Mendeleev Commun., 1997, 7(4), 127–129

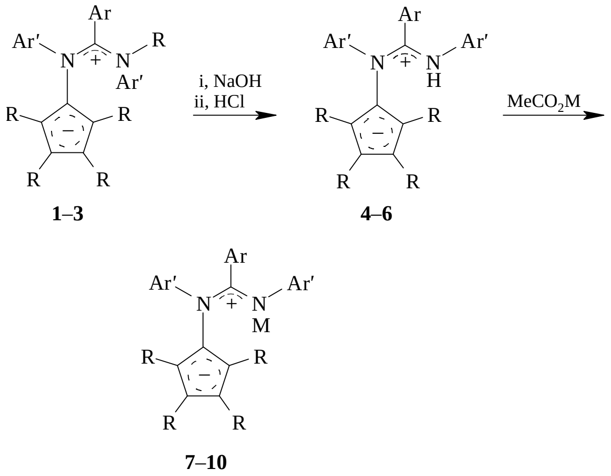
Synthesis and structure of chiral *N*,*N'*-diaryl- -naphthamidinium-*N*-[1,2,3,4-tetra(methoxycarbonyl)cyclopentadien-5-yl] ylides and their metal complexes

Galina A. Dushenko,*[a] Igor E. Mikhailov,[b] Olga E. Kompan,[a] Adolf Zschunke,[c] Gunter Reck,[c] Burkhard Schulz,[c] Clemens Mugge[d] and Vladimir I. Minkin[a]

[a] *Institute of Physical and Organic Chemistry, Rostov State University, 344090 Rostov-on-Don, Russian Federation. Fax: +7 863 228 5667*
[b] *Rostov State Academy of Building, 344022 Rostov-on-Don, Russian Federation. Fax: +7 863 265 5731*
[c] *Federal Institute for Materials Research and Testing, D-12200 Berlin, Germany. Fax: +49 30 811 2029*
[d] *Institute of Chemistry, Humboldt University, D-10115 Berlin, Germany. Fax: +49 30 2093 7343*

Novel chiral *N*,*N'*-diaryl- -naphthamidinium-*N*-[1,2,3,4-tetra(methoxycarbonyl)cyclopentadien-5-yl] ylides and their gold(I) and mercury(II) complexes have been prepared and their structures studied using X-ray crystal analysis and ^{1}H and ^{13}C NMR spectroscopy.

In recent years the area of stereoselective chemistry concerned with the synthesis and application of chiral cyclopentadiene complexes and organometallics has received rapidly growing attention. Among recent applications are catalysts for asymmetric hydrogenation, alkene isomerization, ketone reduction, stereoselective alkene polymerization, stoichiometric reagents for stereoselective cobalt-mediated reactions, addition reactions of allyltitanium to aldehydes and others.[1–4] On the other hand, such traditional chiral ligands as amines and imines continue to find new and useful applications in organic synthesis and supramolecular chemistry. One recent finding is an application of axial chiral amidine ions with biaryl moieties in ‘host–guest’ chemistry.[5]



R = CO$_2$Me
1, **4**, **7**, **8** Ar = $C_{10}H_7$-1, Ar′ = C_6H_4Me-3; M = Au(PPh$_3$) (**7**), M = Hg($C_6H_4NMe_2$-4) (**8**)
2, **5** Ar = $C_{10}H_7$-1, Ar′ = C_6H_4Me-4
3, **6**, **9**, **10** Ar = Ph, Ar′ = C_6H_4Me-4; M = Au(PPh$_3$) (**9**), M = Hg($C_6H_4NMe_2$-4) (**10**)

Scheme 1

Here we report on the synthesis of novel chiral *N*,*N'*-diaryl- -naphthamidinium-*N*-[1,2,3,4-tetra(methoxycarbonyl)cyclopentadien-5-yl] ylides **4** and **5** and their metal complexes **7** and **8**, their X-ray crystal structures and an investigation into the reason for the stability of their chiral forms. The presence of both amidine and cyclopentadiene moieties in molecules **4** and **5** provides these chiral ligands with a bifunctional character and, thus, a diversity in their reactions. The reaction of *N*-methoxycarbonyl-*N*,*N'*, -triarylamidinium-*N'*-[1,2,3,4-tetra(methoxycarbonyl)cyclopentadien-5-yl] ylides **1**–**3**[6] with NaOH in methanol results in elimination of a *N*-methoxycarbonyl group, and subsequent treatment with hydrochloric acid leads to the formation of amidinium *N*-cyclopentadienyl ylides **4**–**6**[†] in 80–85% yields. By coupling ylides **4**–**6** with MeCO$_2$Au(PPh$_3$) or MeCO$_2$Hg($C_6H_4NMe_2$-4) in methanol solution at room temperature for 1–6 h the corresponding metal complexes **7**–**10**[†] were obtained in 85–90% yields (Scheme 1). The complexes **7**–**10** as well as the ylides **4**–**6** are resistant to air and moisture. A similar reaction of penta(methoxycarbonyl)cyclopentadiene[7] with mercury reagent leads to an unstable complex of unidentified structure which rapidly decomposes with elimination of elemental Hg.

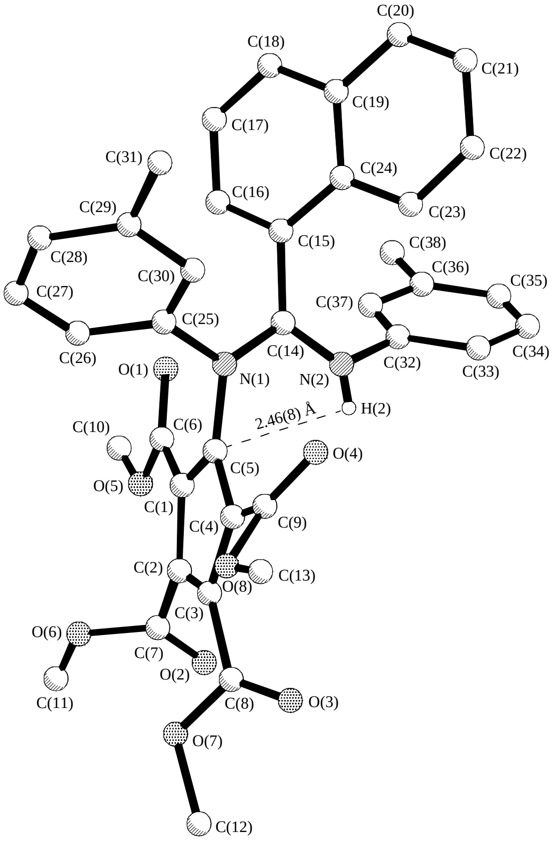


Figure 1 The molecular structure of compound **4**.

The zwitterionic structure of the ylides **4** and **6** has been proved by X-ray diffraction studies[‡] (Figures 1, 2). An equalization of the C–C bond lengths in the five-membered rings [1.37(1)–1.43(1) Å] is characteristic of substituted cyclopentadiene anions.[7] The lengths of the C–N bonds in the amidine moiety are very close in value, 1.32(1) and 1.315(8) Å for **4**, 1.38(1) and 1.31(1) Å for **6**, which is typical of amidine cations.[8] Specific features of the structures **4** and **6** are the *Z*-configuration of the amidine fragment about the C(14)–N(2) (for **4**) or C(14)–N(21) (for **6**) bond, and the short distance between the atoms H (at N) and C of the cyclopentadiene ring attached to N. The plane of the amidine fragment is turned orthogonal to that of the cyclopentadiene ring, which brings this H atom to C of the five-membered ring at a distance of 2.46(8) Å for **4** or 2.25(9) Å for **6** (Figures 1, 2). Such short distances evidence a strong attractive interaction due to the hydrogen bond with the negatively charged cyclopentadienyl ring. A similar type of effective -bonding has long been known for the -complexes of cyclopentadienide anions with Li^+ and Tl^+.[9] Unlike the ylides **4** and **5** their penta(methoxycarbonyl)cyclopentadiene precursor exists in the hydroxyfulvene form where a hydrogen atom bridges two carbonyl oxygens from vicinal CO_2Me groups.[7] It is noteworthy that the structurally-related ylide **3** possesses an *E*-configuration about the same C–N bond, with a stacking interaction[10] between aryl [at N(2)] and cyclopentadiene rings (Scheme 2), causing the deep red colour of this compound.[6] On the contrary, the *Z*-configuration of the ylide **4** impedes the stacking and shifts its UV spectrum to shorter wavelengths [CH_3OH, 260 nm (ε 30200), 290 nm (ε 16000)]. The ylides **4** and **6** differ in certain structural details. The phenyl group at C(14) in **6** can be placed in the plane of the amidine fragment, whereas the bulkier 4-positioned naphthyl group in **4** cannot be placed there and is turned relative to that plane due to steric hindrance [torsion angle N(1)C(14)C(15)C(16) in **4** 62.2(2)°]. The consequence is the chirality of the ylide structure **4**.

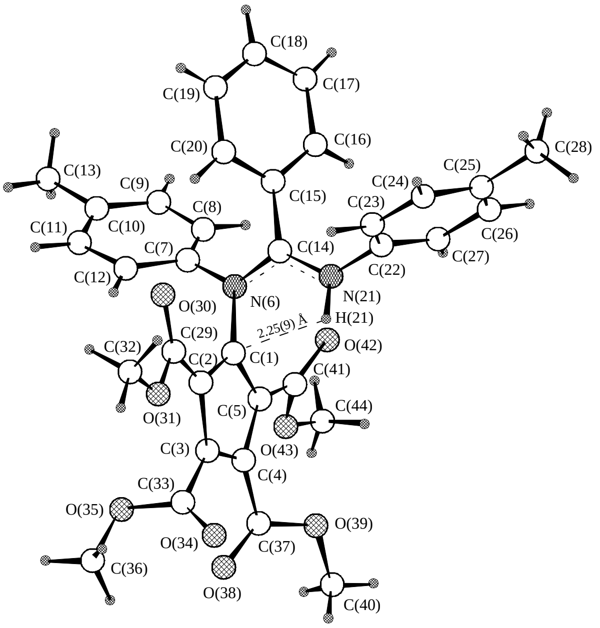


Figure 2 The molecular structure of compound **6**.

[†] Compound **4**: yellow crystals (from diethyl ether), mp 244–245 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.98 (s, 3H, Me), 2.02 (s, 3H, Me), 3.77 (s, 3H, OMe), 3.81 (s, 3H, OMe), 3.86 (s, 3H, OMe), 3.87 (s, 3H, OMe), 6.65–8.32 (m, 15H, Ar), 8.86 (s, 1H, NH). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ: 20.88, 21.06 (Me), 51.24, 51.30, 51.57, 51.85 (OMe), 106.00, 110.67, 117.55, 120.50 (C^{1-5} cp-ring), 122.52, 122.83, 122.91, 124.59, 126.04, 126.29, 126.80, 128.04, 128.07, 128.43, 128.49, 128.69, 130.46, 132.09 (CHAr), 124.33, 130.05, 132.61, 134.91, 138.55, 138.83, 141.67 (quaternary Ar), 165.86 (NCN), 165.50, 165.63, 167.05, 168.40 (C=O). IR (Nujol) ν/cm^{-1}: 3260, 1740, 1720, 1700, 1680, 1610, 1570, 1290, 1220, 1180.

Compound **5**: yellow crystals (from diethyl ether), mp 254–255 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.98 (s, 6H, Me), 3.71 (s, 3H, OMe), 3.75 (s, 3H, OMe), 3.80 (s, 3H, OMe), 3.81 (s, 3H, OMe), 6.59–8.29 (m, 15H, Ar), 8.70 (s, 1H, NH). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ: 20.74, 20.75 (Me), 51.21, 51.22, 51.54, 51.82 (OMe), 105.76, 110.37, 117.70, 120.31 (C^{1-5} cp-ring), 124.39, 124.59, 125.35, 125.39, 126.72, 128.08, 128.08, 128.47, 128.99, 129.24, 130.38, 131.95 (CHAr), 123.12, 124.16, 129.89, 132.26, 132.49, 137.61, 137.66, 139.21 (quaternary Ar), 165.72 (NCN), 165.36, 165.37, 167.07, 168.35 (C=O).

Compound **6**: yellow crystals (from diethyl ether), mp 252–253 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.10 (s, 3H, Me), 2.17 (s, 3H, Me), 3.69 (s, 6H, OMe), 3.76 (s, 6H, OMe), 6.76–7.39 (m, 13H, Ar), 8.52 (s, 1H, NH). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ: 20.86, 20.90 (Me), 51.15, 51.67 (OMe), 107.96, 118.86, 123.90 (C^{1-5} cp-ring), 125.84, 126.50, 128.53, 129.03, 129.75, 130.77, 131.67 (CHAr), 126.64, 132.91, 137.30, 137.69, 138.99 (quaternary Ar), 165.76 (NCN), 165.23, 167.70 (C=O). IR (Nujol) ν/cm^{-1}: 3280, 1740, 1700, 1620, 1610, 1580, 1280, 1230, 1190.

Compound **7**: colourless crystals (from MeOH), mp 223–224 °C. ^1H NMR (300 MHz, C_6D_6) δ: 1.45 (s, 3H, Me), 1.71 (s, 3H, Me), 3.09 (s, 3H, OMe), 3.35 (s, 3H, OMe), 3.73 (s, 3H, OMe), 3.76 (s, 3H, OMe), 6.18–8.73 (m, 15H, Ar). ^{13}C NMR (75.47 MHz, C_6D_6) δ: 20.75, 21.02 (Me), 50.36, 50.68, 50.76, 51.29 (OMe), 107.25, 115.46, 116.85, 123.75 (C^{1-5} cp-ring), 123.96, 124.07, 124.66, 124.88, 125.77, 126.71, 126.72, 127.10, 127.28, 127.69, 128.45, 129.02, 129.18, 130.13, 131.18, 131.58, 134.76, 134.94 (CHAr), 129.52, 130.34, 131.38, 131.89, 132.93, 137.22, 137.79, 144.86, 149.42 (quaternary Ar), 166.43 (NCN), 165.91, 166.42, 167.83, 169.28 (C=O). IR (Nujol) ν/cm^{-1}: 1740, 1700, 1680, 1550, 1280, 1210, 1180.

Compound **8**: colourless crystals (from MeOH), mp 157–158 °C. ^1H NMR (300 MHz, C_6D_6) δ: 1.45 (s, 3H, Me), 1.59 (s, 3H, Me), 2.31 (s, 6H, NMe_2), 3.38 (s, 3H, OMe), 3.46 (s, 3H, OMe), 3.69 (s, 3H, OMe), 3.74 (s, 3H, OMe), 6.10–8.59 (m, 15H, Ar). ^{13}C NMR (75.47 MHz, C_6D_6) δ: 20.68, 20.78 (Me), 39.80 (NMe_2), 50.73, 50.95, 51.59, 51.64 (OMe), 105.52, 115.42, 117.58, 124.99 (C^{1-5} cp-ring), 113.02, 123.00, 123.36, 124.58, 126.12, 126.20, 126.78, 127.24, 128.30, 128.61, 130.85, 131.37, 137.90 (CHAr), 125.69, 130.23, 130.62, 130.78, 132.92, 138.55, 144.66, 146.43, 150.93 (quaternary Ar), 168.69 (NCN), 164.84, 165.95, 168.84, 169.16 (C=O). IR (Nujol) ν/cm^{-1}: 1750, 1720, 1700, 1600, 1530, 1220, 1180.

Compound **9**: colourless crystals (from MeOH), mp 218–219 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.08 (s, 3H, Me), 2.15 (s, 3H, Me), 3.61 (s, 3H, OMe), 3.68 (s, 3H, OMe), 3.74 (s, 3H, OMe), 3.81 (s, 3H, OMe), 6.75–7.48 (m, 13H, Ar). ^{13}C NMR (75.47 MHz, $CDCl_3$) δ: 20.86, 20.91 (Me), 51.16, 51.68 (OMe), 107.93, 118.85, 123.90 (C^{1-5} cp-ring), 125.82, 126.47, 128.52, 129.02, 129.25, 129.74, 130.75, 131.90, 133.98, 134.16 (CHAr), 126.58, 128.52, 132.85, 137.29, 137.68, 138.94 (quaternary Ar), 165.21 (NCN), 165.72, 167.69 (C=O).

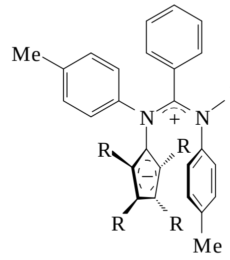
Compound **10**: colourless crystals (from MeOH), mp 158–159 °C. ^1H NMR (300 MHz, C_6H_6) δ: 1.62 (s, 3H, Me), 1.70 (s, 3H, Me), 2.32 (s, 6H, NMe_2), 3.50 (s, 6H, OMe), 3.57 (s, 6H, OMe), 6.40–7.46 (m, 13H, Ar). IR (Nujol) ν/cm^{-1}: 1740, 1710, 1700, 1600, 1520, 1500, 1220, 1180.

Assignments of signals in the ^{13}C NMR spectra were made by APT. Compounds **4**–**10** gave satisfactory elemental analyses.

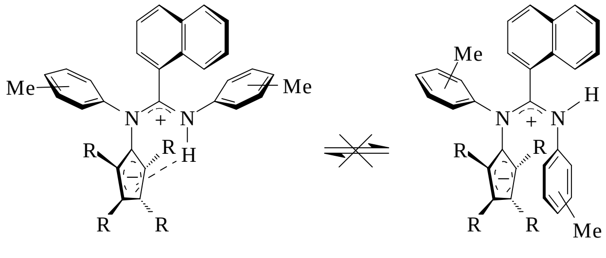
[‡] *Crystal data.* For **4**: $C_{38}H_{34}N_2O_8 \cdot 0.5H_2O$, $M = 655.68$, triclinic, space group $P1$, $a = 10.165(2)$, $b = 13.372(3)$, $c = 14.372(4)$ Å, $\alpha = 114.44(2)$, $\beta = 93.87(2)$, $\gamma = 99.59(2)$°, $V = 1733(2)$ Å^3, $Z = 2$, $d_{calc} = 1.243$ g cm^{-3}.

For **6**: $C_{34}H_{32}N_2O_8$, $M = 596.62$, monoclinic, space group $P2_1/n$, $a = 13.668(3)$, $b = 14.318(4)$, $c = 16.205(3)$ Å, $\alpha = 90.00$, $\beta = 102.93(2)$, $\gamma = 90.00$°, $V = 3091(1)$ Å^3, $Z = 4$, $d_{calc} = 1.177$ g cm^{-3}.

The X-ray diffraction experiment was carried out with a Siemens P3/PC diffractometer for **4** and an Enraf–Nonius CAD-4 for **6** ($T = 293$ K, graphite monochromated MoK radiation, $\lambda = 0.71069$ Å, $\theta/2\theta$ scan technique, $2\theta < 60$°). The structures were solved by direct methods using SHELXTL PLUS programs for **4** and LEPAGE (Spek, 1988) for **6**. Anisotropic (isotropic for H atoms in **6**) least-squares refinement converged at $R = 0.072$, $R_w = 0.069$, $f_{max} = -0.35$ e Å^{-3} for 2138 observed independent reflections with $I > 4\sigma(I)$ (**4**) and at $R = 0.083$, $R_w = 0.086$, $f_{max} = 0.34$ e Å^{-3} for 1951 observed independent reflections with $I > 1\sigma(I)$ (**6**). Hydrogen atom H(2) in **4** was located from a difference map and included in the refinement with fixed $U_{iso} = 0.08$ Å^2; other hydrogen atoms were placed in geometrically calculated positions and included in the refinement in the riding motion approximation with a fixed $U_{iso} = 0.08$ Å^2. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see Notice to Authors, *Mendeleev Commun.*, 1997, issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1135/19. The X-ray experiment for **4** was carried out at the X-Ray Centre of the A. N. Nesmeyanov Institute of Organoelement Compounds, Moscow, Russian Federation; for **6** – at the Federal Institute for Material Research and Testing, Berlin, Germany.



3 (*E*)



4, **5** (*Z*)

4, **5** (*E*)

Scheme 2

From the X-ray structural data, IR (in Nujol) and NMR (in solution) spectra† of the ylides **4**–**6** and their metal complexes **7**–**10** it seems that all the compounds possess a zwitterionic structure both in the solid state and in solution. In the ^{13}C NMR spectra of the compounds **4**–**10** all carbon atom signals in the cyclopentadiene ring appear in the region δ 105–117 ppm. The up-field shift of these signals compared to those of sp^2-hybridized carbon atoms of the cyclopentadiene ring in 5-methyl-1,2,3,4,5-penta(methoxycarbonyl)cyclopentadiene (δ 140.62, 145.46 ppm)[11] bears witness to the localization of negative charge in the five-membered ring. Signals due to the amidine carbon atoms of these compounds are observed at δ 165–169 ppm, which is the characteristic region for positively charged carbon atoms. NMR spectra of the ylides **4**–**6** and their gold and mercury complexes **7**–**10** are fundamentally different. In the ^{1}H NMR spectra of the ylide **6** and its metal complexes **9** and **10** – containing a phenyl substituent at the amidine carbon atom and possessing C_s symmetry – two singlet six-proton signals due to methoxycarbonyl groups are observed at room temperature. Similarly, the ^{13}C NMR spectra of the compounds **6**, **9** and **10** contain signals of pairs of equivalent carbon atoms of both carbonyl and methoxy groups, as well as the cyclopentadiene ring carbon atoms with CO_2Me substituents. In contrast, methoxycarbonyl group protons (^{1}H NMR) and carbons of carbonyl as well as methoxy groups (^{13}C NMR) of the ylides **4** and **5** and their metal derivatives **7** and **8** with a naphthyl substituent at the amidine carbon atom are magnetically inequivalent displaying four separate signals in each case. In addition, C(1) and C(4) atoms of the cyclopentadiene ring which are closer to the amidine fragment than C(2) and C(3) give two different signals. These facts point to the absence of C_s symmetry in molecules **4**, **5** and **7**, **8** with the bulky naphthyl substituents and, therefore, their chiral structure.

By heating a [$^2H_5$]nitrobenzene solution of **4**, **5** and **8** up to 180 °C as well as a [$^2H_8$]toluene solution of **4**, **5** and **7** [for **4** and **5** also in the presence of ‘proton sponge’ 1,8-bis-(dimethylamino)naphthalene] to 110 °C no changes in the NMR spectral patterns were observed. Such spectral behaviour indicates the very stable chiral structure of these compounds. This property may be important considering that for most of the compounds whose chirality is caused by hindered rotation of bulky substituents rigid methylene bridges are usually built up in order to fix a desirable conformation.[5] We suggest that the stability of the chiral structure of naphthamidinium-*N*-cyclopentadienyl ylides and their complexes is determined by the high energy barrier ($G_{180\,°C}$ > 26 kcal mol^{-1}) for hindered rotation of the bulky 1-naphthyl group around the C(14)–C(Ar) bond in the *Z*-configuration of the amidinium fragment. The latter configuration is stabilized by coordination with a metal centre in the complexes **7** and **8** or by a -hydrogen bond in the ligands **4** and **5** (Scheme 2) and is known to have a sufficiently high energy barrier against isomerization to the *E*-form in amidinium ions.[12]

We thank the Volkswagen Foundation (grant no. I/72248) and the Russian Foundation for Basic Research (grant no. 95-03-09559) for financial support.

References

1 R. L. Halterman, *Chem. Rev.*, 1992, **92**, 965.
2 A. A. H. Zeijden, *J. Organomet. Chem.*, 1996, **518**, 147.
3 C. Janiak and H. Schumann, *Adv. Organomet. Chem.*, 1991, **33**, 291.
4 T. Hayashi and A. Jamazaki, *J. Organomet. Chem.*, 1991, **413**, 295.
5 S. Lehr, K. Schulz, M. Bauch and M. W. Gobel, *Angew. Chem.*, 1994, **106**, 1041.
6 I. E. Mikhailov, O. E. Kompan and G. A. Dushenko, *Mendeleev Commun.*, 1991, 121.
7 M. I. Bruce and A. H. White, *Aust. J. Chem.*, 1990, **43**, 949.
8 T. Chivers, J. F. Richardson and N. R. M. Smith, *Inorg. Chem.*, 1985, **24**, 2453.
9 K. S. Waterman and A. Steitwieser, *J. Am. Chem. Soc.*, 1984, **106**, 3138.
10 T. Dahl, *Acta Chem. Scand.*, 1994, **48**, 95.
11 V. I. Minkin, I. E. Mikhailov, G. A. Dushenko, I. A. Yudilevich, R. M. Minyaev, A. Zschunke and K. Mugge, *J. Phys. Org. Chem.*, 1991, **4**, 31.
12 C. L. Perrin, *Stereochemical Aspects of Amidines, Imidates and Related Compounds*, in *The Chemistry of Amidines and Imidates*, eds. S. Patai and Z. Rappoport, J. Wiley, London, 1991, ch. 3, p. 147.

Received: Moscow, 5th January 1997
Cambridge, 21st April 1997; Com. 7/00342K