

## Reactivity of the Macrocyclic Complex $[\text{Ni}(\text{C}_{22}\text{H}_{22}\text{N}_4)]$ Toward Cyanogen

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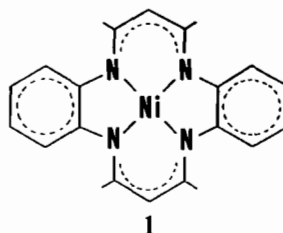
### Abstract

The macrocyclic complex (2,3:9,10-dibenzo-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-2,4,6,9,11,13-hexaenato(2-)- $k^4N$ )nickel(II),  $[\text{Ni}(\text{Bzo}_2\text{Me}_4[14]\text{hexaenatoN}_4)]$  reacts with cyanogen under mild conditions to give addition–insertion to the methine C–H group. The two resulting complexes are characterized by one or two cyanoimino methyl  $-\text{C}(=\text{NH})\text{CN}$  substituents, from which HCN can be easily released to give the corresponding cyano derivatives. The mono cyano complex  $[\text{Ni}(\text{Bzo}_2(\text{CN})\text{Me}_4[14]\text{hexaenatoN}_4)]$  crystallizes in the monoclinic system (space group  $P2_1/n$ ) and has a saddle-shaped structure, in which the benzene and  $\beta$ -diiminato groups are tilted in opposite directions, with respect to the plane defined by the four nitrogen and the nickel atoms ( $\text{C}\equiv\text{N}$  bond distance 1.141(14) Å).

### Introduction

Schiff base complexes are extensively investigated as they may be useful models of biological systems. In particular, tetraaza complexes such as organocobaloximes have been generally employed as  $\text{B}_{12}$  models [1]. In this context, substituted tetraaza[14]-annulenes represent a class of very attractive macrocyclic ligands because of their ability to accommodate a variety of substituents and to adopt different conformations [2]. An additional feature of the metal(II) complexes derived from the dianionic macrocycle is the presence of a C–H methine group capable, in principle, of undergoing addition–insertion reactions with Michael acceptors or nitriles, as already independently found in these and other laboratories for metal carbonylenolate complexes [3, 4].

It appeared therefore interesting to extend to this important class of macrocyclic compounds our previous studies on the reactivity of metallo-organic rings toward nitriles and we report here on the reaction of the dibenzotetramethyltetraaza[14]-annulene nickel complex (1) with cyanogen.



### Experimental

Cyanogen was a Fluka technical product (purity  $\geq 98\%$ ). Alumina (Baker) and silica (Merck 0.04–0.063) were high purity commercial products and used as received. Solvents (Baker Analyzed Reagents) were carefully deoxygenated by three freezing–pump cycles. Argon was a high purity ( $\geq 99.9\%$ ) SIO product.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were performed on a Jeol FX 90Q spectrometer operating in FT mode at 25 °C; IR and UV–Vis spectra on a 781 and on a Lambda 5 Perkin-Elmer spectrophotometers, respectively; the mass spectra on a VG Micromass 16F apparatus; TG-DSC analyses on a Perkin-Elmer TGS-2, DSC-4 equipment.

*Synthesis of (2,3:9,10-Dibenzo-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-2,4,6,9,11,13-hexaenato(2-)- $k^4N$ )nickel(II),  $[\text{Ni}(\text{Bzo}_2\text{Me}_4[14]\text{hexaenatoN}_4)]$  (1)*

This complex was prepared according to ref. 5 and recrystallized from dichloromethane.

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*Synthesis of (2,3:9,10-Dibenzo-6-cyanoiminomethyl-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-2,4,6,9,11,13-hexaenato(2-)-k<sup>4</sup>N)nickel(II), [Ni(Bzo<sub>2</sub>(C<sub>2</sub>N<sub>2</sub>H)Me<sub>4</sub>[14]hexaenatoN<sub>4</sub>)] (2) and of (2,3:9,10-Dibenzo-6,13-bis(cyanoiminomethyl)-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-2,4,6,9,11,13-hexaenato(2-)-k<sup>4</sup>N)nickel(II), [Ni(Bzo<sub>2</sub>(C<sub>2</sub>N<sub>2</sub>H)<sub>2</sub>Me<sub>4</sub>[14]hexaenatoN<sub>4</sub>)] (3)*

Compound 1 (0.4 g, 1 mmol) is suspended in 5 cm<sup>3</sup> of oxygen-free dichloroethane and the suspension is saturated with cyanogen. The reaction mixture is stirred for 6 h, at 40 °C. After cooling, the black solid present in small quantities is filtered off and the solution is carefully chromatographed on a silica column, eluent dichloromethane. Two main green fractions can be isolated, the first of which contains the monocyanoiminomethyl complex 2 and the second one the bis-cyanoiminomethyl derivative 3. Compound 2 is obtained upon solvent removal and recrystallization from dichloromethane–hexane as deep green platelets in 52% yield; melting point (m.p.) > 350 °C. *Anal.* Calc. for C<sub>24</sub>H<sub>22</sub>N<sub>6</sub>Ni: C, 63.60; H, 4.90; N, 18.54. Found: C, 63.48; H, 5.18; N, 18.39%. The IR spectrum (nujol mull) is characterized by two absorptions at 3235 (s, ν(N–H)) and 2190 (vw, ν(C≡N)) cm<sup>-1</sup> and the mass spectrum by a peak at 425 *m/e* (M<sup>+</sup> – HCN). UV–Vis (CHCl<sub>3</sub>, nm, logarithm of extinction coefficient, M<sup>-1</sup> cm<sup>-1</sup>, in parentheses): 268 (4.5), 388 (4.5), 580 (3.7). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ) = 2.07 (s, 6 H, CH<sub>3</sub>), 2.13 (s, 6 H, CH<sub>3</sub>), 4.83 (s, 1 H, CH), 6.66 (cm, 8 H, C<sub>6</sub>H<sub>4</sub>), 10.51 (s, 0.8 H, NH), 11.47 (s, 0.2 H, NH). Compound 3 is obtained upon solvent removal of the second fraction and recrystallization from dichloromethane–hexane as deep green microcrystals in 10% yield; m.p. > 350 °C. *Anal.* Calc. for C<sub>26</sub>H<sub>22</sub>N<sub>8</sub>Ni: C, 61.81; H, 4.36; N, 22.18. Found: C, 61.00; H, 4.56; N, 21.63%. The IR spectrum is characterized by two absorptions at 3235 (s, ν(N–H)) and 2190 (vw, ν(C≡N)) cm<sup>-1</sup> and the mass spectrum by a peak at 450 *m/e* (M<sup>+</sup> – 2 HCN). UV–Vis (CHCl<sub>3</sub>, nm, logarithm of extinction coefficient, M<sup>-1</sup> cm<sup>-1</sup>, in parentheses): 268 (4.5), 383 (4.5), 578 (3.7). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ) = 2.12 (s, 12 H, CH<sub>3</sub>), 6.70 (cm, 8 H, C<sub>6</sub>H<sub>4</sub>), 10.57 (s, 1.3 H, NH), 11.51 (s, 0.7 H, NH).

*Synthesis of (2,3:9,10-Dibenzo-6-cyano-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-2,4,6,9,11,13-hexaenato(2-)-k<sup>4</sup>N)nickel(II), [Ni(Bzo<sub>2</sub>(CN)Me<sub>4</sub>[14]hexaenatoN<sub>4</sub>)] (4) and of (2,3:9,10-Dibenzo-6,13-dicyano-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-2,4,6,9,11,13-hexaenato(2-)-k<sup>4</sup>N)nickel(II), [Ni(Bzo<sub>2</sub>(CN)<sub>2</sub>Me<sub>4</sub>[14]hexaenatoN<sub>4</sub>)] (5)*

*Procedure A.* The reaction mixture of the previous preparation is filtered and the solution is chromatographed on an alumina column, eluent dichloro-

methane. Two main fractions can be isolated: the first dark blue–green one gives, upon solvent evaporation, the monocyano compound 4, whereas the second one, violet in color, gives the dicyano derivative 5. Compound 4 is obtained as dark blue–purple crystals from dichloromethane–hexane in 20% yield; m.p. > 350 °C. *Anal.* Calc. for C<sub>23</sub>H<sub>21</sub>N<sub>5</sub>Ni: C, 64.82; H, 4.97; N, 16.43. Found: C, 64.86; H, 5.00; N, 16.34%. Strong IR absorption at 2183 cm<sup>-1</sup> (ν(C≡N)); MS, *m/e*: 425 (M<sup>+</sup>). UV–Vis (CHCl<sub>3</sub>, nm, logarithm of extinction coefficient, M<sup>-1</sup> cm<sup>-1</sup>, in parentheses): 271 (4.6), 385 (4.5), 564 (3.7). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ) = 2.06 (s, 6 H, CH<sub>3</sub>); 2.38 (s, 6 H, CH<sub>3</sub>), 4.83 (s, 1 H, CH), 6.69 (cm, 8 H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ) = 21.53 (CH<sub>3</sub>), 21.85 (CH<sub>3</sub>), 94.90 (C≡N), 111.45 (CH), 121.10–121.96–124.24–146.34–147.21 (*o*-phenylene), 155.99 (CCH<sub>3</sub>), 160.10 (CCH<sub>3</sub>). Compound 5 is obtained as rose–violet crystals from dichloromethane–hexane in 40% yield; m.p. > 350 °C. *Anal.* Calc. for C<sub>24</sub>H<sub>20</sub>N<sub>6</sub>Ni: C, 63.89; H, 4.47; N, 18.63. Found: C, 63.98; H, 4.49; N, 18.53%. Strong IR absorption at 2183 cm<sup>-1</sup> (ν(C≡N)); MS, *m/e*: 450 (M<sup>+</sup>). UV–Vis (CHCl<sub>3</sub>, nm, logarithm of extinction coefficient, M<sup>-1</sup> cm<sup>-1</sup>, in parentheses): 296 (4.7), 380 (4.6), 558 (3.7). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ) = 2.40 (s, 12 H, CH<sub>3</sub>), 6.80 (cm, 8 H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ) = 21.44 (CH<sub>3</sub>), 96.54 (C≡N), 122.07–124.41–146.26 (*o*-phenylene), 160.91 (CCH<sub>3</sub>).

*Procedure B.* Compound 2 (or 3) (50 mg, 0.11 mmol) is suspended in 5 cm<sup>3</sup> of dioxane and treated with 1 cm<sup>3</sup> of aqueous sodium carbonate. The mixture is heated at 40–50 °C for one minute and compound 4 (or 5) precipitates quantitatively after cooling. This procedure may be modified by employing dichloromethane as solvent and triethylamine as base.

*Crystallography of [Ni(Bzo<sub>2</sub>(CN)Me<sub>4</sub>[14]hexaenatoN<sub>4</sub>)] (4)*

Crystals of suitable size were obtained by recrystallization of 4 from a dichloromethane–methanol solution. A selected crystal was mounted on a Philips PW 1100 four-circle diffractometer and cell constants were obtained from a least-squares fit of the setting angles of 25 reflections. A summary of crystal and intensity collection data is given in Table 1. A total of 3434 unique reflections were recorded out to 2θ(Mo) = 50°.

The structure was solved using Multan80 and refined by block-diagonal least-squares using anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were partially located on a difference Fourier map and not refined. The *R* factor (Σ(|F<sub>o</sub>| – |F<sub>c</sub>||)/|F<sub>o</sub>|) was 0.0778 and *w* = 1. The final fractional atomic coordinates are listed in Table 2.

TABLE 1. Summary of Crystal and Intensity Collection Data for [Ni(Bzo<sub>2</sub>(CN)Me<sub>4</sub>[14]hexaenatoN<sub>4</sub>)] (4)

Formula	C <sub>23</sub> H <sub>21</sub> N <sub>5</sub> Ni
Molecular weight	426.19
Color	purple
Habit	prismatic
Crystal dimensions (mm)	0.1 × 0.2 × 0.4
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	18.848(2)
<i>b</i> (Å)	7.997(1)
<i>c</i> (Å)	12.892(2)
β (°)	90.9(2)
<i>V</i> (Å <sup>3</sup> )	1943.0
Molecules/cell	4
Density (calc.) (g/cm <sup>3</sup> )	1.633
Wavelength (Å)	0.7107
Temperature (°C)	21
Linear absorption coefficient (cm <sup>-1</sup> )	8.66
Diffractometer	Philips PW 1100
2θ range	4° ≤ 2θ ≤ 50°
Scan technique	θ-2θ
Octants	<i>h k l</i> ; $\bar{h} \bar{k} \bar{l}$
Total reflections collected	3588
Unique reflections collected	3434 ( <i>R</i> = 0.07)
Observed reflections ( <i>I</i> > 3σ( <i>I</i> ))	2344
Final residual <i>R</i> ( <i>w</i> = 1)	0.0778

## Results

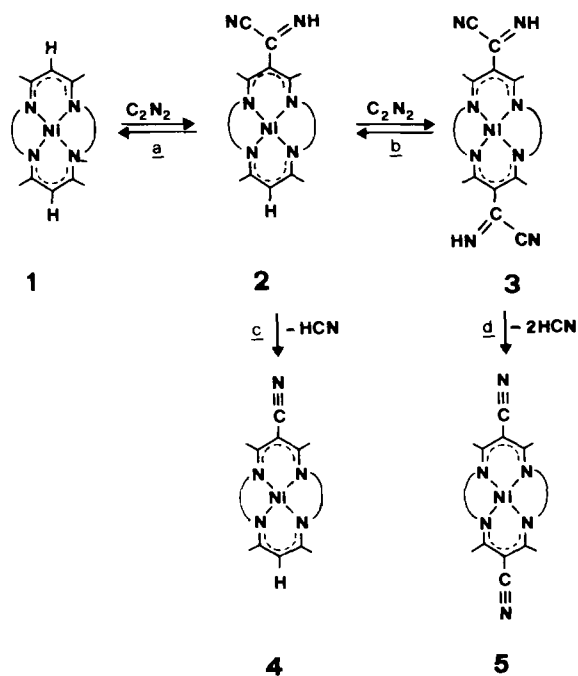
### Synthesis and Characterization

The dibenzotetramethyltetraaza[14]annulene nickel complex (1) reacts with C<sub>2</sub>N<sub>2</sub> in dichloroethane at moderate conditions (6 h, 40 °C, routes a, b in Scheme 1) to give a mixture, which affords by careful chromatography on a silica column the mono- and bis-cyanoimino derivatives 2 and 3. They exhibit a moderate stability and may lose either cyanogen or hydrogen cyanide in solution. The cyanogen addition reaction is reversed in the presence of silica, the conversion of complex 3 to 2 being much easier than the conversion of 2 to 1. This fact makes the chromatographic procedure rather laborious, because of a delicate balance between the opposite requirements of an adequate bands separation and of a high chromatography rate\*. Complexes 2 and 3 lose HCN under basic conditions (alumina, sodium carbonate, or triethylamine) or in the solid state by heating to 150–200 °C to give the corresponding cyano derivatives 4 and 5 (routes c, d in Scheme 1).

\*This reversibility explains the only fair elemental analysis for 3 and the observation (see 'Experimental') that, starting from the same mother solution, a higher yield of 5 (alumina column) is obtained compared with that of the parent complex 3 (silica column).

TABLE 2. Fractional Coordinates and Thermal Parameters for [Ni(Bzo<sub>2</sub>(CN)Me<sub>4</sub>[14]hexaenatoN<sub>4</sub>)] (4)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U<sub>e</sub></i>
Ni	0.2928(1)	0.5803(2)	0.1405(1)	0.0396
N(1)	0.2345(3)	0.5788(10)	0.2530(5)	0.0394
N(2)	0.2189(4)	0.5284(9)	0.0473(5)	0.0389
N(3)	0.3502(3)	0.5815(10)	0.0253(5)	0.0424
N(4)	0.3661(4)	0.6331(10)	0.2362(6)	0.0476
N(5)	-0.0002(5)	0.7425(14)	0.1652(7)	0.0737
C(1)	0.2484(3)	0.4827(9)	0.4367(5)	0.0578
C(2)	0.2938(3)	0.4564(9)	0.5217(5)	0.0495
C(3)	0.3656(3)	0.4963(9)	0.5149(5)	0.0748
C(4)	0.3921(3)	0.5624(9)	0.4231(5)	0.0638
C(5)	0.3468(3)	0.5887(9)	0.3382(5)	0.0523
C(6)	0.2749(3)	0.5488(9)	0.3450(5)	0.0504
C(7)	0.4257(5)	0.7140(12)	0.2077(8)	0.0497
C(8)	0.4433(5)	0.7368(14)	0.1031(9)	0.0587
C(9)	0.4086(5)	0.6730(14)	0.0166(8)	0.0573
C(10)	0.4414(6)	0.7098(19)	-0.0864(9)	0.0851
C(11)	0.4794(6)	0.7767(16)	0.2869(9)	0.0731
C(12)	0.2107(3)	0.3504(9)	-0.1134(5)	0.0572
C(13)	0.2473(3)	0.2740(9)	-0.1939(5)	0.0710
C(14)	0.3197(3)	0.3037(9)	-0.2054(5)	0.0713
C(15)	0.3555(3)	0.4096(9)	-0.1365(5)	0.0629
C(16)	0.3189(3)	0.4859(9)	-0.0560(5)	0.0492
C(17)	0.2465(3)	0.4563(9)	-0.0445(5)	0.0440
C(18)	0.1519(4)	0.5759(13)	0.0606(7)	0.0433
C(19)	0.1284(4)	0.6317(12)	0.1572(7)	0.0448
C(20)	0.1669(5)	0.6288(11)	0.2524(7)	0.0428
C(21)	0.0981(5)	0.5745(15)	-0.0280(7)	0.0586
C(22)	0.0568(5)	0.6952(14)	0.1612(8)	0.0536
C(23)	0.1293(5)	0.6836(13)	0.3483(7)	0.0531



Scheme 1.

The mono- and bis-cyanoiminomethyl complexes **2** and **3** are characterized by IR absorptions at 3235 (s,  $\nu(\text{N-H})$ ) and at 2190 (w,  $\nu(\text{C}\equiv\text{N})$ )  $\text{cm}^{-1}$  due to the  $-\text{C}(=\text{NH})\text{CN}$  substituent, resulting from the addition–insertion of the  $\text{N}\equiv\text{C}-\text{C}\equiv\text{N}$  moiety to the C–H group of the macrocyclic ring. Their  $^1\text{H}$  NMR spectra in  $\text{CDCl}_3$  solution, together with a very small (0.06 ppm) downfield shift of the methyl protons in the substituted diiminato ring, show in addition two well distinct, albeit broad, NH resonances, which may perhaps be attributed to a partial intermolecular interaction of the NH proton with the cyano nitrogen atom or the nickel center.

Complex **2** loses HCN in the temperature range 160–210  $^\circ\text{C}$  ( $\Delta w = -6.0\%$ , scan rate 10  $^\circ\text{C min}^{-1}$ , under nitrogen); this endothermic process ( $\Delta H = 3.7$  kcal  $\text{mol}^{-1}$ ) is followed (210–247  $^\circ\text{C}$ ) by an exothermic structural rearrangement ( $\Delta H = -5.9$  kcal  $\text{mol}^{-1}$ ), so that the conversion of **2** to **4** (see Scheme 1) is enthalpically favoured. Under the same experimental conditions, complex **3** loses two HCN molecules (150–240  $^\circ\text{C}$ ,  $\Delta w = -10.9\%$ ) and in this case only an overall exothermic peak ( $\Delta H = -2.8$  kcal  $\text{mol}^{-1}$ ) centred at 187  $^\circ\text{C}$  can be observed. The EI mass spectra of complexes **2** and **3** are in agreement with the observed thermal behavior: they are, in fact, characterized by peaks at 425 (**2**,  $M^+ - \text{HCN}$ ) and at 450  $m/e$  (**3**,  $M^+ - 2\text{HCN}$ ), the general fragmentation pattern being strictly similar to that exhibited by **4** and **5**, respectively.

The mono- and dicyano complexes **4** and **5** are thermally very stable and they do not lose weight up to 300  $^\circ\text{C}$ . They are characterized by a strong IR absorption at 2183  $\text{cm}^{-1}$  due to the stretching of the  $\text{C}\equiv\text{N}$  group originated from the release of hydrogen cyanide from the cyanoiminomethyl group. This value is about 50  $\text{cm}^{-1}$  lower than the values usually found in organic nitriles [6] or in cyano-substituted acetylacetonate complexes [7], thus suggesting an extensive bond delocalization involving the  $\text{C}\equiv\text{N}$  group. Their  $^1\text{H}$  NMR spectra in  $\text{CDCl}_3$  solution show an appreciable deshielding effect of the cyano substituent at the  $\gamma$ -carbon on the methyl resonances ( $\Delta\delta = 0.33(1)$  ppm).

#### *X-ray Structure of [Ni(Bzo<sub>2</sub>(CN)Me<sub>4</sub>[14]-hexaenatoN<sub>4</sub>)] (4)*

The nickel atom lies on the plane defined by the four nitrogen atoms of the macrocyclic ring (Fig. 1). The structure has a saddle-shaped conformation, in that the benzene and  $\beta$ -diiminato groups are tilted in opposite directions to relieve the steric constrain. The average Ni–N distance in the CN-substituted propane-1,3-diiminato ring (1.852(5) Å) is slightly shorter than that of the unsubstituted one (1.868(5) Å), this last value being remarkably close to that found for the parent compound **1** (1.866(3) Å) [8].

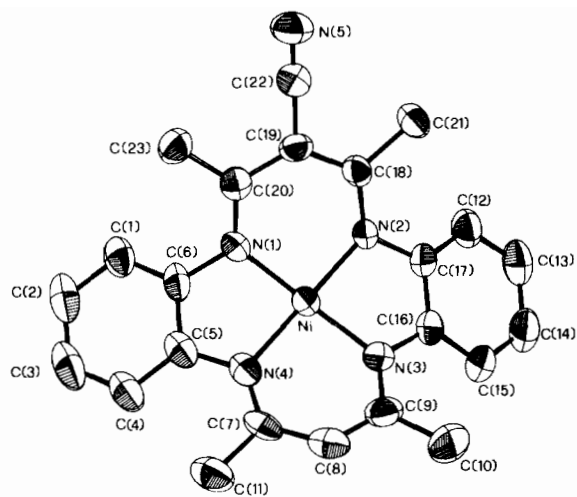


Fig. 1. ORTEP view of  $[\text{Ni}(\text{Bzo}_2(\text{CN})\text{Me}_4[14]\text{hexaenatoN}_4)]$  (**4**). Structural parameters (see also text) are as follows. Distances: Ni–N(1) = 1.833(7); Ni–N(2) = 1.872(7); Ni–N(3) = 1.851(7); Ni–N(4) = 1.886(7); N(1)–C(6) = 1.420(9); N(1)–C(20) = 1.336(11); N(2)–C(17) = 1.422(9); N(2)–C(18) = 1.333(11); N(5)–C(22) = 1.141(14); C(19)–C(22) = 1.444(14). Angles: N(1)–Ni–N(2) = 93.3(3); N(1)–Ni–N(4) = 85.7(3); N(2)–Ni–N(3) = 85.7(3); N(3)–Ni–N(4) = 95.3(3).

In general, it is seen that introduction of a CN substituent in the  $\gamma$  position does not involve significant changes in the structure. A marked delocalization involves the diiminato rings, C–N and C–C bond distances being in the range 1.328(12)–1.352(12) and 1.382(15)–1.416(13) Å, respectively. This delocalization does not extend to the (phenyl)C–N bonds (1.415(10)–1.422(9) Å) as indicated also by the dihedral angle defined, for example, by the C(6)–N(1)–C(20) and N(1)–C(20)–C(23) planes (9.47 $^\circ$ ). As to the cyano substituent, the  $\text{C}\equiv\text{N}$  bond distance (1.141(14) Å) is quite normal and compares well, for example, with that found in acrylonitrile (1.163 Å) [9] or cyanogen (1.127(8) Å) [10], also the C(ring)–C(nitrile) bond distance (1.444(14) Å) falls in the expected range for an  $\text{sp}^2$ – $\text{sp}$  carbon–carbon single bond [11, 12].

#### Discussion

The results obtained indicate that the C–H methine groups of **1** easily undergo addition–insertion reactions by an electrophilically activated nitrile like cyanogen (Scheme 1) to give mono- and bis-cyanoiminomethyl substituted derivatives. This reaction pattern is novel in that the functionalization of the  $\gamma$ -position of six-membered diiminato chelate rings normally requires substitution with acyl groups under basic conditions [2]. From a mechanistic point of view, this reaction is likely to imply a four-center

C...C and N...Ni interaction involving the cyano group, the metal center and the methine carbon atom. Similar interaction was, in fact, postulated in the reaction of the related complex  $[\text{Co}(\text{C}_{22}\text{H}_{22}\text{N}_4)(\text{py})_2]^+$  with nitriles under acidic conditions [13], and in the reaction of a series of macrocyclic bis- $\beta$ -diimine iron(II) complexes with acetonitrile [14]. However, it should be noted that the reaction products are different in these two cases, in that (i) the resulting cyanoiminomethyl substituent is coordinated to the metal center and (ii) the  $\gamma$ -carbon atom adopts an  $\text{sp}^3$  hybridization, which destroys the ring planarity. Thus, the reaction here described discloses a basically new chemical behavior of macrocyclic complexes toward nitriles; this result is not completely unexpected in view of our previous findings on the reactivity of  $\beta$ -carbonylenolato [4] and  $\beta$ -carbonyliminato complexes [15] toward activated nitriles. It appears, therefore, that the addition–insertion reaction of a very electrophilically activated nitrile like cyanogen shown in Scheme 1 represents an expected feature of most metallo-organic rings derived from C–H acid ligands.

The cyanoiminomethyl-substituted complexes 2 and 3 are easily transformed upon heating into the corresponding cyano complexes 4 and 5, this process being enthalpically favoured ( $\Delta H = -2.2$  and  $-2.8$  kcal mol $^{-1}$ , respectively). These figures are the result of an endothermic HCN release accompanied by an exothermic molecular rearrangement, as clearly evidenced for complex 2. The  $\Delta H$  value (3.7 kcal mol $^{-1}$ ) for HCN release found in this case is much lower than the estimated sum (ca. 40 kcal mol $^{-1}$ ) of the contributions due to the individual steps, C–C and N–H bond breaking, H–CN bond forming and C=N to C $\equiv$ N transformation [11, 16], thus suggesting a highly assisted process possibly via intermolecular =NH...N $\equiv$ C– interactions.

The same hydrogen cyanide release takes place also under very smooth basic conditions ('neutral' alumina), so indicating a relative instability of the  $\text{>C-C(=NH)CN}$  assembly. Also the observed reversibility of the cyanogen addition–insertion reaction is consistent with this suggestion. It may seem surprising that similar phenomena have never been observed in  $\beta$ -carbonylenolate complexes; however, it should be pointed out that in these cases an important ligand rearrangement reaction takes place, most likely via a ring opening process, to give a more stable form in which the CN group formally exchanges with the methyl or phenyl substituent at one of the carbonyls [17].

In the present case, the rigid structure of the macrocyclic ring makes this rearrangement impos-

sible, so that complexes 2 and 3 can easily evolve to the corresponding more stable cyano complexes 4 and 5. The success of this synthesis appears interesting as no other examples of macrocyclic complexes with a C $\equiv$ N substituent at the  $\gamma$ -position of  $\beta$ -diiminato groups appear to have been reported.

In conclusion, cyanogen is shown to behave not only as a useful cyanoimination reagent, but, owing to the instability of the resulting  $-\text{C(=NH)CN}$  moiety, also as a mild and selective cyanating agent of electrophilically metal-activated carbon centres.

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