Construction of a Phosphane-based Metallo-synthon Suitable for the Selective Formation of a Tetranuclear Ru_2–Cu_2 Macrocycle

Raymond Ziessel,*[a] Dominique Matt*[b] and Loic Toupet[c]

[a] *Laboratoire de Chimie, d'Electronique et de Photonique Moléculaires, Ecole Européenne des Hautes Etudes des Industries Chimiques de Strasbourg (EHICS), 1 rue Blaise Pascal, F-67008 Strasbourg Cedex, France*

[b] *Groupe de Chimie Inorganique Moléculaire, Ecole Européenne des Hautes Etudes des Industries Chimiques de Strasbourg, 1 rue Blaise Pascal, F-67008 Strasbourg Cedex, France*

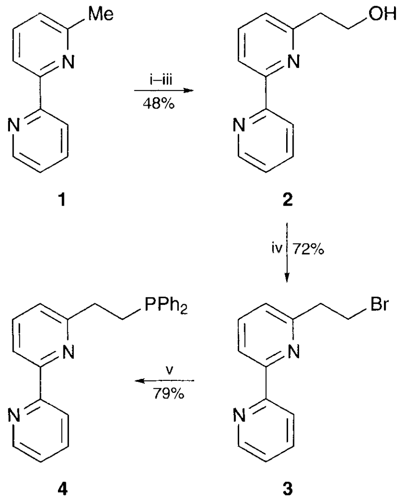
[c] *Groupe Matière Condensée et Matériaux, Université de Rennes 1, Bât. 11B, Campus Beaulieu, F-35042 Rennes Cedex, France*

Metallo-synthon **5**, comprising two hybrid bipyridine-phosphane ligands in a *trans*-arrangement, undergoes self-assembly in the presence of copper(I) affording a 36-membered metallocycle containing two ruthenium and two copper atoms.

The construction of highly organized and logically functionalized structures is one of the major goals of supramolecular chemistry.[1,2] A very efficient methodology for generation of ordered molecular architectures concerns the controlled assembly of several monomeric units around two or more metal ions.[3,4] The codification of such processes is contained in both the preferential stereochemistry of the metal ions used as templates and in the nature (especially topology) of the spacer moieties connecting the individual complexation sites. Polytopic ligands, designed for self-organizing processes, built around transition metal centres which function as spacers have only rarely been employed.[5] Due to the versatility of transition metal centres, it might be anticipated that preorganized metallo-synthons will facilitate, after self-organization, the construction of novel catalytic materials.[6] Furthermore, the presence of a metal-centred spacer may facilitate control of geometric parameters, including separation and relative orientation of the connectors, essential for the assembling process.

We report herein the synthesis, X-ray structure and self-assembling properties of the metallo-synthon **5**. This complex contains the new hybrid bipyridine-phosphane precursor **4**, which was prepared in four steps, Scheme 1.[7] Lithiation of 6-methyl-2,2′-bipyridine[8] followed by reaction with anhydrous paraformaldehyde affords the primary alcohol **2** in 48% yield. Treatment of **2** with HBr–AcOH results in formation of the bromo derivative **3** (72%). Further reaction with Ph_2PLi at low temp. gives the mixed PNN ligand **4** in 79% yield.† The colourless complex **5** is readily obtained (80%) by reaction of **4** (2 equiv.) with $[Ru(CO)_2Cl_2]_n$‡ in methanol at room temp. The $^{31}P\{^1H\}$NMR spectrum of **5** displays a singlet at δ 18.2 (free ligand δ −14.9), showing the equivalence of the two phosphorus atoms. As expected for a *trans*-arrangement of the phosphane ligands, the PCH_2 groups appear as a virtual triplet in the CH_2(bpy)-decoupled ^1H NMR spectrum.[10] The presence of two ν(C=O) stretching vibrations (2052 and 1988 cm^{-1}) in the IR spectrum indicates that the carbonyl ligands occupy *cis* positions.[11] The presence of two Ru–Cl absorption bands (299 and 285 cm^{-1}) is in agreement with their proposed *cis*-arrangement. The *trans*-P_2-*cis*$(CO)_2$-*cis*-Cl_2 stereochemistry was confirmed by a single-crystal X-ray diffraction study (Fig. 1).§

The coordination about the ruthenium atom is close to that of an ideal octahedron, the most important deviations being found for the Cl(1)–Ru–P(1) [84.06(5)°] and Cl(1)–Ru–P(2) [85.73(5)°] angles. The P substituents are oriented so as to minimize steric repulsion with the neighbouring chloride atoms (Fig. 1). Thus, all aryl rings are pointing away from the halogen atoms and are located in the same half-space, while the four methylene carbon atoms are located in a plane perpendicular to the $RuCl_2$ plane and bisecting the Cl–Ru–Cl angle. Similar conformational arrangements have been found in related dichlororuthenium(II) complexes containing $PAr_2(alkyl)$[12a] or



Scheme 1 *Reagents and conditions*: i, $LiNPr^i_2$, −78 °C, THF; ii, anhydrous paraformaldehyde; iii, NH_4Cl–H_2O; iv, HBr–AcOH; v, Ph_2PLi, −78 °C, THF

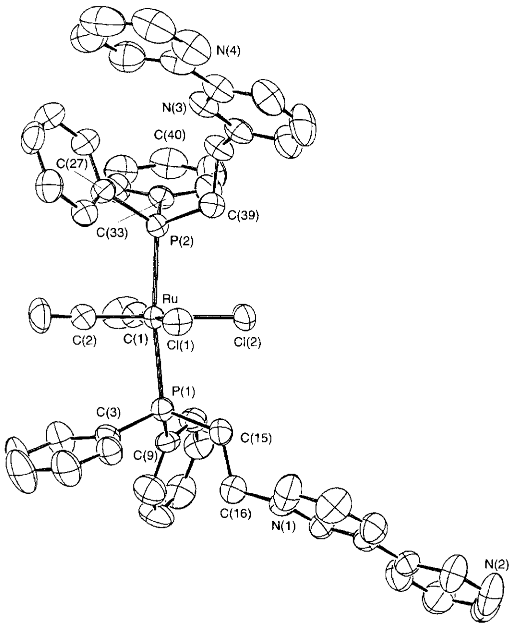
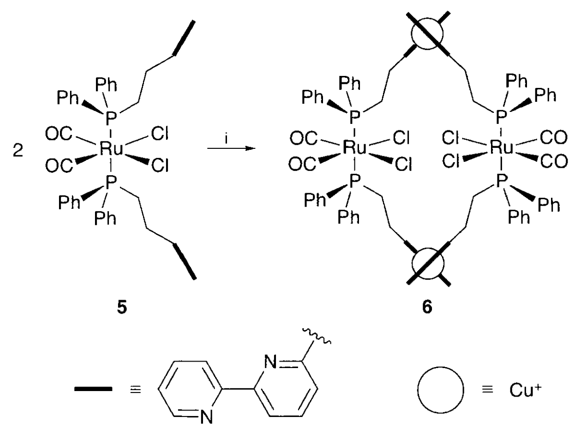


Fig. 1 ORTEP plot of **5** showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ru–P(1) 2.423(2), Ru–P(2) 2.416(2), Ru–Cl(1) 2.420(2), Ru–Cl(2) 2.422(1), Ru–C(2) 1.855(7), Ru–C(1) 1.852(6), P(1)–C(15) 1.834(7), P(2)–C(39) 1.812(6), P(1)–Ru–P(2) 171.6(1), Cl(1)–Ru–C(2) 90.40(6), C(1)–Ru–C(2) 88.8(3), C(15)–P(1)–Ru 112.4(2), P(1)–C(15)–C(16) 117.9(5), C(39)–P(2)–Ru 112.3(2), P(2)–C(39)–C(40) 115.7(5).

PAr(alkyl)$_2$[12b] ligands. In the solid state the two bipyridine subunits also lie in the same half-space. Under the conditions used, only the phosphane subunits (not the bipyridine fragments) enter into complexation with added substrates. The question whether this is due to the softer phosphorus *vs.* nitrogen centres or to the presence in the reaction mixture of acid causing transitory protonation of the bipy moieties cannot be answered at the moment.

One requisite for self-assembly of ditopic ligands is the presence of spacer groups displaying a certain degree of flexibility. In metallo-ligand **5** flexibility arises from rotation around the Ru–P bonds as well as around the CH$_2$–CH$_2$ linkers; the *trans* configuration of the phosphane ligands in complex **5** prevents the bipyridine units from wrapping around a single metal ion. It is noteworthy that the bipyridine subunits are substituted in the α position, a situation which makes this ditopic metallo-synthon particularly suitable for complexation of pseudo-tetrahedral metal ions.[13]



Scheme 2 *Reagents and conditions*: i, [Cu(MeCN)$_4$]ClO$_4$, MeCN–CH$_2$Cl$_2$ (1 : 1), room temp.

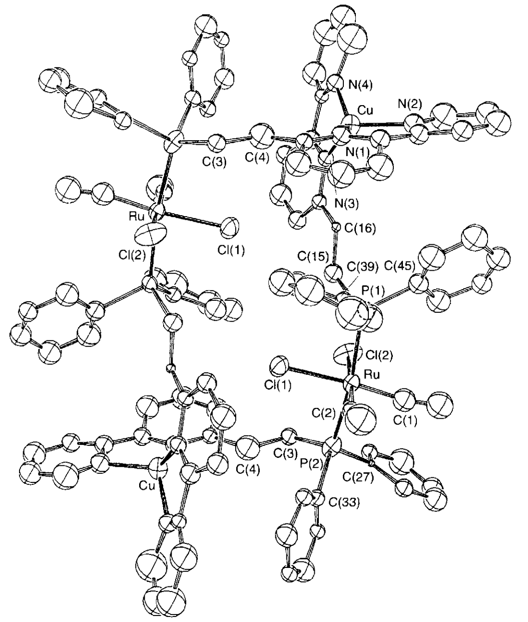


Fig. 2 ORTEP plot of **6** showing 50% probability thermal ellipsoids. Hydrogen atoms and the two perchlorate anions are omitted for clarity. Selected bond distances (Å) and angles (°): Ru–P(1) 2.38(1), Ru–P(2) 2.39(1), Ru–Cl(1) 2.39(1), Ru–Cl(2) 2.45(1), Ru–C(1) 1.81(4), Ru–C(2) 1.86(4), P(1)–C(15) 1.95(4), P(1)–C(45) 1.98(4), P(1)–C(39) 1.84(4), P(2)–C(27) 1.81(3), P(2)–C(33) 1.90(4), P(2)–C(3) 1.86(4), Cu–N(1) 2.04(3), P(2)–C(3) 1.86(4), Cu–N(1) 2.04(3), Cu–N(2) 2.07(3), Cu–N(3) 1.96(3), Cu–N(4) 2.03(3), Cl(1)–Ru–Cl(2) 91(1), C(1)–Ru–C(2) 96(2), P(1)–C(15)–C(16) 113(3), P(2)–C(3)–C(4) 107(3), N(3)–Cu–N(4) 76(1), N(1)–Cu–N(2) 82(1).

Copper(I)-induced self-organization of a 36-membered Ru$_2$Cu$_2$P$_4$N$_8$ metallomacrocycle was achieved by mixing complex **5** (1 equiv.) with [Cu(MeCN)$_4$](ClO$_4$)[14] (1 equiv.) (Scheme 2). The deep-red substance thus obtained (92%) was confirmed as [{Ru^{II}(PNN)$_2$(CO)$_2$Cl$_2$}Cu^{I}]$_2$(ClO$_4$)$_2$. The IR and NMR spectroscopic data are close to those observed for precursor **5** but formation of a 36-membered Ru$_2$Cu$_2$P$_4$N$_8$ metallo-ring was confirmed by X-ray molecular structure determination (Fig. 2).¶ This dication is centrosymmetric with the perchlorate anions remaining uncoordinated and lying outside the cavity. The four coplanar metals form a parallelogram with sides of 8.078(5) Å for Ru(1)···Cu(1) and 6.767(5) Å for Ru(1)···Cu(2) with interior angles of *ca.* 113° for Cu(1)–Ru(1)–Cu(2) and *ca.* 67° for Ru(1)–Cu(2)–Ru(2). Each copper(I) cation displays distorted tetrahedral coordination with a dihedral angle of 102.5(1)° between the mean planes of the bipyridine subunits.[15] The angular parameters about the ruthenium atoms and the phosphorus atoms in **6** compare well with those found in **5**, indicating that ring formation does not generate steric strain within the 'Ru(PNN)$_2$'-spacers [P(1)–Ru–P(2) 169(2), Ru–P(2)–C(3) 112(2), Ru–P(1)–C(15) 109(1)° in complex **6** and P(1)–Ru–P(2) 171.6(1), Ru–P(2)–C(39) 112.3(2) and Ru–P(1)–C(15) 112.4(2)° in complex **5**]. The relative orientation of the *P*-Ph groups and the corresponding Ru–Cl bonds is reminescent of that found in precursor **5**. It is noteworthy that the wrapping of the two bis-bipy metallo-synthons around the two copper centres leads to an achiral complex and not the alternative double-stranded helix. Recent work suggests that steric effects are likely to play a major role in the formation of side-by-side or helical isomers.[16]

Finally, it appears that the *trans*-P,P stereochemistry of complex **5** is particularly well suited for preorganization of the bipyridine chelators. To the best of our knowledge, complex **5** constitues the first example of a bipyridine-driven self-organization based on a transition metal synthon, and also a rare example where a phosphane ligand is used for self-assembly.[4,17] This clearly opens the way for construction of novel organized heteronuclear systems containing catalytic centres.

Received, 30th June 1995; Com. 5/04223B

Footnotes

† *Selected data* for **4**: R_f = 0.62 (alumina, CH$_2$Cl$_2$–hexane 9 : 1); ^{1}H NMR (CDCl$_3$, 25 °C) δ 8.69 (ddd, 1 H, H$_{6'}$, $^3J_{H,H}$ 4.8 Hz, $^4J_{H,H}$ 1.0 Hz, $^5J_{H,H}$ 0.8 Hz), 8.51 (dm, 1 H, H$_3$′, $^3J_{H,H}$ 7.6 Hz), 8.28 (dm, 1 H, H$_3$, $^3J_{H,H}$ 7.9 Hz), 7.79 (td, 1 H, H$_{4'}$, $^3J_{H4',H5'}$ = $^3J_{H4',H3'}$ 7.6 Hz, $^4J_{H,H}$ 1.3 Hz), 7.69 (t, 1 H, H$_4$, $^3J_{H4,H3}$ = $^3J_{H4,H5}$ 7.8 Hz), 7.59–7.35 (10 H, PPh$_2$), 7.27 (m, 1 H, H$_{5'}$), 7.12 (d, 1 H, H$_5$, $^3J_{H,H}$ 7.6 Hz), 3.05 (δ$_A$) and 2.69 (δ$_B$) (two multiplets of an A$_2$B$_2$X system, with A = PCH$_2$, $^2J_{P,A}$ 9 Hz and B = PCH$_2$C*H*$_2$, 4 H); ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C) δ 160.88 (d, C$_q$P, $^2J_{CP}$ 13 Hz), 156.27 (C$_q$, bipy), 155.42 (C$_q$, bipy), 148.91 (C$_q$, bipy), 138.61–118.32 (C$_{aromatic}$), 34.40 (d, CH$_2$P, J_{CP} 17 Hz), 27.67 (d, CH$_2$-bipy, $^2J_{CP}$ 13 Hz); ^{31}P{^{1}H}NMR (CDCl$_3$, 25 °C) δ −14.9; MS(EI) *m/z* 384 (ligand 4 + O).

For **5**: mp 185 °C (slow decomp.); UV–VIS (MeCN) λ$_{max}$/nm (ε/dm^3 mol^{-1} cm^{-1}) 283 (21200), 224 (19900); ^{1}H NMR (CD$_2$Cl$_2$, 25 °C) δ 8.62 (d, 2 H, $^3J_{H,H}$ 4.7 Hz), 8.46 (d, 2 H, $^3J_{H,H}$ 8.0 Hz), 8.17 (d, 2 H, $^3J_{H,H}$ 8.0 Hz), 7.93 (m, 8 H), 7.81 (td, 2 H, $^3J_{H,H}$ 7.8 Hz, $^4J_{H,H}$ 1.8 Hz), 7.63 (t, 2 H, $^3J_{H,H}$ 7.8 Hz), 7.50 (m, 12 H), 7.29 (m, 2 H), 7.00 (d, 2 H, $^3J_{H,H}$ 7.6 Hz), 3.51 (m, 4 H), 2.75 (m, 4 H); ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C) δ 192.47 (d, Ru–CO, $^2J_{C,P}$ 11 Hz), 159.87 (C$_q$, bpy), 156.33 (C$_q$, bpy), 155.43 (C$_q$, bpy), 148.95 (C$_q$, bpy), 137.16–118.49 (C$_{aromatic}$), 31.75 (s, CH$_2$-bpy), 23.29 [pseudo t, CH$_2$P, $J_{C,P}$ 14.5 Hz and 13.2 Hz, (^1J and ^3J not assigned)]; ^{31}P{^{1}H} NMR {[^{2}H$_6$]acetone–acetone (1 : 9), 25 °C} δ 18.2; IR (KBr pellet) ν/cm^{-1}, 3054w, 2052s (ν$_{CO}$), 1998s (ν$_{CO}$), 1579m, 1431m, 1133m, 1104m; Far IR (polythene) ν/cm^{-1} 299(ν$_{Ru-Cl}$), 285(ν$_{Ru-Cl}$); MS (FAB$^+$ in *m*-NBA as matrix) *m/z* 964.9 (M$^+$ + H, expected isotopic profile).

For **6**: mp > 200 °C; UV–VIS (MeCN) λ$_{max}$/nm (ε/dm^3 mol^{-1} cm^{-1}): 442(14300), 292(138000), 260(127000), 213(153000); ^{31}P{^{1}H} NMR (CD$_3$CN, 25 °C) δ 19.52; MS (FAB$^+$ in *m*-NBA) *m/z* 2158.9 (M$^+$ − ClO$_4$, expected isotopic profile), 2057.8 (M − 2 ClO$_4$), 1029.1 (M − Cu − 2 ClO$_4$); IR (KBr pellets) ν/cm^{-1} 3063w, 2050s (ν$_{CO}$), 1987s (ν$_{CO}$), 1597m, 1567m, 1453s, 1089vs (ν_{ClO_4}), 773s. Far IR (polythene) ν/cm^{-1} 304(ν_{Ru-Cl}), 280(ν_{Ru-Cl}).

‡ This polymeric ruthenium(II) complex was prepared in acidic media [HCO_2H (99%)–HCl (conc.) (7 : 1)] according to ref. 9.

§ *Crystal data* for **5**: $C_{50}H_{42}Cl_2N_4O_2P_2Ru$, $M = 964.8$; colourless crystals ($0.15 \times 0.25 \times 0.25$ mm); monoclinic, $P2_1/c$, $a = 14.570(6)$, $b = 22.426(9)$, $c = 13.982(8)$ Å, $\beta = 93.71(5)°$, $V = 4559(2)$ Å^3, $Z = 4$, $D_c = 1.406$ g cm^{-3}, $F(000) = 1976$, $\mu = 5.66$ cm^{-1}. A suitable crystal of **5** was obtained by slow evaporation of a dichloromethane–hexane solution of complex **5** at room temp. Data were collected on an ENRAF–NONIUS CAD4 diffractometer at room temp. with graphite-monochromated Mo-Kα radiation ($\lambda = 0.70926$ Å). The cell parameters were obtained by fitting a set of 25 high-theta reflections. The data collection ($2\theta_{max} = 50°$, scan ω–$2\theta = 1$, $t_{max} = 60$ s, ranges h 0–16, k 0–25, l −15 to 15, intensity controls without appreciable decay (0.2%) gives 7656 reflections from which 3416 independent ($R_{int} = 0.020$) with $I > 3\sigma(I)$. After Lorenz and polarization corrections, the structure was solved by direct methods, revealing many non-hydrogen atoms of the molecule. The remaining atoms were found after successive scale-factor and Fourier difference calculations. After isotropic ($R = 0.085$), then anisotropic refinement ($R = 0.065$), all the hydrogen atoms were found by Fourier difference (between 0.52 and 0.23 e Å^{-3}). The whole structure was refined by the full-matrix least-squares technique [use of F magnitude; x, y, z, β_{ij} for Ru, Cl, P, O, N and C atoms and x, y, z for H atoms; 677 variables and 3416 observations; $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{-1/2}$ with $R = 0.033$, $R_w = 0.031$ and $S_w = 2.22$ (residual $\Delta\rho \leqslant 0.21$ e Å^{-3}). Atomic scattering factors from International Tables for X-ray Crystallography (1974). All calculations were performed on a Digital Micro VAX 3100 computer with the MolEN[18] package (Enraf-Nonius, 1990). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

¶ *Crystal data* for **6**: $C_{100}H_{84}Cl_6Cu_2N_8O_{12}P_4Ru_2$, $M = 2255.66$, cherry-red crystals ($0.25 \times 0.25 \times 0.30$ mm), monoclinic, $C2/c$, $a = 23.34(1)$, $b = 13.539(9)$, $c = 32.22(3)$ Å, $\beta = 91.41(7)°$, $V = 10181(14)$ Å^3, $Z = 8$, $D_c = 1.471$ g cm^{-3}, $F(000) = 4576$, $\mu = 9.79$ cm^{-1}. Suitable crystals were obtained by slow evaporation of an acetonitrile–toluene solution of **6** at room temp. The structure was solved as described above for **5**, $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{-1/2}$ with $R = 0.109$, $R_w = 0.122$.

References

1 See for example: J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1304; S. Lindsey, *New. J. Chem.*, 1991, **15**, 153; G. M. Whitesides, J. P. Mathias and C. T. Seto, *Science*, 1991, **254**, 1312; D. Philp and J. F. Stoddart, *Synlett*, 1991, 445.

2 C. Piguet, G. Hopfgartner, B. Bosquet, O. Schaad and A. F. Williams, *J. Am. Chem. Soc.*, 1994, **116**, 9092.

3 Among the recent examples listed below many metal-induced organization processes have not been specifically named self-assembly, *e.g.* reactions leading to (i) polynuclear macrocyclic transition metal complexes: A. A. Bahsoun and R. Ziessel, *Nouv. J. Chim.*, 1985, **9**, 225; A. W. Maverick, S. C. Buckingham, Q. Yao, J. R. Bradbury and G. Stanley, *J. Am. Chem. Soc.*, 1986, **108**, 7430; G. A. Fox and C. G. Pierpont, *J. Chem. Soc., Chem. Commun.*, 1988, 806; M. Fujita, J. Yazaki and K. Ogura, *J. Am. Chem. Soc.*, 1990, **112**, 5645; P. Braunstein, B. Ostwald, A. Tiripicchio and M. Tiripicchio-Camellini, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1140; (ii) oligomeric organometallic materials: W. Kläui, D. Matt, F. Balegroune and D. Grandjean, *Acta Crystallogr. Sect. C*, 1991, **47**, 1614; D. Matt and A. Van Dorsselaer, *Polyhedron*, 1991, **10**, 1521.

4 A. L. Airey, G. F. Swiegers, A. C. Willis and S. B. Wild, *J. Chem. Soc., Chem. Commun.*, 1995, 695.

5 M. S. Goodman, V. Jubian and A. D. Hamilton, *Tetrahedron Lett.*, 1995, **36**, 2551.

6 C. L. Hill and X. Zhang, *Nature*, 1995, **273**, 324.

7 Some phosphane-oligopyridine ligands have been reported previously but these do not contain a CH_2–CH_2 bridge: R. Ziessel, *Tetrahedron Lett.*, 1989, **30**, 463; M. Grassi, G. DeMunno, F. Nicolo and S. Lo Schiavo, *J. Chem. Soc., Dalton Trans.*, 1992, 2367; G. Newkome, *Chem. Rev.*, 1993, **93**, 2067; R.-H. Uang, C.-K. Chan, S.-M. Peng and C.-M. Che, *J. Chem. Soc., Chem. Commun.*, 1994, 2561.

8 Th. Kauffmann, J. König and A. Waltermann, *Chem. Ber.*, 1976, **109**, 3864.

9 R. Colton and R. H. Farthing, *Aust. J. Chem.*, 1967, **20**, 1283.

10 E. M. Hyde, J. D. Kennedy and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1977, 1571.

11 M. J. Cleare and W. P. Griffith, *J. Chem. Soc. A*, 1969, 372; C. F. J. Barnard, J. A. Daniels, J. Jeffery and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1976, 953.

12 (*a*) D. W. Krassowski, J. H. Nelson, K. R. Brower, D. Hauenstein and R. A. Jacobson, *Inorg. Chem.*, 1988, **27**, 4294; (*b*) L. D. Brown, C. F. J. Barnard, J. A. Daniels, R. J. Mawby and J. A. Ibers, *Inorg. Chem.*, 1978, **17**, 2932.

13 D. R. McMillin, J. R. Kirchhoff and K. V. Goodwin, *Coord. Chem. Rev.*, 1985, **64**, 83.

14 B. J. Hathaway, D. G. Holah and J. D. Poslethwaite, *J. Chem. Soc.*, 1961, 3215.

15 For dihedral angles between bipyridine chelates see: A. Juris and R. Ziessel, *Inorg. Chim. Acta*, 1994, **225**, 251 and references cited therein.

16 A. Bilyk and M. M. Harding, *J. Chem. Soc., Dalton Trans.*, 1994, 77; A. Bilyk, M. M. Harding, P. Turner and T. W. Hambley, *J. Chem. Soc., Dalton Trans.*, 1994, 2783.

17 See for example: C. A. McAuliffe and W. Levason, *Phosphine, Arsine and Stibine Complexes of the Transition Elements*, Elsevier, Amsterdam, 1979; *The Chemistry of Organo-phosphorus Compounds*, ed. F. R. Hartley, Wiley, Chichester, 1990, vol. 1.

18 C. K. Fair, in MolEN. An Interactive Intelligent System for Crystal Structure Analysis. Enraf-Nonius, Delft, 1990.