, *113*, 4787; *Angew. Chem. Int. Ed.* **2001**, *40*, 4651.

[17] Crystal data for **1**: crystal dimensions $0.15 \times 0.30 \times 0.60$ mm, monoclinic, space group $P2_1/c$, $a = 21.14(1)$, $b = 27.16(1)$, $c = 19.274(9)$ Å, $\beta = 104.99(1)^\circ$, $V = 10689(1)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.321$ g cm^{-3}, $2\theta_{\max} = 43.8^\circ$, $\mathrm{Mo}_{K\alpha}$ ($\lambda = 0.710730$ Å), θ-2θ scan, $T = 298$ K, 13445 measured reflections, 12909 independent reflections ($R_{\mathrm{int}} = 0.0268$), 12391 reflections included in the refinement. Lorentz, polarization corrections were applied, $\mu = 0.867$ mm^{-1}, $(\Delta/\sigma) = 0.095$, 1262 parameters refined, $R1 = 0.0624$ (for 8482 reflections with $I > 2\sigma(I)$), $wR2 = 0.1453$ (on F^2). Max./min. residual peaks in the final difference map 0.619/−0.414 e Å^{-3}. A crystal of **1** was mounted in a glass capillary with drops of mother liquor because of its sensitivity to air exposure. The structure was solved by direct methods using SHELXS-86 and refined by full-matrix least-squares techniques on F^2 using SHELXL-93. All non-hydrogen atoms were refined anisotropically, except for the solvent molecules, which were refined isotropically. All hydrogen atoms were introduced at calculated positions as riding on bonded atoms. CCDC-180394 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[18] a) K. L. Taft, G. C. Papaefthymiou, S. J. Lippard, *Science* **1993**, *259*, 1302; b) A. Caneschi, A. Cornia, S. J. Lippard, G. C.Papaefthymiou, R. Sessoli, *Inorg. Chim. Acta* **1996**, *243*, 295.

[19] B. P. Murch, F. C. Bradley, P. D. Boyle, V. Papaefthymiou, L. Que, Jr., *J. Am. Chem. Soc.* **1987**, *109*, 7993.

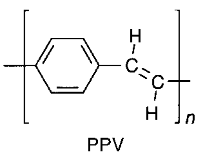
[20] T. Smith, S. A. Friedberg, *Phys. Rev.* **1968**, *176*, 660.

[21] R. Hoffmann, *Sci. Am.* **1993**, *268*, 66.

Poly(*p*-phenylenephosphaalkene): A π-Conjugated Macromolecule Containing P=C Bonds in the Main Chain[**]

Vincent A. Wright and Derek P. Gates*

Approximately twenty years ago, several examples of stable neutral compounds possessing acyclic (p – p) π bonds involving the heavier p-block elements were prepared.[1] Subsequently, the synthesis, structures, and reactivity of numerous low-coordinate molecules has received extensive study and continues to attract considerable attention.[2] Despite current interest in the preparation of organic macromolecules possessing π-conjugated backbones,[3] to our knowledge, the incorporation of heavy-element multiple bonds into a π-conjugated polymer is unprecedented.[4, 5] Furthermore, the incorporation of inorganic elements into the polymer backbone is synthetically challenging and often results in materials with unique properties.[6] Therefore, the development of methods to prepare π-conjugated polymers containing heavier main-group (p – p) π bonds is of fundamental interest, and may ultimately lead to materials with novel properties.[7] The poly(*p*-phenylenevinylene)s (PPVs) are an exciting class of luminescent organic macromolecules containing C=C bonds which pose many synthetic challenges.[3a,c, 8] However, the possible incorporation of other stable multiple bonds, such as the well-established P=C moiety,[9] into the PPV structure has not been explored.[10] Herein, we report the synthesis and characterization of a poly(*p*-phenylenephosphaalkene), a π-conjugated macromolecule containing phosphorus(III) – carbon double bonds in the polymer backbone.



PPV

An elegant and general route to phosphorus(III) – carbon double bonds involves the rapid and thermodynamically favorable [1,3]-silatropic rearrangement of an acylphosphane to a phosphaalkene (Scheme 1).[1a] From a preparative standpoint, this method is probably the most convenient and versatile route to phosphaalkenes with minimal steric protection.[11] We initiated our investigations by preparing model compounds **1** and **2** for the polymer **3**, under conditions chosen to mimic a typical condensation polymerization. Therefore, phosphaalkene **1** was prepared in the absence of solvent by stirring mesitylene-2-carboxylic acid chloride and $\mathrm{PhP(SiMe_3)_2}$ at 50 °C for several days. Analysis of the reaction mixture by ^{31}P NMR spectroscopy showed only two signals

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