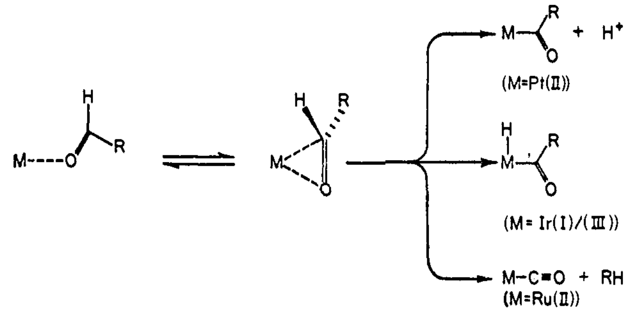
Scheme I. Suggested Mechanism for the Reactions of Transition Metal–Aldehyde Complexes



can rearrange via hydrogen migrations to each of the observed products with minimal geometric reorganizations.[23]

**Acknowledgments.** We thank the Merck Foundation for partial financial support and Engelhardt Industries for loan of the platinum metals.

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(11) Anal. Calcd for $C_{38}H_{29}ClO_2P_2Pt$: C, 56.32; H. 3.58; Cl, 4.38; P, 7.66. Found: C, 56.08; H, 3.59; Cl, 4.59; P, 7.90. Spectral data: IR (Nujol) 1695, 1625 $cm^{-1}$; $^1H$ NMR (90 MHz, $COCl_3$) $\tau$ −0.566 (d, 1 H, $J_{PH}$ = 2 Hz), 2.0–3.0 (m, ~28 H); $^{31}P[^1H]$ ($CH_2Cl_2$) $\tau$ 30.12 (d), 48.54 (d) ($J_{AB}$ = 391 Hz). For these and other $^{31}P$ data, downfield shifts are positive.
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(14) This mechanism was recently demonstrated by Suggs in the reaction of quinoline-8-carboxaldehyde with rhodium(I).[6]
(15) Spectral data: IR (Nujol) 2110 (w), 1635 $cm^{-1}$ (s); $^1H$ NMR (90 MHz, $CDCl_3$) 2.0–2.9 (m, 14 H, Ph–H), 4.5 (m, 1 H, olefin), 5.0 (m, 2 H, olefin), 5.7 (m, 1 H, olefin), 7.5 (m, ~8 H, alkyl), 26.12 (d, 1 H, $J_{PH}$ = 15 Hz).
(16) Anal. Calcd for $C_{38}H_{30}Cl_2O_2P_2Ru$: C, 60.32; H, 3.97; Cl, 9.11; P, 9.51. Found: C, 60.48; H, 3.88; Cl, 9.71; P. 9.14. Spectral data: IR ($CH_2Cl_2$) 1646 $cm^{-1}$ (s); IR (Nujol) 372 $cm^{-1}$ (m); $^1H$ NMR (90 MHz in $CDCl_3$) $\tau$ 0.6 ($J_{PH}$ = 9 Hz, 2 H), 2.9–4.1 (m, 28 H); $^{31}P[^1H]$ $\tau$ 51.7(s).
(17) Purple ruthenium(II)–phosphine complexes have recently attracted attention, as they are usually five-coordinated and often catalytically active. See M. A. A. F. de C. T. Carrondo, B. N. Chaudret, D. J. Cole-Hamilton, A. C. Skapski, and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 463 (1978), and references therein.
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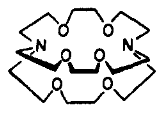
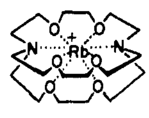
## Synthesis and X-ray Structure of $N[(CH_2)_2O(2,6\text{-}C_6H_3N)O(CH_2)_2]_3N$: a $D_3$ Macrobicyclic Ligand Capped by Two $sp^2$ Nitrogen Atoms

*Sir:*

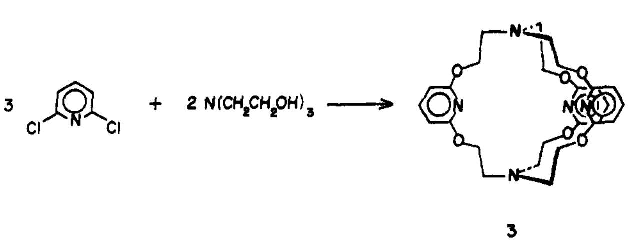
In 1970 (in a preliminary form), Weiss et al.[1] reported the molecular structure of the noncomplexed diazabicyclopolyether **1** (C-2.2.2) as well as of the corresponding rubidium cryptate **2** [Rb⁺⊂2.2.2]. The free ligand **1** was shown to possess the endo-endo (in-in)[2] N configurations, in which the N–N distance was 6.872 (9) Å, a value slightly larger than that of **2** (6.008 Å).[1] In free cryptands, it has been generally assumed that the N lone pairs are either in the in-in, in-out, or out-out configurations.[3] In published structural representations of cryptands, these molecules are generally depicted in the in-in configuration for convenience in seeming correlation with the corresponding cryptates. However, a brief synopsis of cryptand literature suggests that few researchers are aware of the Weiss et al.[1] paper, since ~30–40% of the structural representations of C-2.2.2 are inadvertently and/or erroneously drawn in the out-out configuration. The correctness of the generally accepted concept of describing cryptand bridging nitrogen atoms as being only in the in or out configuration is now in question, since we herein report the X-ray crystal structure of **3**, in which *the bridgehead nitrogen atoms possess a planar configuration with crystallographically equivalent 120° bond angles.*



**1**



**2**



**3**

To a mixture of triethanolamine (10 mmol) with excess oil-free sodium hydride in xylene, 2,6-dichloropyridine **4** (15 mmol) in xylene was added. The mixture was refluxed for 36 h and worked up by previously described procedures[4] to afford (5%) **3**, as colorless crystals:[5] mp 228 °C dec; NMR (100 MHz) ($CDCl_3$) $\delta$ 3.08 (t, $NCH_2$, $J$ = 6 Hz, 12 H), 4.32 (t, $OCH_2$, $J$ = 6 Hz, 12 H), 6.13 (d, 3,5-PyrH, $J$ = 8 Hz, 6 H), 7.30 (t, 4-PyrH, $J$ = 8 Hz, 3 H); IR (KBr) 1580, 1250, 1145 $cm^{-1}$; UV ($CH_3CN$) $\lambda_{max}$ 276 ($3.10 \times 10^6$), 258 (sh, $2.36 \times 10^6$), 225 ($7.50 \times 10^6$); mass spectrum *m/e* 523 ($M^+$), 412 ($M^+ - 111$). Numerous other macrocycles and oligomeric products were isolated and characterized.[6]

The molecular structure of **3** was established by X-ray crystallographic methods indicating: Trigonal space group $R\bar{3}c$, with rhombohedral axes $a$ = 10.937 (2) Å, $\alpha$ = 83.33 (2)°, $Z$ = 2, $d_c$ = 1.355 g $cm^{-3}$, $R$ = 0.060 for 430 unique observed data collected on an Enraf-Nonius CAD-4 diffractometer. The macrobicyclic cryptand **3** has been found to possess $D_3$ symmetry in the crystal, deviating from ideal $D_{3h}$ symmetry by a slight twist about the $C_3$ axis (Figure 1). Figure 2 shows that all bond distances and angles are near their expected values except for the very surprising C–N–C angle of 120 ± 0.5° for the bridgehead, amine nitrogen atoms. Figure 3 shows a stereoscopic view of **3**.

Thus, since cryptand nitrogen atoms in **3** are planar $sp^2$

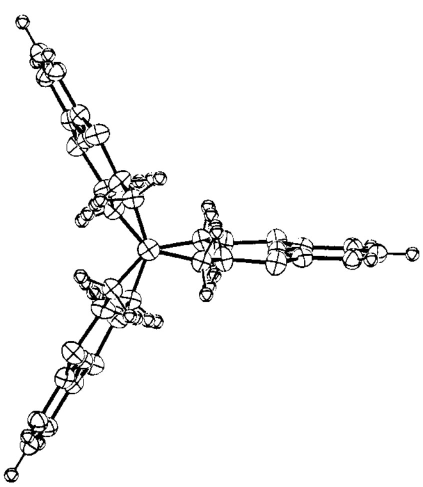


Figure 1. ORTEP[7] drawing of **3** projected down the N-N axis, illustrating nonhydrogen atoms by 40% probability thermal ellipsoids and hydrogen atoms by spheres of arbitrary radius.

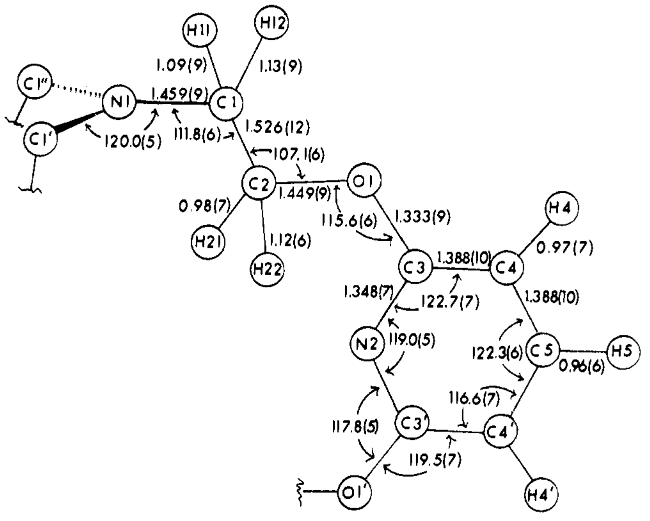


Figure 2. Bond distances and angles of cryptand **3**.

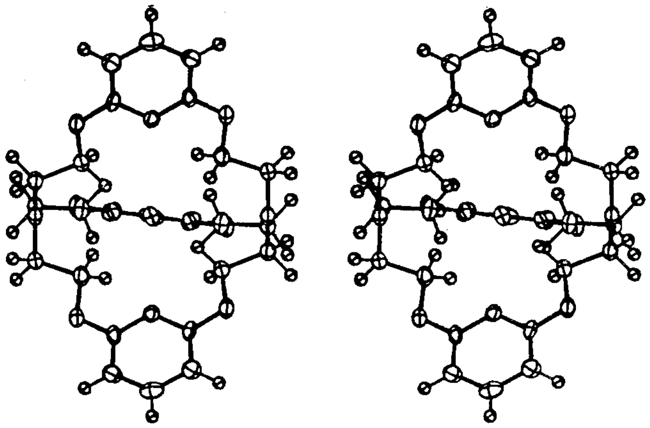


Figure 3. Stereoscopic representation of **3** viewed approximately down a twofold axis.

hybridized, rather than the anticipated sp$^3$ configuration, the generally accepted in-in and out-out pictorial representation need *not* adequately represent these macropolycyclic structures. Skeletal rigidity of the bridges or intramolecular hinderence imposed by substituents on the bridges apparently may determine the bridgehead nitrogen configurations. Crystallographic details, as well as the synthesis and reactions of similar cryptands, will be the subject of a later paper.

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**Supplementary Material Available:** Table of the positional and thermal parameters (1 page). Ordering information is given on any current masthead page.

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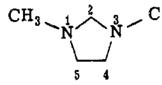
## Ring-Chain Tautomerism in 1,3-Dimethylimidazolidine on the NMR Time Scale[1]

*Sir:*

Intramolecular organic rate processes studied at equilibrium by NMR spectroscopy have included bond rotations, atomic inversions, pentacoordinate pseudorotations, sigmatropic shifts, and proton transfers.[2] We report here the first example of a new reaction class that can be studied by this method, ring-chain tautomerism. This process is well known in heterocyclic chemistry[3] but has not previously been subject to study by the DNMR method.

At room temperature 1,3-dimethylimidazolidine (**1**, 1,3-dimethyl-1,3-diazolidine or 1,3-dimethyltetrahydroimida-

**1**



zole) in $CF_3CO_2H$ gives the $^1$H spectrum illustrated at the bottom of Figure 1. At first glance, the spectrum appears to be unremarkable, with the $NCH_2N$ resonance at $\delta$ 5.2, the $NCH_2CH_2N$ at 4.3, and the $NCH_3$ at 3.4. In addition, however, there are two puzzling small resonances from $\delta$ 7.7 to 8.5, one that is very broad and one that is relatively sharp. The spectrum is identical in $CF_3CO_2D$, except for the absence of the broad peak at $\delta$ 7.7–8.4, which hence can be assigned to the $^+$NH protons. Consequently, the sharper peak at $\delta$ 8.4–8.5 cannot be from $^+$NH protons. Integration of the $^+$NH peak shows that the diazolidine is ~50% protonated under these conditions. The equilibrium between unprotonated (**1**) and monoprotonated (**1**-H$^+$) forms must be fast on the NMR time scale, since separate resonances are not observed and the H-N-C-H couplings are absent.

The rather low-field location of the $\delta$ 8.4 peak suggested to us an aldehyde-like structure (**2**), which can be readily obtained from the diazolidine by ring-chain tautomerism (eq 1).[4] The anisotropy of the C=N double bond should deshield the

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