dination plane. Thus, the second double bond is in position to attack above the coordinated plane. Energetic differences between the perpendicular and in-plane coordinated olefin could contribute to the activation energy,[11,12] and this, coupled with a very unfavorable energetic pathway for the chair to TBC activation energy,[22] could dramatically inhibit the second substitution step to form the chelate ring. In our earlier published work[3] involving [$PdCl_2$·CND-1,5] we did in fact have positive indication that the chelation step was inhibitited kinetically (without a good explanation for the inhibition). Thus, reaction of [$PdCl_2$·2PhCN] with CND-1,5 results in immediate precipitation of material with stoichiometry Pd_3Cl_6·$(CND\text{-}1,5)_2$. We characterized the material as a "linear polymer" with bridging halogens and bridging dienes. This precipitate, over period of 24 h in contact with mother liquor, rearranges quantitatively to chelated [$PdCl_2$·CND-1,5]. We now contend that monodentate CND-1,5 (probably as a chair) attacks a second palladium substrate in a kinetically controlled oligomerization process. The inhibited process (chelation) ultimately leads to the thermodynamic monomer product.

Rearrangement of [$PdCl_2$·1,4-COD] to [$PdCl_2$·1,5-COD]. Conversion of coordinated 1,4-COD to coordinated 1,5-COD should be favored by as much as 4 kcal/mol from the conformational energy standpoint alone, enough of a stabilization to overcome the fact that free COD-1,4 is more stable than free COD-1,5 by ca. 2 kcal/mol.[1f,23] There are suggestions in the literature that metal ion promotion of the COD-1,4 to COD-1,5 rearrangement is possible.[4,24] However, in every case reported there was the possibility of metals selectively binding and concentrating COD-1,5 which could have been present as an impurity in the COD-1,4 or COD-1,3 that was available (although very high purities were claimed). In the present case, at the beginning of reaction, no [$PdCl_2$·COD-1,5] was detectable by ^1H NMR. As described in the Experimental Section, the initial [$PdCl_2$·COD-1,4] resonances gradually disappeared and were replaced by [PdCl·COD-1,5] resonances.[25] Given the present results, one would expect that a mixture of COD-1,4 and COD-1,5 would be stoichiometrically converted completely to [$PdCl_2$·COD-1,5], possibly again with a primary driving force being conformational relaxation in the coordination sphere. We suggest the general possibility of converting a mixture of olefins to a single coordinated olefin, given the conformational driving force and the low-energy pathway (in the present case probably involving Pd-H formation).

Conclusion

In this paper we have initiated a comprehensive study of metal-diolefin interactions. We have shown that relatively small conformational energy effects can have a major influence on the kinetics and thermodynamics of complex formation. We are now expanding the scope of this work to other diene systems and to calorimetric measurements of the enthalpies of diene complexation reactions.

Acknowledgment. We thank Professor F. Anet for supplying us with atom coordinates calculated as described in ref 1e,i. This work was partially supported by the National Science Foundation (Grant CHE-7822691 and an NSF Summer Faculty Fellowship to G.R.W), by the University of California Intramural Research Fund, by a Cottrell Research Grant (G.R.W.), and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. The department's Bruker WH-90 NMR instrument and Spex Ramalog were purchased in part by NSF equipment funds and by University Biomedical Sciences Support Funds.

Supplementary Material Available: A listing of structure factors (Table S1) and fractional coordinates, temperature factors, bond lengths, bond angles, and torsion angles (Table S2) for [$PdCl_2$·CND-1,5] and A listing structure factors (Table S3) and fractional coordinates, temperature factors, bond lengths, bond angles, and torsion angles (Table S4) for [$PdCl_2$·COD-1,4] (41 pages). Ordering information is given on any current masthead page.

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(25) The rapidity of formation of [$PdCl_2$·COD-1,5] reported in ref 4 and 24 is surprising in view of our observation of the slowness of the homogeneous rearrangement. The earlier rapid formation of [$PdCl_2$·COD-1,5] would be expected if COD-1,5 were initially present or possibly if the rearrangement followed a different path.

[2.2.2]Paracyclophane, a Novel Type of Metal Cation Complexing Agent (π-Prismand)

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Contribution from the Laboratoire d'Etudes Dynamiques et Structurales de la Sélectivité II, Université Scientifique et Médicale de Grenoble, B.P. 53X, 38041 Grenoble Cedex, France, and Laboratoire d'Energétique électrochimique, E.N.S.E.E.G., B.P. 44, 38041 Grenoble Cedex, France. *Received March 4, 1980*

Abstract: A novel type of cryptation involving only the π-binding sites of the cavity [2.2.2]paracyclophane is evidenced through solubility and ^1H NMR studies. The stability constant, in methanol, of the 1:1 complex of [2.2.2]paracyclophane with silver triflate is approximately 100-fold higher than those of the usual π-charge-transfer complexes of arenes with silver cation. The well-defined, sharp-melting, crystalline, 1:1 complex has been isolated and characterized.

Although many crown ethers contain aromatic rings,[1] there exist only a few claims of the aromatic subunit serving as a π donor in these systems in complexation with metal or ammonium salts.[2,3] Sousa and co-workers[4] have described the perturbation induced by metal ion guests on the emission properties and ^{13}C chemical shifts of the naphtalene unit of crown ether hosts.

† Université Scientifique et Médicale de Grenoble.
‡ E.N.S.E.E.G.

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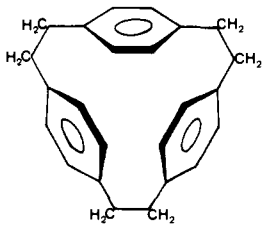

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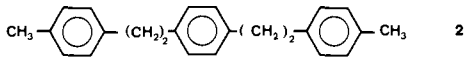

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Figure 1. Structural formula and codes. The *Chemical Abstracts* names are as follows: **1**, tetracyclo[14.2.2.2^{4,7}.2^{10,13}]tetracosa-4,6,10,12,16,18,19,21,23-nonaene; **2**, 1,4-bis(*p*-methylphenethyl)benzene.

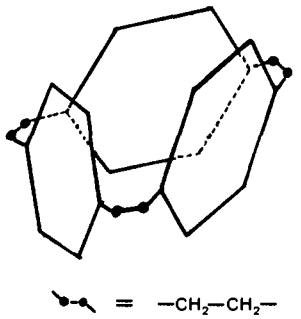

Figure 2. Spatial shape of **1**.

We wish to report here the first example of "π-cryptation". The [2.2.2]paracyclophane **1** (Figure 1) was prepared by the modified Würtz reaction, as described by Tabushi.[5] The open-chain compound **2** was also obtained in the reaction. Corey–Pauling–Koltun space-filling molecular models of **1** show a rigid prismatic juxtaposition of the three benzene nuclei (diameter of the cavity ca. 2 Å). The paracyclophane **1** thus appeared capable of enclosing certain metal cations in its molecular cavity. It seemed possible that it would manifest stronger complexing properties than those observed with the usual arenes. Because of its spatial shape, we named **1** "π-prismand" (Figure II). We investigated silver ion as the ligand, since the benzene ring is a soft donor.

Results and Discussion

The isolation of a 1:1 silver trifluoromethanesulfonate (triflate) complex of **1** as a stable crystalline powder at room temperature was effected by evaporating the solvent from a solution obtained by mixing equimolecular amounts of **1** and silver triflate in dry tetrahydrofuran. The melting point of the recrystallized complex is sharp (192 °C) and 24 °C higher than the melting point of **1**. The elemental analysis is within acceptable limits. The field desorption mass spectrum shows ions corresponding to $[\mathbf{1},Ag]^+$ and to $[\mathbf{1}]^{+\cdot}$. X-ray powder diffraction studies using the Debye–Scherrer method[6] indicate that the powder is a stoichiometric compound and not a mixture; the complex is free of uncomplexed cyclophane and silver salt.

Whereas the solubility of CF_3SO_3Ag in chloroform is not significantly affected by an equimolecular amount to **2**, it is strongly enhanced in the presence of **1**. The strong complexing ability of **1** was clearly evidenced through ^1H NMR studies in $CDCl_3$ or CD_3OD solution.

Table I. ^1H NMR Data (100 MHz, 25 °C) of **1** and **2** Solutions in $CDCl_3$,[a] Free or in the Presence of CF_3SO_3Ag (1:1 Molar Ratio)

	δ			
	1	**1**-CF_3SO_3Ag	**2**	**2**-CF_3SO_3Ag
$H_{aromatic}$	6.68	7.03	7.10 7.09	7.09 7.07
$H_{(CH_2-CH_2)}$	2.92	3.04	2.87	2.88

[a] Within a range of temperature from −55 °C to +25 °C, single sharp signals are observed.

Whereas the ^1H NMR spectrum of **2** is practically unchanged in the presence of 1 equiv of silver triflate, compound **1** exhibits large shifts (Table I). The downfield shift of the aromatic protons are mainly due to a decrease in the π-electron density of the complexed benzene nuclei.[2b]

The addition of silver triflate to **1** in less than stoichiometric amounts results in two sets of resonances, one indicative of free **1** and the second of the complexed species. No exchange between complexed and free species is observed in $CDCl_3$ from −55 °C to +25 °C. The strength of the interaction in the complex is further indicated by the fact that no free **1** is observed at 1:1 mole ratio of the reagents. When the same experiments are performed with **2** a single set of resonances is observed.

When a sample containing a 2:1 mixture of **1** and CF_3SO_3Ag in $CDCl_3$ is heated in a sealed tube, a line broadening is observed for both proton signals of the uncomplexed and complexed species. The coalescence of the signals occurs near 52 °C for the aromatic protons and near 31 °C for the benzylic protons, indicating exchange rates of $k_{Ar} = 77.7\ s^{-1}$ and $k_{CH_2} = 26.7\ s^{-1}$, respectively. At the coalescence temperature, the free energy of activation can be calculated by using the Eyring rate equation ($\Delta G^{\ddagger}_{52\,°C} = 16.2$ kcal mol^{-1}; $\Delta G^{\ddagger}_{31\,°C} = 15.8$ kcal mol^{-1}).

The stability constant of the complex can be estimated by ^1H NMR studies above the coalescence temperature by means of the Benesi–Hildebrand equation[7] (see Experimental Section). Lack of solubility in $CDCl_3$ of the silver salt, which is used in large excess in this method, obliged us to perform the measurements in CD_3OD solutions.[8] The equilibrium constant thus obtained is 195 ± 10 L mol^{-1} at 24 °C, while the known values for aromatic compound–silver salt interactions, in methanol, are of the order of 2–3 L mol^{-1}.[9]

The observed temperature invariance of the ^1H NMR spectrum of the 1:1 complex [**1**–CF_3SO_3Ag], which retains its symmetry even at −55 °C, and the comparison of the results obtained with **1** and **2** seem to rule out the alternative of an external complex and favor the hypothesis of the incorporation of the silver cation inside the cavity of the [2.2.2]cyclophane. The "cryptate effect" augments the stability of the complex approximately 100-fold *even though only π-binding sites are involved.*

We are now exploring the synthesis of other π-cryptands.

Experimental Section

All chemicals were reagent grade. Commercial silver triflate was thoroughly vacuum dried at 40 °C. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl immediately prior to use. All other solvents were fractionally distilled and stored in a N_2 atmosphere.

Melting points are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker WP 100 CW and WP 100 multinuclei Fourier transform spectrometers, respectively. Chemical shifts are in parts per million (δ) relative to internal Me_4Si, with $CDCl_3$ and CD_3OD as solvents

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and lock compounds. Field desorption mass spectra were run on a Kratos AEI MS 30 double-focusing mass spectrometer equipped with high-temperature-activated wire emitters. Analytical and preparative high-pressure liquid chromatographies were performed on either a Waters 440 (detector UV, λ = 254 nm) or a Prep LC 500 (detector, differential refractometer) apparatus, respectively.

Materials. [2.2.2]Paracyclophane (**1**) was prepared by the modified Wurtz condensation of paraxylylene chloride in the presence of a catalytic amount of tetraphenylethylene as described by Tabushi and co-workers.[5] From the crude solid, **1** and **2** were obtained as a mixture by column chromatography (silica, hexane–benzene) and then separated by repeated recrystallization from ethanol. A more rapid and convenient separation of **1** and **2** was performed by preparative HPLC (Prep PAK-500/C_{18} column; mobile phase methanol). [2.2.2]Paracyclophane (**1**): mp 168 °C; ^{1}H NMR ($CDCl_3$) see Table I; ^{1}H NMR (CD_3OD) δ 2.47 (CH_2), 6.23 (Ar); ^{13}C NMR ($CDCl_3$) featured resonances at δ 33.56 (CH_2), 128.35, and 136.56 (Ar). *p*-bis(2-*p*-tolylethyl)benzene (**2**): mp 142–143 °C; ^{1}H NMR ($CDCl_3$) see Table I.

1:1 Silver Triflate Complex of 1. Into a solution of 25.7 mg (0.1 mmol) of silver triflate in 8 mL of freshly distilled THF was added 31.2 mg (0.1 mmol) of **1**. The mixture was magnetically stirred at room temperature for ten minutes and the solvent evaporated under reduced pressure to give a stoichiometric amount of the 1:1 silver triflate complex as a whitish crystalline powder. The crude complex was dissolved in hexane–dichloromethane and allowed to evaporate very slowly in the darkness at room temperature to give tiny colorless needles: mp 192 °C; ^{1}H NMR ($CDCl_3$) see Table I; ^{1}H NMR (CD_3OD) δ 2.57 (CH_2), 6.42 (Ar); ^{13}C NMR featured resonances at δ 33.01 (CH_2), 125.95, and 138.19 (Ar); field desorption mass spectrum *m/e* 312 (M^+), 419 (^{107}Ag + M)$^+$, 420 (^{109}Ag + M)$^+$. Anal. Calcd for $C_{25}H_{24}F_3SO_3Ag$: C, 52.72; H, 4.21. Found: C, 52.43; H, 4.28.

Use of up to 4:1 molar ratio of silver triflate to cyclophane did not affect the character of product or yield to any extent; only the mono-complex of **1** could be detected.

Determination of the Stability Constant. Considering the equilibrium A + D $\rightleftarrows$ AD, where A and D represent the acceptor and donor molecules and AD represents the π-molecular complex, we can use the following equation, derived from the Benesi-Hildebrand equation:[7]

$$\frac{1}{\Delta} = \frac{1}{K_c}\frac{1}{\Delta_o}\frac{1}{a_o} + \frac{1}{\Delta_o}$$

where Δ = observed shift of the donor protons for the system in equilibrium relative to the shift for the pure donor in solution, Δ_o = shift for the pure complex relative to the shift for the pure donor in solution, K_c = equilibrium constant, and a_0 = acceptor concentration. K_c was evaluated graphically, plotting $1/\Delta$ vs. $1/a_o$ (see Table II).

Table II. Values of Complexation Constant K_c from ^{1}H NMR Chemical Shifts with Measurement in CD_3OD at 24 °C[a]

acceptor–donor system	conditions[b]	proton measured	Δ_o, Hz	K_c, L mol^{-1}
CF_3SO_3Ag–[2.2.2]PCP	$a_o >> d_o$	H aliph	20.2	197 ± 8
		H arom	41.7	189 ± 5

[a] For each concentration, three spectra were averaged to obtain the chemical shift of the individual protons. [b] a_o, acceptor concentration; d_o, donor concentration.

In this study, we kept the donor concentration fixed while the concentrations of the acceptor were varied and we measured the shifts of the donor protons in the complexing media. The physical method chosen here for studying weak complexes requires a large excess of the acceptor ($AgCF_3SO_3$) compared with that of the donor ([2.2.2]PCP). Deuterated methanol (CD_3OD) was used; this solvent dissolves a large amount of silver salt as well as smaller amounts of cyclophane. a standard solution of cyclophane in CD_3OD was prepared with a concentration just sufficient to observe a measurable NMR spectrum (0.01 M). Molar ratios of silver triflate to cyclophane were varied from 2 to 10 in the preparation of a series of NMR samples (200 μL in volume).

The NMR instrument was internally locked on a CD_3OD peak and chemical shifts were measured at 24 °C with Me_4Si as an external reference and an estimated accuracy of ±0.3 Hz.

Dynamic FTNMR Studies of Hindered Metal–Cage Rotation in Twelve-Vertex *closo*-Phosphinometallacarborane Complexes†

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Abstract: Dynamic ^{1}H and ^{31}P{^{1}H} FTNMR spectra of a series of 12-vertex *closo*-phosphinometallacarboranes are presented which suggest that the metal vertex undergoes hindered rotation with respect to the five-membered face of the carborane cage. Studies of the Rh(III) and Ir(III) complexes, [L_2HM(carb)], where L = PPh_3, PEt_3, or PMe_2Ph and carb = 1,2-, 1,7-, or 1,12-$C_2B_9H_{10}R$ (R = H, Me, Ph, or *n*-Bu), the Ru(IV) complex, [2,2-$(PPh_3)_2$-2,2-H_2-2,1,7-$RuC_2B_9H_{11}$], the Ru(II) complex, [2,2-$(PPh_3)_2$-2-CO-2,1,7-$RuC_2B_9H_{11}$], and the Ru(II) and Rh(I) complexes, [3,3-$(PPh_3)_2$-3-$(H)_n$-4-C_5H_5N-3,1,2-$MC_2B_9H_{10}$] (n = 0, M = Rh; n = 1, M = Ru), constitute the first direct determination of rotational barriers in solution for [ML_n] moieties with respect to planar η^5-bonded ligands in which the π system is continuous. Free energies of activation ($\Delta G^{\ddagger}$) vary from <8.4 to >17.5 kcal/mol.

The potential barrier to internal rotation about the n-fold axis in organometallic π-complexes containing a cyclic η^n-C_nR_n ligand (n = 3–8) is so low[2,3] that it evidently cannot be measured directly by dynamic FTNMR in solution. Although free energies of activation for complexes with noncontinuous π-systems (i.e., polyenes,[4] polyenyls,[5] *nido*-5,6-$C_2B_8H_{11}$,[6] and *nido*-$B_{10}H_{12}^{2-}$[7]) have been reported, no barriers have thus far appeared for complexes containing continuous but nonuniform π systems such as those containing C-substituents[8] or one or more heteroatoms in the π-bonding network.[9] Extended Hückel molecular orbital cal-

† A preliminary account of this work has been presented. T. B. Marder, J. A. Doi, R. T. Baker, and M. F. Hawthorne, Pacific Conference on Chemistry and Spectroscopy, Pasadena, CA, October 1979.

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