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radical (**3**) to, eventually, naphthaldehyde without affecting any of the reactions that form ether **2** (O_2 does not react rapidly with I·). This prediction also is verified by experiment. The quantum yield of ether formation is essentially unaffected by the addition of oxygen to the reaction mixture; however, the quantum yield for total disappearance of iodide **1** more than doubles when oxygen is present.

The last step in the proposed mechanism is the reaction of the naphthylmethyl radical with $I_2^{-}\cdot$ to regenerate **1** and form iodide ion. The evidence for this step is that the rates of consumption of the radical and $I_2^{-}\cdot$, in the absence of oxygen, are approximately the same.

In sum, our kinetic, spectroscopic, and product studies implicate a secondary reaction of iodine atoms with alkyl iodide **1** as the product generating step in this photosolvolysis reaction. The complex formed in this step may rapidly dissociate into separated ions or may react directly with solvent. There is no evidence in this system for the direct photochemical generation of carbonium ions or for their formation by electron transfer from the naphthylmethyl radical to iodine atoms. However, it must be noted that the mechanism for photosolvolysis of these halides may depend strongly upon the identity of the halogen atom and the structure of the alkyl group. We are continuing to explore the photosolvolysis mechanism of iodide **1** and its relationship to the other systems that have been reported.

Acknowledgment. We thank Professor Robert L. Strong of Renssalaer Polytechnic Institute for some very helpful suggestions and comments, John Hurst of this department for the use of his computer programs, and James Wehmer of this department for his assistance with the laser apparatus. This work was supported by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Catalysis by Solvated Transition-Metal Cations. Novel Catalytic Transformations of Alkenes by Tetrakis(acetonitrile)palladium Ditetrafluoroborate. Evidence for the Formation of Incipient Carbonium Ions as Intermediates

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An important requirement of homogeneous catalysts is that they have the ability to create vacant coordination sites by dissociation of weakly held ligands. Transition-metal cations solvated in weakly coordinating solvents and having noncoordinating counteranions would be expected to meet this criterion. Furthermore, the catalytic properties of such compounds should be subject to modification in a predictable way by the stepwise substitution of solvent molecules by other more strongly binding ligands. In this context, we report the catalytic properties of $[Pd(CH_3CN)_4](BF_4)_2$ (**1**) and its trisphosphine derivative $[Pd(CH_3CN)(PPh_3)_3](BF_4)_2$ (**2**). As detailed below, the chemistry associated with **1** was found to differ very significantly from that observed with analogous neutral Pd(II) compounds, such as $Pd(PhCN)_2Cl_2$, $PdCl_2$, and $Pd(OAC)_2$, as well as other conventional, neutral transition–metal compounds on one hand and traditional Lewis acids such as $AlCl_3$ on the other.

Compound **1** was synthesized through the interaction of palladium metal with 2 equiv of nitrosyl tetrafluoroborate in acetonitrile.[1] Following precipitation by the addition of methylene chloride, an air-sensitive yellow solid was isolated.[2] Addition of an excess of PPh_3 to **1**, suspended in methylene chloride, resulted in the quantitative formation of **2**, isolated as air-stable, pale greenish yellow solid.[3]

Dropwise addition of styrene to an acetonitrile solution of **1** resulted in the immediate and quantitative precipitation of polystyrene (eq 1). When a monomer to catalyst ratio of 100:1

$$\mathrm{PhCH{=}CH_2} \xrightarrow[\text{room temperature, } \mathrm{CH_3CN}]{\mathrm{Pd(CH_3CN)_4^{2+}}} \text{polystyrene} \qquad (1)$$

was used, a polymer of average molecular weight ~70 000 was obtained.[4] Catalytic polymerization of styrene has not been observed with neutral Pd(II) compounds;[5] **2** was also found to be inactive under identical conditions. Significantly, another electrophilic cation, Ag^+, also catalyzes polymerization of styrene,[6] although at an appreciably higher temperature (70 °C vs. room temperature for **1**).

Compound **1** also catalyzed the oligomerization of unactivated olefins such as ethylene. In a typical reaction, a solution containing 0.1 mmol of **1** in 0.3 mL of CH_3CN was exposed to ethylene (at 1200 psi) at 40 °C for 60 h. At the end of this period, a colorless organic layer (~0.9 mL) was found to have been formed over the original acetonitrile layer.[7] Analysis[8] of this layer revealed it to be an approximately equal mixture of C_4-, C_6-, C_8- as well as a small amount of C_{10}-internal monoolefins, the overall reaction representing a "turnover" of 200 equiv (relative to **1**) of ethylene (eq 2). The formation of internal olefins is not surprising since

$$\mathrm{CH_2{=}CH_2} \xrightarrow[40\ ^\circ\mathrm{C},\ \mathrm{CH_3CN}]{\mathrm{Pd(CH_3CN)_4^{2+}}} \mathrm{C_4H_8},\ \mathrm{C_6H_{12}},\ \mathrm{C_8H_{16}}, \text{ and } \mathrm{C_{10}H_{20}}\text{-internal monoolefins} \qquad (2)$$

1 in acetonitrile solution or chloroform suspension was found to convert both 1-butene and *cis*-2-butene to the thermodynamic equilibrium mixture of *trans*-2-butene, *cis*-2-butene, and 1-butene (observed percentages are 67%, 28% and 5%, respectively),[9] within 1 h at room temperature. *In Addition, this equilibrium mixture was converted to butene dimers in <2 days.* The catalytic formation of C_8-monoolefins from butenes indicate that the oligomerization of ethylene by **1** may proceed through discrete dimerization steps. Significantly, unlike most ethylene oligomerization catalysts,[11] the oligomerization of ethylene by **1** does not stop at the dimer stage. This may be due to the fact that while neutral, electron-rich transition-metal centers bind ethylene more strongly than butenes,[12] in the case of electrophilic $Pd(CH_3CN)_4^{2+}$, with minimal steric requirements, the bulky electron-rich butenes may be able to compete effectively with ethylene in the dimerization process. As an extension of the above argument, one would predict that substitution of some of the CH_3CN molecules in **1** by other bulkier, more electron-donating ligands would favor the formation of C_4- over C_6- and C_8-monoolefins, and indeed in

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(1) R. F. Schramm and B. B. Wayland, *Chem. Commun.*, 898 (1968).

(2) Anal. Calcd for $[Pd(CH_3CN)_4](BF_4)_2$: C, 21.7; H, 2.7; N, 12.6. Found: C, 21.8; H, 2.9; N, 12.3. IR (Nujol) $\bar{\nu}(C{\equiv}N)$ 2335 cm^{-1}; $\bar{\nu}(BF_4^-)$ 1100–1000, 760 cm^{-1}.

(3) ^{31}P NMR ($CDCl_3$, −40 °C) δP_1 34.5 (1 P, t), δP_2 27.6 (2 P, d); IR (nujol) $\bar{\nu}(C{\equiv}N)$ 2375, 2335 cm^{-1}; $\bar{\nu}(BF_4^-)$ 1100–1000, 760 cm^{-1}.

(4) Molecular weights of polymers determined by gel permeation chromatography using standard polystyrene samples as calibrants.

(5) P. M. Maitlis, "The Organic Chemistry of Palladium", Vol. II, Academic Press, New York, 1971, Chapter I.

(6) (a) M. M. T. Khan and A. E. Martell, "Homogeneous Catalysis by Metal Complexes", Vol. II, Academic Press, New York, 1974, Chapter 6. (b) J. P. Hermans and G. Smets, *J. Polym. Sci., Part A*, **3**, 3175 (1965).

(7) A trace of palladium metal was sometimes observed following depressurization. This was found to be inactive in a separate experiment.

(8) Hydrocarbon samples were analyzed by standard gas chromatographic–mass spectrometric techniques.

(9) Typical reported percentages were 69%, 25%, and 6%, respectively.[10]

(10) (a) M. Tuner, J. v. Jouanne, H.-D. Brauer, and H. Kelm, *J. Mol. Catal.*, **5**, 425, 433, 477 (1979); (b) C. A. Tolman, *J. Am. Chem. Soc.*, **94**, 2994 (1972).

(11) G. Lefebvre and Y. Chauvin, *Aspects Homogeneous Catal.*, **1**, 107 (1970).

(12) (a) F. R. Hartley, *Chem. Rev.*, **73**, 163 (1973); (b) C. A. Tolman, *J. Am. Chem. Soc.*, **96**, 2780 (1974).

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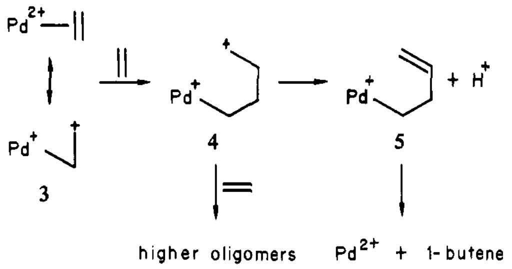
Scheme I

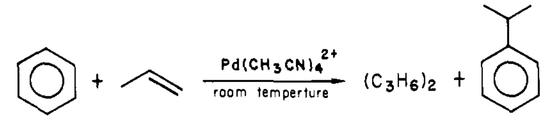


chloroform solution, $[Pd(CH_3CN)(PPh_3)_3](BF_4)_2$, (**2**) was found to catalyze the conversion of ethylene (at 1200 psi) to C_4-monoolefins *exclusively* at 40 °C (eq 3).

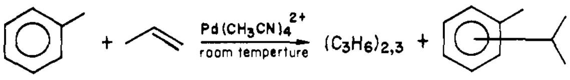
$$CH_2{=}CH_2 \xrightarrow[40\ °C,\ CHCl_3]{Pd(CH_3CN)(PPh_3)_3^{2+}} C_4H_8\text{-monoolefins exclusively} \quad (3)$$

In addition to the use of acetonitrile as solvent, **1** as a suspension in chloroform, benzene, or toluene was also found to catalyze the oligomerization of olefins. *Addition of small quantities of water to the reaction mixture in any* solvent *system invariably caused the deposition of metallic palladium together with the formation of oxygenated organic products through a mechanism similar to Wacker process.*[13b] *Furthermore, the use of CD_3CN as solvent caused no appreciable incorporation of deuterium in the organic products.* A possible mechanism for the catalytic oligomerization of olefins by **1** would be one which involves direct nucleophilic attack on a coordinated olefin by a second olefin (Scheme I). Nucleophilic attack on olefins bound to transition-metal centers is a well-documented phenomenon,[13] and in view of the strongly electrophilic nature of **1**, participation of even weak nucleophiles such as olefins in a similar reaction step seems feasible. The resulting palladium bound carbonium ion species **4**[14] can further react with olefins to produce higher oligomers or, alternatively, may deprotonate to **5**, the resulting proton then cleaving the Pd–C bond in a well-precedented step[15] to produe butene and regenerate the catalyst.

In accordance with the mechanism postulated in Scheme I, other weak nucleophiles such as arenes should also take part in an analogous nucleophilic attack on a coordinated olefin, and indeed passage of propylene through a benzene or toluene suspension of **1** resulted in the formation of significant amounts (>15% compared to olefin oligomers)[16] of arene alkylation products (eq 4 and 5).[17] Use of a 1:1 mixture of benzene and toluene resulted in the formation of isopropylbenzene and isopropyltoluenes in the ratio of 1:1.5, reflecting the somewhat greater nucleophilicity of toluene.

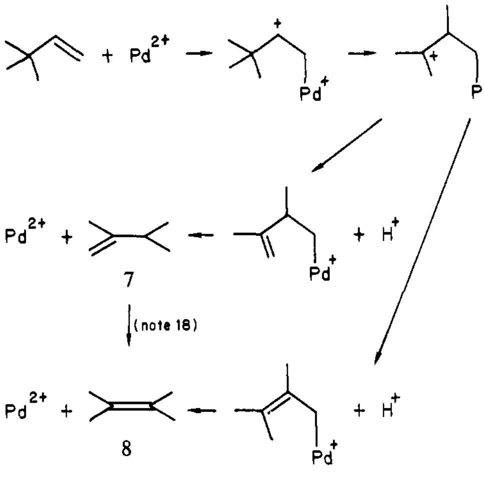


(4)



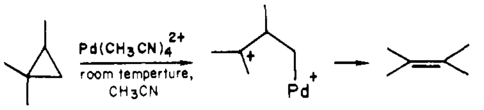
(5)

Scheme II



Significantly, the weaker transition-metal electrophiles, **2**, $PdCl_2$, and $RhCl_3$, produced only small amounts of olefin dimers and no arene alkylation products under identical conditions. On the other hand, the nontransition-metal electrophile, $AlCl_3$, produced only alkylated arenes and no olefin oligomers.

If incipient carbonium ions such as **3** are indeed formed through the interaction of **1** with olefins, then **1** should catalyze the carbonium ion induced rearrangements of suitably substituted olefins. Indeed, **1**, in acetonitrile, was found to catalyze the rearrangement of *tert*-butylethylene to tetramethylethylene, at room temperature (Scheme II). Tetramethylethylene was also the major product in the reaction of 1,1,2-trimethylcyclopropane with **1** (eq 6). Interestingly, no isomerization of *tert*-butylethylene was observed with the compounds **2**, $PdCl_2$, $RhCl_3$, and $AlCl_3$ *even in the presence of trace amounts of water.*[19]



(6)

Because of the dissociation of H^+, an analogous mechanism for the catalytic isomerization of olefins by electrophilic transition-metal centers would lead to the formation of significant amounts of crossover products, especially in polar solvents. Indeed, it has been reported[20] that in the $Pd(PhCN)_2Cl_2$ catalyzed isomerization of 1-pentene to 2-pentenes, significant amounts (>15%) of 2-pentene-d_1 and -d_3 are formed, stating with 1-pentene-d_2 *even when the reaction was carried out in benzene.*

In conclusion, it seems obvious that solvated transition-metal cations, by virtue of the presence of weakly bound ligands, are capable of acting as versatile catalysts. Moreover, the catalytic properties of such compounds are readily modified by the substitution of some of the solvent molecules by other more strongly binding ligands.

In addition, the study indicates that incipient carbonium ions may be generated by the interaction of olefins with electrophilic transition-metal centers, and such species may play an important role in transition-metal catalyzed oligomerization, polymerization, and isomerization of olefins.[21] From a practical standpoint, **1** should act as a good initiator for cationic polymerization reactions. Indeed, in addition to the polymerization of styrene (vide supra), **1** was also found to catalyze the rapid polymerization of such diverse monomers as RC≡CH (R = H, Ph),[23] 1,3-cyclohexadiene,

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(13) See, for example, (a) A. J. Birch and I. D. Jenkins in "Transition Metal Organometallics in Organic Synthesis", Vol. I, H. Alper, Ed., Academic Press, New York, 1975, Chapter 1. (b) P. M. Henry, "Palladium Catalyzed Oxidation of Hydrocarbons", D. Reidel, Dordrecht, Holland, 1979, p 41.

(14) The carbonium ion is most probably stabilized by acetonitrile coordination.

(15) (a) U. Belluco, U. Croatto, P. Uguglìati, and R. Pietropaolo, *Inorg. Chem.*, **6**, 718 (1967); (b) U. Belluco, M. Giustiniani, and M. Graziani, *J. Am. Chem. Soc.*, **89**, 6494 (1967).

(16) Due to competition between olefin oligomerization and arene alkylation reactions, the relative amount of products obtained was found to vary with the olefin concentration.

(17) In acetonitrile solution, the rate of propylene oligomerization was slower, and only trace amounts of arene alkylation products were obtained, probably due to stabilization of the carbonium ion by acetonitrile coordination.

(18) In a seperate experiment, **1** in acetonitrile was found to catalyze the rapid isomerization of 2,3-dimethyl-1-butene (**7**) to tetramethylethylene (**8**).

(19) In case of **1**, addition of water resulted in the deposition of metallic palladium and the formation of *tert*-butyl methyl ketone in amounts proportional to the amount of added water, through a mechanism similar to Wacker process.[13b]

(20) D. Bingham, B. Hudson, D. E. Webster, and P. B. Wells, *J. Chem. Soc., Dalton Trans.*, 1521 (1974).

(21) The initiation of cationic polymerization of olefins by electrophilic metal compounds, e.g., $TiCl_4$, may take place through such a mechanistic step.[22]

(22) P. Sigwalt, *Makromol. Chem.*, **175**, 1017 (1974).

and phenylcyclopropane to high molecular weight polymers at room temperature.

Acknowledgment. Support of this research by the Department of Chemistry and through grants from the Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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(23) For phenylacetylene, using monomer to catalyst ratio of 100:1, polymer of average molecular weight ~10 000 was obtained in acetonitrile. Significantly, poly(phenylacetylene) thus isolated has one of the highest molecular weights recorded so far.[24]

(24) For other synthetic routes to high molecular weight poly(phenylacetylene), see (a) T. J. Katz and S. J. Lee, *J. Am. Chem. Soc.*, **102**, 422 (1980); (b) F. R. Navarro and M. F. Farona, *J. Polym. Sci., Polym. Chem.*, **14**, 2335 (1976); (c) T. Masuda, N. Sasaki, and T. Higashimura, *Macromolecules*, **8**, 717 (1975).

Planar, Pleated, and Saddle-Shaped Structures of the Phthalocyanine Dianion in Two Novel Multidentate Oxygen-Donor Complexes of Dipotassium Phthalocyanine

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Received March 9, 1981
Revised Manuscript Received May 18, 1981

The phthalocyanine macrocycle is most often found in the planar conformation and is generally presumed to be a very rigid system.[1] Although substantial nonplanar conformations of the macrocycle are known,[2] the potential flexibility of the ring is not widely appreciated despite its similarity to the flexible and isoelectronic porphyrin ring system.[3] In this paper we report on the flexibility of the phthalocyanine dianion as observed from the x-ray structural analysis of two novel, multidentate oxygen-donor complexes of dipotassium phthalocyanine, $K_2Pc(18\text{-crown-6})_2\cdot$benzene($^3/_2$) (**1**) and $K_2Pc(\text{diglyme})_2$ (**2**). Such species are readily prepared as a consequence of the previously unknown solubility of the dialkali metal phthalocyanines in common oxygen-donor solvents or solvents containing oxygen-donor ligands.[4,5]

Crystals of **1** were obtained from benzene containing K_2Pc[6] and excess 18-crown-6. X-ray analysis was performed on a green prism (0.25 × 0.25 × 0.30 mm) mounted in a glass capillary.[7]

Compound **1** crystallizes as the trimacrocyclic sandwich complex illustrated in Figure 1. The unit cell contains two crystallographically independent monomers and three molecules of benzene. Pc is flanked by two potassium ions and two molecules of crown ether.

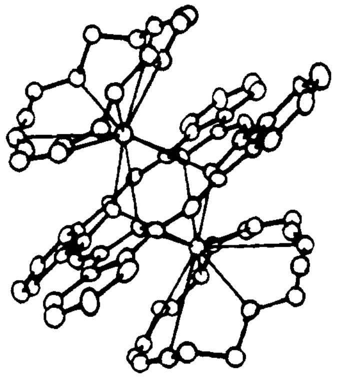

Figure 1. Perspective view of the trimacrocyclic $K_2Pc(18\text{-crown-6})_2$ complex.

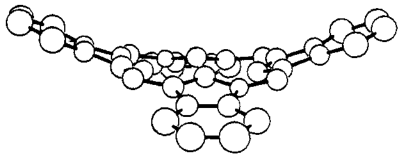

Figure 2. Saddle-shaped phthalocyanine dianion in $K_2Pc(\text{diglyme})_2$.

Table I. Phthalocyanine Interatomic Distances (Å)

bond	type	**1**, mean value	**2**, mean value
N-N	isoindole	2.782 (7)[a]	2.80 (1)
C-N	isoindole	1.362 (5)	1.36 (2)
C-N	azamethine	1.340 (1)	1.37 (2)
Cα-Cβ	pyrrole	1.473 (9)	1.46 (2)
C-C	benzene	1.414 (6)	1.41 (1)
N-K	all	2.91 (2)	2.78 (4)
O-K	all	3.39 (7)	3.03 (5)

[a] Values in parentheses are estimated variances of the mean calculated as $(\Sigma(x-\bar{x})^2/[n(n-1)])^{1/2}$.

Bond distances (Table I) and angles in the dianions are similar to those found in the coordinated ligand.[8] The conformation of the two independent centrosymmetric dianions differs, with one ion being nearly planar.[9] In the other ion (Figure 1) the relative upward and downward tilting of the isoindole rings out of the inner 4-N least-squares plane gives the dianion a pleated conformation similar to that observed in $Sn(Pc)Cl_2$.[10] The tilting of the rings takes place by rotation about the C-N azamethine bonds and leads to maximum carbon atom displacements from the 4-N least-squares plane of ±1.265 (5) Å.[11] The marked difference in conformation between the dianions shows the flexibility of the phthalocyanine system and correlates with the different packing environments of the dianions.

As a crown ether complex, **1** is atypical in that potassium is external to the 18-crown-6 cavity.[12] The location of the K^+ ions (1.6 Å from the mean O plane) clearly indicates competitive coordination between the ligands with the N-K and O-K distances (Table I) suggesting a high degree of structural integrity for the K_2Pc core. Significant changes in conformation from that of the

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(1) See, for instance: Wells, A. F. "Structural Inorganic Chemistry", 3rd ed.; Oxford University Press: London, 1962; Chapter 25. See also ref 8.

(2) See, for example, ref 10, 17, and 18. See also: Gieren, A.; Hoppe, W. *J. Chem. Soc., Chem. Commun.* **1971**, 413. Ukei, K. *Acta Crystollogr., Sect. B* **1973**, *B29*, 2290.

(3) See, for instance: Fleischer, E. B. *Acc. Chem. Res.* **1970**, *3*, 105. Hamor, M. J.; Hamor, T. A.; Hoard, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 1938. Silvers, S.; Tulinsky, A. *Ibid.* **1964**, *86*, 927. Also see ref 15.

(4) Ziolo, R. F.; Günther, W. H. H. "Abstracts of Papers", 2nd Symposium on Macrocyclic Compounds, Provo, UT, Aug 1978; Thermochemical Institute, Brigham, Young University: Provo, UT, 1978; Abstract II2.

(5) Ziolo, R. F.; Günther, W. H. H. "Abstracts of Papers", American Chemical Society/Chemical of Japan Chemical Congress, Honolulu, HI, April 1979; American Chemical Society: Washington, DC, 1979; INOR 62.

(6) Moser, F. H.; Thomas, A. L. *ACS Monogr.* **1963**, *No. 157*, 112.

(7) Space group $P\bar{1}$; $a = 11.878$ (5), $b = 20.915$ (8), $c = 13.056$ (4) Å; $\alpha = 90.93$ (3), $\beta = 97.36$ (3), $\gamma = 90.64$ (3)°; $Z = 2$ (23 °C). A total of 7736 reflections were measured (CAD 4) for $\theta < 45°$, of which 3109 were considered to be observed. Full matrix least-squares refinement (559 variables) produced agreement factors of $R = 0.117$ and $R_w = 0.142$. The crown ether rings were found to be disordered and were approximated, therefore, by placing the atoms at the locations of highest electron density from a ΔF map. This approximation gave rise to a featureless final ΔF map.

(8) Boucher, L. J. in "Coordination Chemistry of Macrocyclic Compounds"; Melson, G. A., Ed., Plenum Press: New York, 1979, Chapter 7.

(9) Distances of the Pc atoms from the linear 4-N least-squares plane reach ±0.232 Å, while the dihedral angle between neighboring isoindole least-squares planes is 3.1°. Dihedral angles between the 4-N plane and the isoindole rings are 1.6 and 2.1°.

(10) Rogers, D.; Osborn, R. S. *J. Chem. Soc., Chem. Commun*, **1971**, 840.

(11) Dihedral angles between isoindole rings and the 4-N plane are 5.2 and 15.9°; between isoindole neighbors, 12.6°. A slight sideways tilt (ruffle) occurs in the 5.2° ring.

(12) Dalley, N. K. In "Synthetic Multidentate Macrocyclic Compounds"; Izatt, R. M. and Christensen, J. J., Eds.; Academic Press: New York, 1978; Chapter 4.

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