

Writing and Revising
the Disciplines

Edited by

JONATHAN MONROE

CORNELL UNIVERSITY PRESS

Ithaca and London

Writing (and Drawing) Chemistry

ROALD HOFFMANN (Chemistry)

IN the chemical profession our stock in trade is not the book, but the scientific (chemical) article, published in a periodical. I have written 450 of them in my years at Cornell University; my colleague Harold Scheraga has published over 1000. We have promoted an assistant professor to tenure at Cornell with 11 published papers, and we have not promoted one with over 80.

THE NATURE OF THE BEAST

It is instructive to see the article untamed, roaming its range. For this I would like to begin with some pages from the chemical journal that is arguably the world's best (at least in inorganic and organic chemistry, not in physical chemistry or biochemistry); publication venues and their prestige carry much baggage of history and fashion. The journal is not an American one. It is *Angewandte Chemie*, published out of Germany, it appears simultaneously in German and English editions. Despite its name, the journal contains precious little applied chemistry.

Angewandte Chemie, under the inspired and proactive leadership of its editor, Peter Götz, has cultivated an effective mix of largely solicited review or feature articles, short highlights, and many "Communications." These are brief accounts of novel chemistry, presumably worthy of urgent publication. And publication, following review by one to three anonymous (to the author) referees, is certainly rapid. Several Communications in the Nov. 2, 1998 issue of the journal carry June submission dates; the latest is dated July 1, 1998. For my friends in the humanities (I'm there

too; I have been waiting over two years for a paper to appear in the *Canadian Review of Comparative Literature*, all I can say is "It can be done."

Let us leaf (see figures 1–5) through some pages in the Nov. 2, 1998 issue of *Angewandte Chemie* which arrived in my mailbox the week of November 9. (The original lecture on which this text is based was presented on Nov. 16, 1998.)

From these five sequential pages, as well as perusal of a greater sample, one notes:

(1) The authorship is international.

(2) There are many authors per paper; one of the differences between the sciences and the humanities and arts (theater and film are exceptions), is that the sciences have mastered the ethics of collaboration.

(3) The usual scholarly apparatus is there: author affiliations, end-notes (often numerous), acknowledgments of granting agencies and individual assistance or discussion.

(4) An unusual feature, particular to *Angewandte Chemie*, is the mandatory inclusion at the end of any experimental paper of an experimental section, detailing procedures for at least part of the experiments carried out.

(5) Most striking is the remarkable density of graphic material, most of it quasi-iconic representations of microscopic molecular structure. It is this feature of chemistry—the high graphical content of the literature and the science—which led me to include the parenthetical clause in my title (see Hoffmann and Laszlo, 1991). I will return to it, for now I hope I have convinced you that it is not my stylistic prejudice when I say that it is impossible to write chemistry without drawing molecules.

I also note that while there are some graphs and plots of observables, these are relatively few. And still fewer equations. This is not physics.

Is what these figures present typical? Yes, it certainly is so, of the literature of organic, inorganic, and biological chemistry. Physical chemistry is quite different, for its literature (viewed phenomenologically) carries more equations, and fewer depictions of molecules.

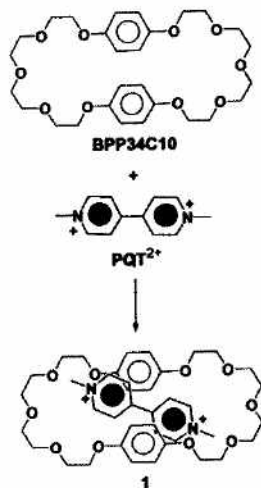
CALIXARENES

Let us now zoom in on one article, and read it together. I do this for the ostensible reason of analyzing this contemporary text as a text. But I must also 'fess up; I do it because I will not pass up the chance of teaching any audience, including the audience of the present volume, some chemistry.

A New Motif for the Self-Assembly of [2]Pseudorotaxanes; 1,2-Bis(pyridinium)ethane Axles and [24]Crown-8 Ether Wheels**

Stephen J. Loeb* and James A. Wisner

The threading of the paraquat dication PQT^{2+} through the cavity of bis(paraphenylene)[34]crown-10 (BPP34C10) to form the [2]pseudorotaxane [(BPP34C10)(PQT)] $^{2+}$ (**1**) was the genesis of a diverse range of molecules that contain mechanical linkages (rotaxanes, catenanes, molecular shuttles, and switches) derived from this basic interaction, and stands as a landmark discovery in the area of supramolecular chemistry (Scheme 1).^[1] Many examples of rotaxanes have

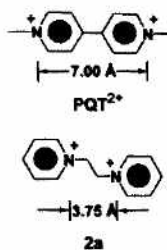


Scheme 1. Formation of the [2]pseudorotaxane **1** by insertion of the linear dicationic axle PQT^{2+} through the cavity of the neutral crown ether wheel BPP34C10.

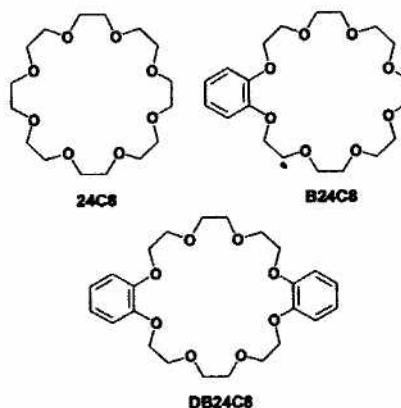
now been reported involving π stacking between electron-rich and electron-poor aromatic rings,^[2] hydrogen bonding between secondary dialkylammonium ions and crown ethers^[3] or between amides and large ring lactams,^[4] hydrophobic interactions within the cavity of a cyclodextrin,^[5,6] and metal-ligand interactions between transition metal ions and cyclic ligands.^[7-9] In many of these systems the ion-dipole interaction between positively charged atoms of one component and the Lewis basic atoms of the other component makes a significant contribution to the binding. Although these electrostatic interactions are not directional and predictable in the same manner as hydrogen bonds or metal-ligand

bonds, they are nonetheless extremely important. For example, the PQT^{2+} ion in **1** is tilted away from perpendicular by 62° so as to maximize the $\text{N}^+ \cdots \text{O}$ interactions and also form weak $\text{CH} \cdots \text{O}$ hydrogen bonds along with the major π -stacking components.^[1]

Herein, we present a new motif for the design of [2]pseudorotaxanes based on the simple concept of optimizing $\text{N}^+ \cdots \text{O}$ interactions between pyridinium ions and simple crown ethers.^[10] The $\text{N}^+ - \text{N}^+$ distance in PQT^{2+} is about 7.00 Å while in the isomeric 1,2-bis(pyridinium)ethane dication **2a** it is only about 3.75 Å (Scheme 2). Although Stoddart et al. have reported that the interaction between dibenzylparaquat and DB24C8 is negligible,^[11,12] an examination of CPK and computer models suggested a good match between **2a** (the "axle") and the 24-membered crown ethers (wheels) 24C8, B24C8, and DB24C8 (Scheme 3) that should



Scheme 2. Comparison of the intramolecular $\text{N}^+ - \text{N}^+$ distances in the isomeric pyridinium ions PQT^{2+} and [pyCH₂CH₂py] $^{2+}$ (**2a**).



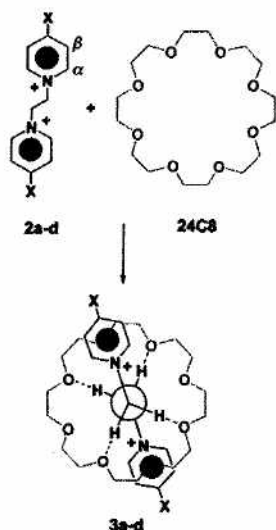
Scheme 3. Formation of [2]pseudorotaxanes from 24C8, B24C8, and DB24C8.

optimize the $\text{N}^+ \cdots \text{O}$ interactions. Scheme 4 shows how two sets of $\text{N}^+ \cdots \text{O}$ interactions might be accompanied by a series of four $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds that are formed with alternate oxygen atoms in the crown ether. The question remains as to whether these interactions are sufficient to produce a stable [2]pseudorotaxane in the absence of the π -stacking interactions found in **1** and related molecules.

The addition of one equivalent of 24C8 to a solution of one equivalent of **2a**(BF₄)₂ in MeCN gave the [2]pseudorotaxane **5a**. An association constant K_a of 165 M^{-1} was measured for this interaction by ¹H NMR titration in MeCN at 298 K. By variation of the substituent X on the pyridinium ring other axes can be incorporated and a more detailed understanding of the overall interaction can be obtained. The strength of the interaction can be controlled by varying X as shown in Table 1. In particular, the introduction of the electron-with-

[*] Prof. Dr. S. J. Loeb, J. A. Wisner
Department of Chemistry and Biochemistry
University of Windsor
Windsor, ON, N9B 3P4 (Canada)
Fax: (+1) 519-973-7098
E-mail: loeb@uwindsor.ca

[**] Financial support for this work was provided by the Natural Sciences and Engineering Research Council of Canada.



Scheme 4. Newman projection along the C-C vector of the $N^+CH_2CH_2N^+$ portion of the dication $[XpyCH_2CH_2pyX]^{2+}$, **2a-d**, ($X = H, Me, Ph, CO_2Et$). This combination of $N^+ \cdots O$ ion-dipole interactions and C-H \cdots O hydrogen bonds might stabilize the formation of [2]pseudorotaxanes with **24C8**.

a charge transfer absorption band at about 370 nm (Figure 1). In addition, **3d-5d** show significant downfield shifts ($\delta =$

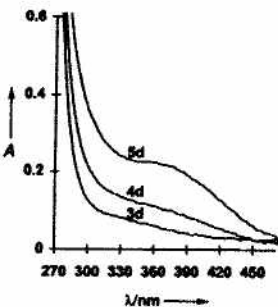


Figure 1. UV absorption spectra of **3d**, **4d**, and **5d**. The intensity of the charge-transfer band in the region 270–470 nm increases with increased capacity for π -stacking interactions.

drawing group CO_2Et results in the largest association constant for the interactions with each of the three crown ethers.

Incorporation of aromatic groups into the crown ether provides the possibility of π stacking between the pyridinium rings and the catechol rings of the crown ether. In the 1H NMR spectra of the two pseudorotaxanes derived from **2a** ($X = CO_2Et$) with **B24C8** (**4d**) and **DB24C8** (**5d**) π stacking in solution is clearly evident: the signals for the β protons of the pyridine group shift upfield ($\delta = 8.56, 8.36,$ and 8.14 for the pseudorotaxanes with **24C8**, **B24C8**, and **DB24C8**, respectively). This trend is mirrored by a uniform increase in K_a from 320 to 740 to $1200 M^{-1}$ and an increase in the intensity of

0.20–0.31) for the α and NCH_2 protons, which is indicative of the formation of C-H \cdots O hydrogen bonds to the oxygen atoms of the crown ether.

These results and the threading conformation proposed in Scheme 4 are supported by the solid-state structure of $[(EtO_2CpyCH_2CH_2pyCO_2Et)(DB24C8)]^{2+}$ (**5d**; $py = C_5H_4N^+$).^[11] Figures 2 and 3 show different views of the threading of the dicationic axle through the cavity of the **DB24C8** macrocycle. The [2]pseudorotaxane is stabilized by 1) eight $N^+ \cdots O$ interactions ($N-O$ 3.76–4.88 Å), 2) eight C-H \cdots O hydrogen bonds (the four predicted ones between the bridging ethane unit and alternate ether oxygen atoms as well as four others between α -pyridinium hydrogen atoms and symmetry related $O5$ atoms

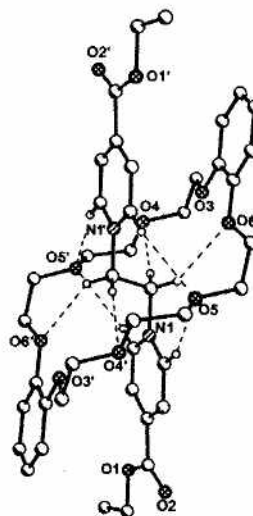


Figure 2. A ball-and-stick representation of the crystal structure of **5d**, formed from $[EtO_2CpyCH_2CH_2pyCO_2Et]^{2+}$ (**2d**) and **DB24C8**.

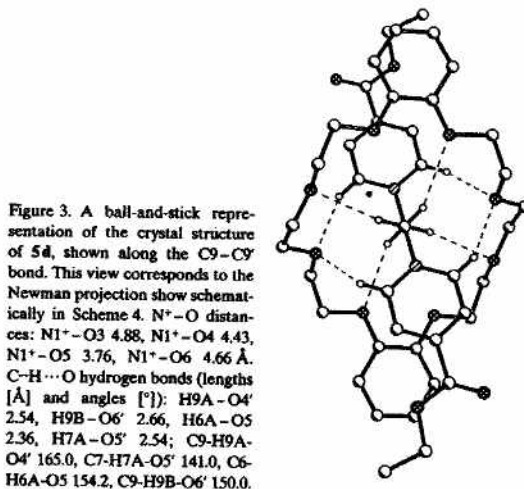


Figure 3. A ball-and-stick representation of the crystal structure of **5d**, shown along the $C9-C9'$ bond. This view corresponds to the Newman projection shown schematically in Scheme 4. $N^+ \cdots O$ distances: $N1^+ \cdots O3$ 4.88, $N1^+ \cdots O4$ 4.43, $N1^+ \cdots O5$ 3.76, $N1^+ \cdots O6$ 4.66 Å. C-H \cdots O hydrogen bonds (lengths [Å] and angles [°]): $H9A \cdots O4'$ 2.54, $H9B \cdots O6'$ 2.66, $H6A \cdots O5$ 2.36, $H7A \cdots O5'$ 2.54; $C9-H9A \cdots O4'$ 165.0, $C7-H7A \cdots O5'$ 141.0, $C6-H6A \cdots O5$ 154.2, $C9-H9B \cdots O6'$ 150.0.

Table 1. Association constants (K_a) and free energies of complexation (ΔG) for **3a-d**, **4a-d**, and **5a-d** formed from $[X-pyCH_2CH_2py-X]^{2+}$, **2a-d**, and **24C8**, **B24C8**, or **DB24C8** in MeCN at 298 K.^[a]

X	24C8		B24C8		DB24C8	
	K_a [M^{-1}]	$-\Delta G$ [$kJ mol^{-1}$]	K_a [M^{-1}]	$-\Delta G$ [$kJ mol^{-1}$]	K_a [M^{-1}]	$-\Delta G$ [$kJ mol^{-1}$]
H (a)	165	12.7	195	13.1	180	12.9
Me (b)	105	11.6	205	13.2	230	13.5
Ph ^[b] (c)	160	12.6	300	14.2	320	14.3
CO_2Et ^[b] (d)	320	14.3	740	16.4	1200	17.6

[a] Sample concentrations 2.0×10^{-3} – $5.0 \times 10^{-3} M$. [b] Chemical exchange was slow on the NMR time scale and peaks were observed for both complexed and uncomplexed species. K_a was determined by integration from a 1:1 mixture. All other K_a values were determined by NMR titration experiments by using the program EQNMR.^[10] Estimated errors: < 10% for $K_a > 100$.

(C–O 2.36–2.66 Å), and 3) π -stacking interactions between the electron-rich catechol rings of the crown ether and the electron-poor aromatic rings and ester group of the pyridinium salt.

The new binding motif for the formation of [2]pseudorotaxanes presented herein demonstrates for the first time that simple crown ethers can be used to form [2]pseudorotaxanes. The ability to easily tune the interaction strength and the availability of these simple components bodes well for the extension of this motif to more complex supramolecular systems with interlocked [n]rotaxanes and [n]catenanes.

Experimental Section

All pyridinium bromide salts were prepared by the literature method.^[14] The BF₄⁻ salts were precipitated from water by the addition of NaBF₄ or NH₄BF₄ and recrystallized before use. DB24C8 was purchased from Aldrich and used as received. B24C8 and 24C8 were prepared by literature methods.^[15] In a typical experiment, [2]pseudorotaxanes were formed in solution by mixing equimolar solutions of 2a(BF₄)₂–d(BF₄)₂ and crown ether in MeCN. Typical data for [2]pseudorotaxanes in which X = CO₂Et: 3d: ¹H NMR (300 MHz, CD₃CN, 298 K): δ = 9.27 (d, 4H, J = 5.3 Hz; α -pyH), 8.56 (d, 4H, J = 5.3 Hz; β -pyH), 5.40 (s, 4H; NCH₂), 4.50 (q, 4H, J = 7.1 Hz; C(O)OCH₂), 3.50 (s, 32H; OCH₂), 1.44 (t, 6H, J = 7.1 Hz; CH₃); ES-MS *m/z* (%): 770 (5) [M – BF₄]⁺, 341 (100) [M – 2BF₄]²⁺. 4d: ¹H NMR (300 MHz, CD₃CN, 298 K): δ = 9.24 (d, 4H, J = 6.4 Hz; α -pyH), 8.36 (d, 4H, J = 6.4 Hz; β -pyH), 6.80 (m, 4H; Ar), 5.46 (s, 4H; NCH₂), 4.47 (q, 4H, J = 7.1 Hz; C(O)OCH₂), 4.02 (m, 4H; ArOCH₂), 3.94 (m, 4H; OCH₂), 4.83 (m, 8H; OCH₂), 3.63 (m, 4H; OCH₂), 3.43 (m, 4H; OCH₂), 3.18 (m, 4H; OCH₂), 1.44 (t, 6H, J = 7.1 Hz; CH₃); ES-MS *m/z* (%): 818 (7) [M – BF₄]⁺, 365 (100) [M – 2BF₄]²⁺. 5d: ¹H NMR (300 MHz, CD₃CN, 298 K): δ = 9.24 (d, 4H, J = 6.7 Hz; α -pyH), 8.14 (d, 4H, J = 6.7 Hz; β -pyH), 6.74 (m, 8H; Ar), 5.58 (s, 4H; NCH₂), 4.40 (q, 4H, J = 7.1 Hz; C(O)OCH₂), 4.00 (m, 24H; OCH₂), 1.44 (t, 6H, J = 7.1 Hz; CH₃); ES-MS *m/z* (%): 865 (12) [M – BF₄]⁺, 389 (100) [M – 2BF₄]²⁺.

Received: April 28, 1998 [Z11791IE]

German version: *Angew. Chem.* 1998, 110, 3010–3013

Keywords: crown compounds • rotaxanes • self-assembly • supramolecular chemistry

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J. F. Stoddart, A. J. P. White, D. J. Williams, *Chem. Commun.* 1996, 1387–1388.

- [13] Crystal structure data for 5d(BF₄)₂: monoclinic, space group P2₁/c, *a* = 13.2421(4), *b* = 15.7037(5), *c* = 12.1739(4) Å, β = 94.909(1)°, *V* = 2522.3(1) Å³, *Z* = 2, ρ_{calc} = 1.308 g cm⁻³, $2\theta_{\text{max}}$ = 45.0°, MoK α radiation (λ = 0.71073 Å), *T* = 296 K. A pale yellow crystal with dimensions 0.2 × 0.2 × 0.3 mm was grown by vapor diffusion of isopropyl ether into a solution of 5d in MeCN and mounted on a fibre. The 3280 unique reflections (*R*_{int} = 0.0715) were integrated from frame data obtained from programmed hemisphere scan routine on a Siemens SMART CCD diffractometer. Decay (<1%) was monitored by 50 standard data frames measured at the beginning and end of data collection. Systematic absences in the diffraction data and determined unit-cell parameters were consistent with the space group P2₁/c. Lorentzian-polarization correction and semi-empirical absorption correction, based on redundant data at varying effective azimuthal angles, were applied to the data (μ = 0.112 cm⁻¹, min./max. transmission = 0.221/0.492). The structure was solved by direct methods, with Fourier syntheses, and refined with full-matrix least-squares methods against $|F^2|$ data to give *R*(*F*) = 0.0815, *wR*(*F*²) = 0.2271, *GOF* = 1.033, *N*_p/*N*_t = 3275/354. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as idealized contributions. Scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 5.03 program library (Sheldrick, G. M., Madison, WI). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101459. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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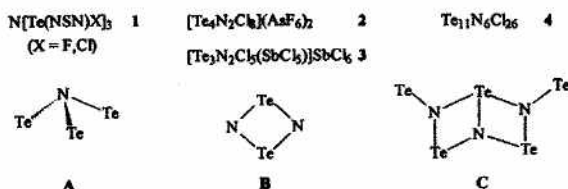
[Te₃N₆(TeCl₄)₄]-Tellurium Nitride Stabilized by Tellurium Tetrachloride

Werner Massa, Carsten Lau, Michael Möhlen, Bernhard Neumüller, and Kurt Dehnicke*

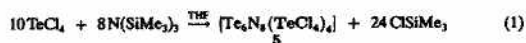
Exactly 100 years ago tellurium nitride was first obtained by the reaction of tellurium tetrabromide with liquid ammonia.^[1] The composition TeN was ascribed to this yellow, extremely poorly soluble, and highly explosive substance. Considering the analogy to the crystallographically well characterized homologues S₄N₄^[2] and Se₄N₄,^[3] this assignment has not been entirely ruled out to this day.^[4] However, later analytical work made the composition Te₃N₄ with tetravalent tellurium probable.^[5–7] The tellurium compounds with nitride functionalities which were characterized in recent years also derive from tellurium(+IV). Among these are the complexes of type 1 with X = Cl^[8] and F,^[9] which correspond to the structure motif A with pyramidal nitride functionality, and the nitride

* Prof. Dr. K. Dehnicke, Prof. Dr. W. Massa, Dr. C. Lau, Dr. M. Möhlen, Priv.-Doz. Dr. B. Neumüller
Fachbereich Chemie der Universität
Hans-Meerwein-Strasse, D-35032 Marburg (Germany)
Fax: (+49) 6421-28-8917

halides 2^[10] and 3^[11] with the structure motif B and trigonal-planar nitride functionality, which is also realized in 4 with the structure motif C.



We now found a method of approach to tellurium nitride stabilized by $TeCl_4$ molecules in the reaction of tellurium tetrachloride with tris(trimethylsilyl)amine in THF [Eq. (1)]. This tellurium nitride can be obtained in more than 80% yield.



Compound 5 forms pale yellow, moisture-sensitive, non-explosive crystals. According to the crystal structure analysis^[12] these crystals still contain 7.5 equivalents of THF per formula unit, four of which enter into weak bonding interactions with the atoms Te1 and Te2. With 271.3 pm their Te–O distances agree with the Te–O bond lengths of 273.1 pm in $[TeCl_4(OPCl_2)]_2$.^[16] The core of the structure of $[5 \cdot 4THF] \cdot 3.5THF$ consists of the rhombic dodecahedral unit Te_6N_6 , in which the tellurium atoms form the corners of a distorted octahedron and the nitrogen atoms occupy the faces of the octahedron as μ_3 ligands (Figure 1). Four of these

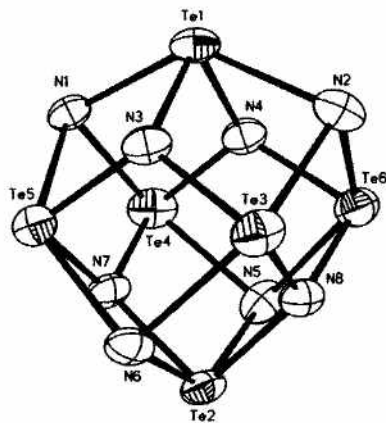


Figure 1. View of the Te_6N_6 core in the structure of $[5 \cdot 4THF] \cdot 3.5THF$. Displacement ellipsoids are at the 30% probability level at 223 K.

nitrogen atoms are coordinated with $TeCl_4$ molecules, the chlorine atoms of which adjust themselves well to the shape of the Te_6N_6 core due to the steric effect of the free electron pair at the tellurium atom (Figure 2). At the same time, with 304–331 pm the distances of the chlorine ligands of the $TeCl_4$ molecules to the Te atoms of the core which are not

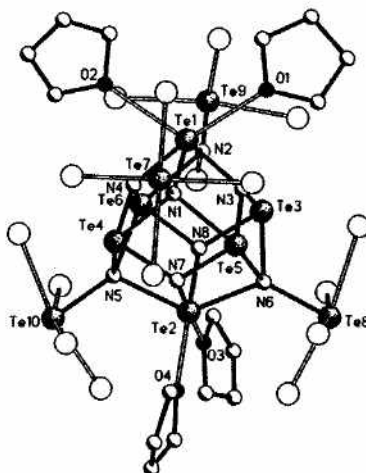


Figure 2. Molecular structure of $[5 \cdot 4THF]$ in the crystal. In the disordered $TeCl_4$ groups at Te(8–10) only the more strongly occupied orientations are shown. Selected average bond lengths [pm] and angles [°] (standard deviations taken from the mean of the single values): Te(1–6)–N(1,2,5,6) 228.5(6), Te(7–10)–N(1,2,5,6) 204.0(6), Te(1–6)–N(3,4,7,8) 201.3(6), Te(1,2)–O(1–4) 271.3(8), Te–Cl 251.6(4); Te–N(1,2,5,6)–Te 95.5(2), Te–N(3,4,7,8)–Te 114.4(2), Te–N(1,2,5,6)–Te(7–10) 121.0(2).

coordinated with THF are clearly below the van der Waals sum of radii (381 pm). Since the shielding of the Te_6N_6 core obtained thereby is not yet perfect, the tellurium atoms Te1 and Te2 which are facing each other are solvated by THF molecules. This results in Te_6N_6 molecules which are isolated from one another in the crystal lattice because of their jacket and thus lose their explosive character. Upon heating under argon $5 \cdot 7.5THF$ loses tetrahydrofuran at 83 °C. From 141 °C onwards 5 is intrinsically unstable with dinitrogen evolution and blackening under separation of tellurium beginning. At 168 °C, finally, $TeCl_4$ can be observed as yellow sublimate.

The $TeCl_4$ molecules bonded to the nitrogen atoms N(1,2,5,6) cause not only a restriction of the Te–N–Te bond angles of the Te_6N_6 skeleton from 114.4° to 95.5° at N(3,4,7,8), but also a stretching of the affected Te–N bonds of the Te_6N_6 core to 228.5 pm on average; all the other Te–N distances are only 201.3 pm. As a result, the latter are only a bit shorter than the Te–N bonds of the nitride functionality in the molecular complex 1 with 203.1 pm for X = F^[9] and 206.1 pm for X = Cl.^[8] Almost the same length is also shown by the Te–N bonds of the $TeCl_4$ molecules which are connected to the Te_6N_6 skeleton (av 204.0 pm). Te–N bonds which are a little shorter with an approximate length of 198 pm were observed in the cationic complexes 2 and 3.^[10,11] In all cases these distances approximately meet the value of 199 pm for Te–N single bonds.^[17] An approximately planar surrounding of the tellurium atoms by the four chlorine atoms as given in 5 is also observed in the polymeric structure of phenyltellurium trichloride.^[18]

In THF 5 shows dynamic behavior in the ¹²⁵Te NMR spectrum. Only two signals of different intensities are observed at $\delta = 716$ for the coordinated $TeCl_4$ molecules

and at $\delta = 567$ for the tellurium atoms of the Te_6N_8 core. This is in accord with the idea of a synchronized change of location for the four TeCl_4 molecules on the Te_6N_8 surface. Detachment of the TeCl_4 molecules does not take place in this process; the ^{125}Te NMR signal of TeCl_4 in THF is at $\delta = 1036$.^[19] Because of their disorder behavior the change of location of the TeCl_4 molecules is also indicated in the crystalline state, even at 223 K. In contrast, the THF molecules which are only loosely bonded are subject to quick exchange according to the ^1H NMR spectrum.

Received: May 20, 1998 [Z 11886 IE]

German version: *Angew. Chem.* 1998, 110, 3008–3010

Keywords: nitride · nitrogen · tellurium

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 [13] Crystal structure determination of $[\text{5} \cdot 4\text{THF}] \cdot 3.5\text{THF}$ ($\text{C}_{50}\text{H}_{104}\text{Cl}_4\text{N}_8\text{O}_{12}\text{Te}_{10}$, $M_r = 2496.06$): A colorless crystal (ca. $0.54 \times 0.54 \times 0.45$ mm) was analyzed with an area detector system (IPDS, Stoe) at -50°C with $\text{MoK}\alpha$ radiation ($\lambda = 71.069$ pm, graphite monochromator). Unit cell monoclinic, $a = 2291.7(2)$, $b = 1222.7(1)$, $c = 5356.0(5)$ pm, $\beta = 101.74(1)^\circ$; $V = 14694 \times 10^{-30}$ m³, space group $I2/a$, $Z = 8$, $\rho_{\text{calc}} = 2.257$ Mg m⁻³, $\mu(\text{MoK}\alpha) = 4.53$ mm⁻¹, $F(000) = 9184$. Because of a rapid decline in intensity at increasing diffraction angle, data were only collected up to $\theta = 24^\circ$, $\Phi = 0-250^\circ$, $\Delta\Phi = 1^\circ$, $t = 1$ min per record. Of 55355 reflections collected, 11290 were independent ($R_{\text{int}} = 0.060$) and 7648 observed ($I \geq 2\sigma(I)$). Measurement at even lower temperature was not possible, since a phase transition apparently occurs at approximately 220 K. Below this temperature diffuse streaks occur along the nevertheless very long c axis with maxima corresponding to a double superstructure. Semiempirical absorption corrections (from equivalent reflections) were carried out, and the structure was solved by direct methods and refined against all F^2 data^[14] by full matrix. The TeCl_4 molecules bonded to the Te_6N_8 core showed strong disorder. Three of them had to be described by split atom models, which in two cases showed also a shift component in addition to a rotational component. All atoms, just as those of the core, could be refined with individual anisotropic displacement parameters. The four THF molecules coordinated at the core could be refined without using split positions, but with large anisotropic displacement parameters. The 3.5 THF molecules per molecule additionally fitted into gaps of the packing, one of which was situated on a twofold axis, and showed very strong motion and/or disorder. A model refined with split positions for two THF molecules converged at $wR_2 = 0.1182$ (all reflections) and $R = 0.0404$ (observed reflections).

Because of the less than satisfactory possibility of describing the electron density blurred over this solvent range, its contribution to the structure factors was calculated by way of Back-Fourier transformation^[15] and subtracted from the data set. Thereafter, the main structure $[\text{5} \cdot 4\text{THF}]$ could be refined with clearly improved accuracy ($wR_2 = 0.0901$, $R = 0.0348$, residual electron density $0.95/-0.79$ e Å⁻³). The geometrical details documented here refer to this refinement. The structure determined at 223 K has the character of a high-temperature form in which the solvate molecules and TeCl_4 groups show high mobility or disorder. As documented in the quite physically meaningful shapes of displacement ellipsoids ($U_{\text{eq}} = 0.054-0.083$ Å²) of all atoms of the Te_6N_8 core, its orientation is not noticeably involved. Thus, no significant influence on the geometry is expected. Crystallographic data (excluding structure factors) for the structure reported in this paper (those obtained by Back-Fourier transformation as well as those obtained according to the disorder model) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101 663 and CCDC-101 664. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Langmuir–Blodgett Films of Single-Molecule Nanomagnets**

Miguel Clemente-León, Hélène Soyer,
 Eugenio Coronado,* Christophe Mingotaud,*
 Carlos J. Gómez-García, and Pierre Delhaès

The discovery that individual molecules can act as magnets of nanometer size is a very recent one.^[1,2] The most thoroughly studied single-molecule magnets are the mixed-valence manganese clusters $[\text{Mn}_{12}\text{O}_{12}(\text{carboxylate})_{16}]$ (carboxylate = acetate,^[1,3] propionate,^[4] benzoate,^[5] and 4-methylbenzoate^[6]), referred to here as Mn_{12} . The current excitement for this kind of magnetic cluster is primarily due to

[*] Prof. Dr. E. Coronado, M. Clemente-León, Dr. C. J. Gómez-García
 Dept. Química Inorgánica, Univ. de Valencia
 Dr. Moliner 50, E-46100 Burjassot (Spain)
 Fax: (+34) 96-3864322
 E-mail: eugenio.coronado@uv.es
 Dr. C. Mingotaud, H. Soyer, Dr. P. Delhaès
 Centre de Recherche Paul Pascal – CNRS
 Avenue A. Schweitzer, F-33600 Pessac (France)
 Fax: (+33) 556845600
 E-mail: mingotaud@axpp.crpp.u-bordeaux.fr

[**] This work was supported by the Ministerio de Educación y Cultura (Grant No. MAT98-0880) and the EU. M.C.-L. thanks the Generalitat Valenciana for a predoctoral fellowship. We thank the Spanish CICYT and the Generalitat Valenciana for the financial support to purchase the SQUID magnetometer.

The paper is "Directed Positioning of Organometallic Fragments inside a Calix[4]arene Cavity," by Catherine Wieser-Jeunesse, Dominique Matt and André De Cian (see figures 6–9), all from the Université Louis Pasteur, located on rue Blaise Pascal in multicultural Strasbourg, Alsace, France.

The article is about three pages long. Almost one page contains experimental detail. Half a page is the endnote apparatus. The body of the article is then about one and a half printed pages, of which roughly a third consists of graphical material: three schemes and a figure.

Let us begin to read the article. To a lay audience, the title is almost comprehensible ("organometallic" being an understandable subject area construction, metals + organic), except for "Calix[4]arene." It is clear that this is a name of a molecule or class of molecules. But what molecules? Our entrance to this small garden of molecular delights is barred (temporarily) by a cognitive disjunction, an angel bearing the awesome sword of nomenclature. Is "calixarene" some systematic scientific name? It couldn't be that calyxes of flowers, or chalices (à la the holy grail) sneak into the chemists' world?

Have no fear. Does it make you feel better when I tell you that half the physical chemists in the world also don't know what a calixarene is?

"Calix[4]arene" is indeed a descriptive, so-called "trivial" name for a class of molecules. The representative of interest to the authors is drawn out in Scheme 1 of the Wieser-Jeunesse, Matt, and De Cian paper (see Figure 10 = Scheme 1). It consists of four (that's the "4" in calix[4]arene) six-carbon benzene rings, which are also called arenes. Each of the four bears an oxygen atom, which is actually almost the only atom whose symbol is explicitly given. And hanging off the four oxygens is a little tail, reconstructed by the chemist from the part iconic, part symbolic, zigzag as a $\text{CH}_2\text{CH}_2\text{CH}_3$ or "n-propyl" group. The four arene rings are linked by another zig (a CH_2 group) into a ring. For all the world, the core of the molecule looks like a square of Balkan dancers, tripping lightly, yet energetically on the molecular scene.

And why "calix"? Precisely because it looked like a chalice to David Gutsche, the maker of the first representative of this class (Nickon and Silvermith, 1987). You wouldn't want to see its systematic official name, and neither would 99.999% of chemists. Calix[4]arene serves just fine. And yes, there are calix[5]arenes . . .

Let us begin with the rather long first paragraph of the paper:

A major attraction of cone-shaped calix[4]arenes concerns the presence of a macrocyclic cavity defined by four symmetrically sited phenoxy rings.^[1] To date, exploitation of such organized structures has mostly relied on converg-

spectroscopy of ^{15}N -labeled calmodulin. Measurements were made at 15°C on a Varian Inova 500 MHz NMR spectrometer, and the protein concentration was 1 mM in $\text{H}_2\text{O}/\text{D}_2\text{O}$ (9/1) at pH 6.8. Figure 2 displays a small region of ^{15}N - ^1H correlation spectra of calmodulin. Figure 2a shows the conventional HSQC spectrum obtained without the use of

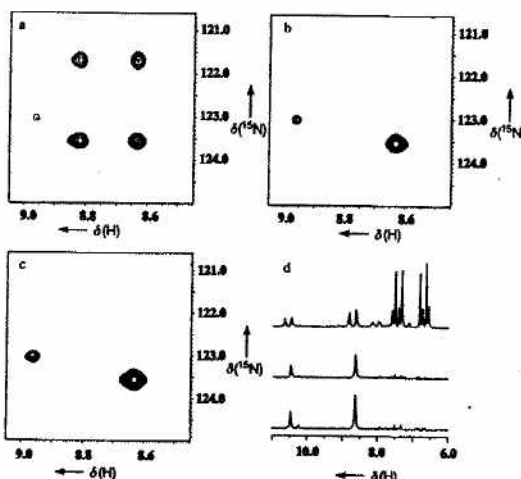


Figure 2. Contour plots of ^{15}N - ^1H correlation spectra of ^{15}N -labeled calmodulin. a) Conventional HSQC spectrum, obtained without decoupling during the t_1 and t_2 periods. b) Spectrum recorded in a conventional TROSY experiment.^[4] c) Spectrum recorded in a sensitivity-enhanced TROSY experiment (see text). d) One-dimensional cross sections from the spectra a-c at $\delta(^{15}\text{N}) = 123.6$ (from top to bottom). The peaks between 6 and 8 ppm in the HSQC cross section correspond to the cross-peak multiplets at the ^{15}N frequency ($\omega_{\text{N}} - \pi^1J_{\text{NH}}$), which is not observed by TROSY experiments. Spectra b and c, which were recorded and processed with the same parameters, have been scaled to the same noise level. The spacing factor between two consecutive contour lines is 1.2.

decoupling during the t_1 and t_2 periods. It is notable that even at 500 MHz there are significant differences in line width between the four individual multiplets. Figures 2b and 2c are taken from spectra recorded in conventional and sensitivity-enhanced TROSY experiments, respectively. Comparison of Figures 2b and 2c, as well as all other correlation peaks (not shown here), shows that a uniform enhancement in sensitivity of all peaks by a factor of $\sqrt{2}$ was achieved without introducing any artifacts.

The introduction of the TROSY experiment makes NMR spectroscopy a promising technique for studying the structure and function of larger biomolecules. We have improved the sensitivity of the original 2D TROSY experiment by a factor of $\sqrt{2}$ by using different phase cycling and data-processing schemes. This improvement will doubtless have widespread practical application in high-field NMR studies of large proteins.

Received: June 19, 1998 [Z120141E]
German version: *Angew. Chem.* 1998, 110, 3019–3021

Keywords: NMR spectroscopy • proteins

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[8] Note added in proof: A reviewer's comments alerted us to a difference between Varian and Bruker spectrometers, which requires that the y-axis receiver phases be inverted. It is also necessary to invert the y-axis pulse phases. In the pulse sequence of Figure 1, the particular phase cycling means that only the phase of the second 90° ^1H pulse needs to be considered. For optimal sensitivity, the phase of this pulse should be $-y$ for Varian and $+y$ for Bruker. If this phase is inverted then the "steady-state" enhancement, described by Pervushin et al. (*J. Am. Chem. Soc.* 1996, 118, 6394–6400) after this manuscript was submitted, will be lost. The sensitivity enhancement presented in this work is independent of the phase of this pulse and a $\sqrt{2}$ enhancement is gained over the corresponding TROSY experiment that has the same phase for this pulse.

Directed Positioning of Organometallic Fragments Inside a Calix[4]arene Cavity

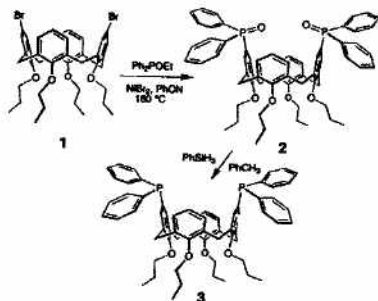
Catherine Wieser-Jeunesse, Dominique Matt,* and André De Cian

A major attraction of cone-shaped calix[4]arenes concerns the presence of a macrocyclic cavity defined by four symmetrically sited phenoxy rings.^[1] To date, exploitation of such organized structures has mostly relied on converging π systems on the inner side that facilitate weak binding of various substrates,^[2] including certain metal cations.^[3] Surprisingly, despite increasing interest in the application of calixarenes as ligands in transition metal chemistry,^[4] the

- [*] Dr. D. Matt, Dr. C. Wieser-Jeunesse
Université Louis Pasteur, UMR 7513 CNRS
Groupe de Chimie Inorganique Moléculaire
1 rue Blaise Pascal, F-67008 Strasbourg Cedex (France)
Fax: (+33) 3-88-617852
E-mail: dmatt@chimie.u-strasbg.fr
Dr. A. De Cian
Université Louis Pasteur, UMR 7513 CNRS
Laboratoire de Cristallogénie et Chimie Structurale
4 rue Blaise Pascal, F-67008 Strasbourg Cedex (France)

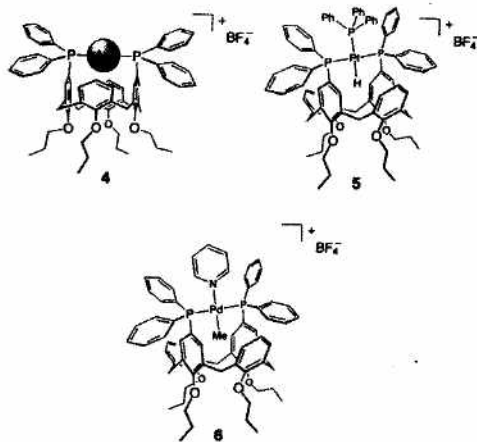
interior of the cavity has not been used to entrap or confine reactive fragments bound to transition metal ions.^[5] Such architectures could possess the capability to promote metal-centered reactions that are sterically constrained, thereby allowing combined shape control and regioselectivity.^[6] Furthermore, it is likely that the cavity walls will afford protection of highly reactive "M-R" units against undesired side reactions. We now report the first calix[4]arenes with organometallic fragments positioned inside the larger opening of the cavity.

Our approach to the construction of such systems exploits the coordinative properties of the hemispherical ligand **3**, a calix[4]arene bearing two P^{III} centers located on distal *p*-carbon atoms of the upper rim. Diphosphane **3** was conveniently prepared in two steps from **1**^[7] by using well-established procedures:^[8] diphosphorylation of **1** with Ph₂POEt/NiBr₂ resulted in formation of the di(phosphane oxide) **2**, which was then quantitatively reduced with PhSiH₃ to afford **3** (Scheme 1).



Scheme 1. Synthesis of the hemispherical ligand **3** in two steps.

Diphosphane **3** seems to be an ideal scaffold on which to assemble *trans*-chelate complexes: for example it reacts with one equivalent of AgBF₄ to form complex **4**. The FAB mass spectrum of **4** exhibits an intense signal at *m/z* 1069.6 with the appropriate isotopic profile for the (4 - BF₄)⁺ ion. NMR data collected for **4** show the molecule to possess C₂ symmetry,



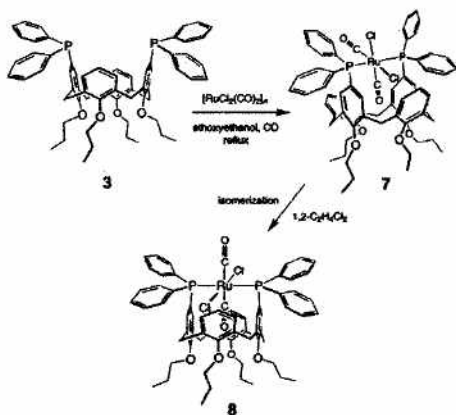
with the chemical shift found for the ³¹P NMR signal being exactly as expected for the assigned structure.^[9]

The above studies serve to indicate, not unsurprisingly, that the phosphane groups remain readily accessible for complexation with Ag⁺ ions; more challenging targets were then sought. Treatment of **3** with [PtH(thf)(PPh₃)₂]⁺ in refluxing THF afforded the platinum(II) complex **5** quantitatively. As for **4**, the ¹H and ¹³C NMR data indicate an apparent C₂-symmetry for the calixarene skeleton. Furthermore, the ³¹P NMR spectrum unambiguously establishes the *trans*-spanning behavior of the diphosphane as well as the presence of two types of phosphorus atoms (the phosphorus atoms on the calixarene appear as a doublet with ¹⁹⁵Pt satellites at δ = 15.0; J(P,P') = 20 Hz, J(P,Pt) = 2706 Hz). The bulky PPh₃ ligand, positioned *trans* to the hydride ligand, forces the Pt-H bond to point inside the calixarene cavity. The signal for the hydride atoms appears approximately 1.3 ppm upfield with respect to the related [PtH(PPh₃)₃]⁺ ion,^[10] thus reflecting the high shielding effect of the two phenoxy rings that border the hydride atom. In contrast to other complexes of the type [PtH(PPh₃)₂(P⁺P⁻)]⁺ that contain a *trans*-spanning diphosphane,^[11] complex **5** is inert towards *cis/trans* isomerization in solution. Since only the *trans* isomer has the necessary stereochemical features to position the hydride atom group inside the cavity, the reluctance to isomerize attests to the stability of the inclusion complex.

With the aim to entrap larger metallo-fragments inside the cavity, a solution of **3** in THF was treated with the cationic alkylpalladium complex [PdMe(cod)(thf)]BF₄ (cod = cyclooctadiene). Subsequent addition of pyridine resulted in the quantitative formation of complex **6**. Characteristic features of the ¹H NMR spectrum are the presence of a triplet for the methyl group at δ = -0.79, a solitary AB quartet for the ArCH₂Ar bridges, and a virtual triplet for four (*o*-P)-ArH hydrogen atoms (|³J(PH) + ⁵J(PH)| = 9 Hz). In the ³¹P NMR spectrum the phosphorus atoms appear as a singlet at δ = 27.0. Two-dimensional NOESY spectra (500 MHz) indicate that the methyl hydrogen atoms lie in close proximity to the phenolic CH bonds of the two phosphorus-substituted phenoxy rings. Taking into account that the bulky pyridine ligand does not allow gyroscopic spinning of the pyridine-Pd-Me fragment around the P-P axis, these findings clearly establish that the methyl group is locked inside the cavity.

A further illustration of the unique complexing properties of calixarene **3** concerns the positioning of octahedral metal centers at the entrance of the cavity. Treatment of commercial ruthenium trichloride with carbon monoxide in boiling ethoxyethanol followed by the addition of **3** afforded the Ru^{II} complex **7** in high yield (Scheme 2). The *cis* arrangement of the two carbonyl units was inferred from the infrared spectrum, which showed two absorption bands in the CO region ($\nu = 2072(\text{s})$ and $1995(\text{s}) \text{ cm}^{-1}$). Complex **7** slowly isomerizes in 1,2-dichloroethane into the *trans,trans,trans* isomer **8** ($\nu(\text{C}\equiv\text{O}) = 1924(\text{s}) \text{ cm}^{-1}$). The *trans*-spanning behavior of the diphosphane was confirmed by an X-ray diffraction study (Figure 1). The most remarkable feature of this structure is the entrapment of one metal carbonyl unit inside the calixarene cavity, the CO ligand being exactly intercalated

FIGURE 7



Scheme 2. Positioning of octahedral ruthenium units at the mouth of calixarene 3.

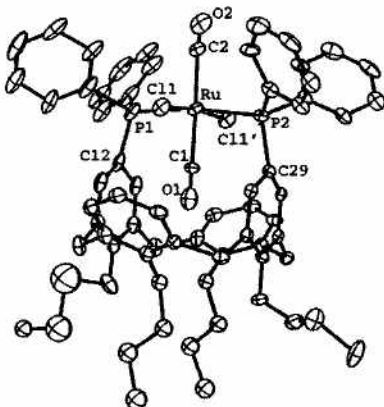


Figure 1. Structure of complex 8 (ORTEP). Selected bond lengths [pm] and angles [°]: Ru–P1 240.9(5), Ru–P2 240.3(5), Ru–Cl1 196(2), Ru–Cl2 188(2), Ru–C1 241.0(3), P1–C12 182(2), P2–C29 184(1); P1–Ru–P2 172.2(3), Cl–Ru–Cl 171.9(2), Ru–P(1)–C(12) 106.6(5), Ru–P(2)–C(29) 107.2(5). The molecule possesses a mirror plane containing the phosphorus and ruthenium atoms. Each carbon atom of the propyl groups that are linked to the OArP rings are disordered over two positions.

between the two bordering P-substituted phenyl rings. The distance between these planes and the CO ligand axis is rather short (about 2.75 Å), thus suggesting a bonding interaction between the sandwiched CO and the two PPh rings. The relatively low $\bar{\nu}(\text{CO})$ frequency (1924(s) cm^{-1} compared with 1998 cm^{-1} for *trans,trans,trans*-[RuCl₂(CO)₂(PPh₃)₂]^[12]) supports this assumption.

Experimental Section

All reactions were carried out in dry solvents under purified nitrogen.

2: Yield: 82%; m.p. > 280°C; ¹H NMR (300 MHz, CDCl₃, 25°C): δ = 7.76–7.69 and 7.54–7.48 (20H, PPh₂), 7.40 (d, 4H, *m*-H of OArP, ³J(P,H) = 12 Hz), 6.24 and 6.02 (AB₂ spin system, 6H, *m*- and *p*-H of

OAr, ³J = 7.5 Hz), 4.42 and 3.12 (AB spin system, 8H, ArCH₂Ar, ³J(A,B) = 13 Hz), 4.08 (pseudo t, 4H, OCH₂, ³J ≈ 8 Hz), 3.60 (t, 4H, OCH₂, ³J = 8 Hz), 1.94 (m, 4H, OCH₂CH₂), 1.82 (m, 4H, OCH₂CH₂), 1.06 (t, CH₃, ³J = 8 Hz), 0.90 (t, CH₃, ³J = 8 Hz); ¹³C{¹H} NMR (50 MHz, CDCl₃, 25°C): δ = 161.52 and 155.12 (2s, arom. C_q-O), 137.67–122.31 (arom. C atoms), 77.14 and 76.74 (2s, OCH₂), 30.96 (s, ArCH₂), 23.51 and 23.17 (2s, CH₂CH₂), 10.84 and 9.86 (2s, CH₃); ³¹P{¹H} NMR (121 MHz, CDCl₃, 25°C): δ = 29.4 (s, PPh₂); elemental analyses calcd for C₆₄H₆₀O₆P₂ · 0.5CHCl₃ (993.18 + 59.69): C 73.58, H 6.37; found: C 74.00, H 6.37.

3: Yield: 75%; m.p. 230–233°C; ¹H NMR (300 MHz, CDCl₃, 25°C): δ = 7.37–7.33 (20H, PPh₂), 7.06 (d, 4H, *m*-H of OArP, ³J(P,H) = 8 Hz), 6.29 and 6.11 (AB₂ spin system, 6H, *m* and *p*-H of OAr, ³J = 8 Hz), 4.41 and 3.06 (AB spin system, 8H, ArCH₂Ar, ³J(A,B) = 13 Hz), 4.03 (pseudo t, 4H, OCH₂, ³J ≈ 8 Hz), 3.63 (t, 4H, OCH₂, ³J = 8 Hz), 2.00 (m, 4H, OCH₂CH₂), 1.81 (m, 4H, OCH₂CH₂), 1.06 (t, CH₃, ³J = 7.5 Hz), 0.91 (t, CH₃, ³J = 7.5 Hz); ¹³C{¹H} NMR (50 MHz, CDCl₃, 25°C): δ = 159.80 and 155.10 (2s, arom. C_q-O), 137.25–122.02 (arom. C atoms), 77.00 and 76.60 (2s, OCH₂), 30.94 (s, ArCH₂Ar), 23.51 and 23.15 (2s, CH₂CH₂), 10.82 and 9.93 (2s, CH₃); ³¹P{¹H} NMR (121 MHz, CDCl₃, 25°C): δ = -6.4 (s, PPh₂); elemental analyses calcd for C₆₄H₆₀O₆P₂ (961.18): C 79.98, H 6.92; found: C 80.18, H 6.74.

4: Yield: 80%; m.p. 187–190°C (decomp); ¹H NMR (300 MHz, CDCl₃, 25°C): δ = 7.43–7.37 (24H, arom. H), 6.82 (s, 4H, *m*-H of OArP), 6.18 (t of B₂A spin system, 2H, *p*-H of OAr, ³J = 8 Hz), 4.40 and 3.05 (AB spin system, 8H, ArCH₂Ar, ³J(A,B) = 13 Hz), 4.01 (pseudo t, 4H, OCH₂, ³J ≈ 8 Hz), 3.70 (t, 4H, OCH₂, ³J = 8 Hz), 1.98 (m, 4H, OCH₂CH₂), 1.89 (m, 4H, OCH₂CH₂), 1.09 (t, CH₃, ³J = 7.5 Hz), 0.83 (t, CH₃, ³J = 7.5 Hz); ¹³C{¹H} NMR (50 MHz, CDCl₃, 25°C): δ = 157.18 and 156.85 (2s, arom. C_q-O), 136.09–123.02 (arom. C atoms), 77.64 and 76.59 (2s, OCH₂), 30.85 (s, ArCH₂Ar), 23.91 and 23.57 (2s, CH₂CH₂), 10.79 and 9.80 (2s, CH₃); ³¹P{¹H} NMR (121 MHz, CDCl₃, 25°C): δ = 10.4 (two d, PPh₂, ¹J(¹⁰⁹Ag,P) = 503 Hz, ¹J(¹⁰⁹Ag,P) = 580 Hz); MS (FAB): *m/z* calcd for C₆₄H₆₀O₆P₂Ag [M - BF₄]⁻: 1069; found 1069.6; elemental analyses calcd for C₆₄H₆₀BF₄O₆P₂Ag (1155.86): C 66.51, H 5.76; found: C 66.66, H 5.43.

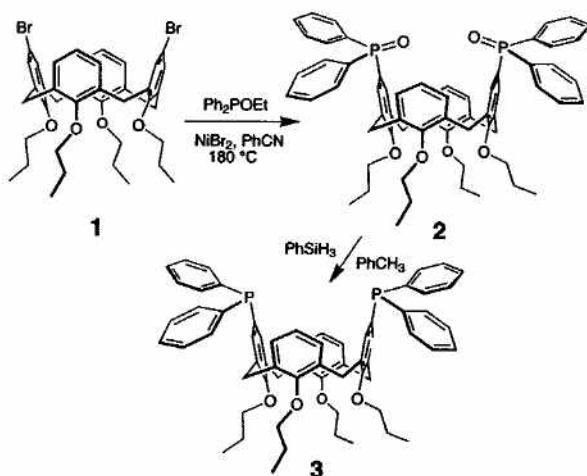
5: Yield: 73%; m.p. 226–230°C; ¹H NMR (300 MHz, CDCl₃, 25°C): δ = 7.42–7.02 and 6.87 (43H, arom. H), 6.24 (t of B₂A spin system, 2H, *p*-H of OAr, ³J(A,B) = 6 Hz), 4.44 and 3.09 (AB spin system, 8H, ArCH₂Ar, ³J(A,B) = 13 Hz), 4.04 (pseudo t, 4H, OCH₂, ³J ≈ 6 Hz), 3.69 (t, 4H, OCH₂, ³J = 7 Hz), 1.97 (m, 4H, OCH₂CH₂), 1.89 (m, 4H, OCH₂CH₂), 1.10 (t, CH₃, ³J = 9 Hz), 0.92 (t, CH₃, ³J = 7 Hz), -6.93 (dt with Pt satellites, 1H, PtH, ³J(H,P_{ax}) = 17 Hz, ³J(H,P_{eq}) = 167 Hz); ¹³C{¹H} NMR (50 MHz, CDCl₃, 25°C): δ = 157.39 and 156.70 (2s, arom. C_q-O), 136.40–122.43 (arom. C atoms), 77.90 and 76.65 (2s, OCH₂), 30.93 (s, ArCH₂), 23.51 and 22.94 (2s, CH₂CH₂), 10.74 and 9.77 (2s, CH₂CH₂); ³¹P{¹H} NMR (121 MHz, CDCl₃, 25°C): δ = 24.2 (t with Pt satellites, PPh₂, ³J(P,P) = 20 Hz, ¹J(P,Pt) = 2120 Hz), 15.0 (d, PPh₂, ³J(P,P) = 20, ¹J(P,Pt) = 2706 Hz); MS (FAB): *m/z* calcd for C₆₄H₆₀O₆P₂Pt [M - BF₄]⁻: 1418.5; found: 1418.8 (expected isotopic profile); elemental analyses calcd for C₆₄H₆₂BF₄O₆P₂Pt (1506.38): C 65.38, H 5.49; found: C 65.18, H 5.43.

6: Yield: 81%; m.p. 163–166°C (decomp); ¹H NMR (300 MHz, CD₂Cl₂, 25°C): δ = 7.79 (d, 2H, *o*-H of pyridine), 7.52 (t, 1H, *p*-H of pyridine, ³J = 5 Hz), 7.32–7.24 (20H, PPh₂), 7.06–7.00 (m, 6H, *m*- and *p*-H of OAr), 6.79 (m br, 2H, *m*-H of pyridine), 6.62 (virtual t, 4H, AA'XX'A'A' spin system (X = P), 4H, *m*-H of OArP, ³J(P,H) + ³J(P',H) = 9 Hz), 4.56 and 3.24 (AB spin system, 8H, ArCH₂Ar, ³J(A,B) = 13 Hz), 4.15 (pseudo t, 4H, OCH₂, ³J ≈ 8 Hz), 3.81 (t, 4H, OCH₂, ³J = 7 Hz), 2.06 (m, 4H, OCH₂CH₂), 1.97 (m, 4H, OCH₂CH₂), 1.15 (t, CH₃, ³J = 7 Hz), 0.96 (t, CH₃, ³J = 7 Hz), -0.79 (t, 3H, Pd-CH₃, ³J(P,H) = 6 Hz); ¹³C{¹H} NMR (CD₂Cl₂, 50 MHz, 25°C): δ = 157.95 and 157.59 (2s, arom. C_q-O), 151.66–121.56 (arom. C atoms), 78.32 and 77.08 (2s, OCH₂), 31.32 (s, ArCH₂Ar), 23.98 (s, CH₂CH₂), 11.00 and 9.98 (2s, CH₃); ³¹P{¹H} NMR (CD₂Cl₂, 121 MHz, 25°C): δ = 27.0 (s, PPh₂); MS (FAB): *m/z* calcd for C₆₈H₆₀O₆P₂Pd [M - pyridine - BF₄]⁻: 1081; found: 1081.1 (expected isotopic profile); elemental analyses calcd for C₆₈H₆₄BF₄NO₆P₂Pd (1248.53): C 67.34, H 5.95, N 1.12; found: C 67.41, H 6.10, N 0.93.

7: Yield: 84%; m.p. > 280°C; IR (KBr): $\bar{\nu}(\text{C}=\text{O}) = 2072(\text{s})$ and $1995(\text{s}) \text{cm}^{-1}$; ¹H NMR (500 MHz, CD₂Cl₂, 25°C): δ = 8.31–8.28 and 7.36–7.34 (20H, PPh₂), 6.82 (virtual t, 4H, *m*-H of OArP), 6.81 and 6.65 (B₂A spin system, 6H, *m*- and *p*-H of OAr, ³J(A,B) = 6 Hz), 4.47 and 3.19 (AB spin system, 8H, ArCH₂Ar, ³J(A,B) = 13 Hz), 3.99 (pseudo t, 4H,

FIGURE 8

FIGURE 10



Scheme 1. Synthesis of the hemispherical ligand 3 in two steps.

ing π systems on the inner side that facilitate weak binding of various substrates,^[2] including certain metal cations.^{[3]1}

To make sense of the words we need to look at the picture, Scheme 1, again. The beetle quadrille is sort of cone-shaped. “Phenoxy” is a chemical word for the combination of an oxygen with an arene ring; the same grouping plays a role in molecules as diverse (and as common) as vanillin, aspirin, and mescaline. “Macrocyclic” is a fancy word for “big ring.” The addition to Latinate expressions to express learnedness has not vanished, even if chemists in general know precious little Latin.

In the second sentence of the introductory paragraph there is some delimitation of the current interest in the molecule that is central to this study, the rhetorical intent clear, to provide a space for the *raison-d'être* of this study. The “ π -systems” referred to are the electrons cruising above and below the face of the six-carbon arene rings that make up the calixarene; there is a long, long history both of the importance of this subset of electrons, and their tangible involvement in the stability of that ring. If you want to know more, a combination of a dose of Pynchon’s *Gravity’s Rainbow* and an organic chemistry course by one of my colleagues will help. Wieser-Jeunesse, Matt, and De Cian say that others have been playing with these electrons, using them to bind weakly to metal cations (positive ions).

1. The bracketed numbers are the endnote references in the original text.

The background to all this work is a desire to achieve control (shall we malign that obsession as male, when a woman is one of the co-authors of this work?) over the way molecules react and their structures. The thinking is geometrical, almost billiard ball-like, on the microscopic level. Molecules are an in-between land, yes—they are quantum objects, and yet, in so many heuristically useful ways, they are also little structures, to be ingeniously assembled, disassembled, constructed. The architectonic thinking is very clear in this paragraph.

The authors continue:

Surprisingly, despite increasing interest in the application of calixarenes as ligands in transition metal chemistry ^[4] the interior of the cavity has not been used to entrap or confine reactive fragments bound to transition metal ions.^[5]

Here there is a reaching out to another type of chemistry (inorganic chemistry, which studies metal ions), and a furthering of the rhetorical strategy. There is no doubt that the authors will provide us with the utility lacking in the previous work:

Such architectures could possess the capability to promote metal-centered reactions that are sterically constrained, thereby allowing combined shape control and regioselectivity.^[6]

We see more geometrical descriptors, further aspirations to control, just a little more jargon. The paragraph ends with the claim of this paper very clearly announced:

We now report the first calix[4]arenes with organometallic fragments positioned inside the larger opening of the cavity.

I would characterize the jargon as moderate at this level, and the claims actually not exaggerated. The rhetorical posture is—to me—acceptable.

The authors next get down to business:

Our approach to the construction of such systems exploits the coordinative properties of the hemispherical ligand **3**, a calix[4]arene bearing two P^{III} centers located on distal p-carbon atoms of the upper rim. Diphosphane **3** was conveniently prepared in two steps from **1**^[7] by using well-established procedures:^[8] diphosphorylation of **1** with Ph₂POEt/NiBr₂ resulted in formation of the di(phosphane oxide) **2**, which was then quantitatively reduced with PhSiH₃ to afford **3** (Scheme 1).

What Wieser-Jeunesse, Matt, and De Cian are doing is pretty easy to describe. They take the calixarene (they don't tell us in what quantity) **1**,² which has two bromine atoms at the top of two of the four arene rings, and using these bromide handles, change them to more complicated groupings containing a phosphorus and an oxygen, then remove an oxygen. The experimental section does not actually give details of the synthesis, but provides the physical proof for the structure of compounds/molecules **2** and **3**. Real substances are manipulated, many physical transformations made, much labor, real work. None of that is detailed here. The authors speak, as chemists today do, of molecules that they do not see, but for which they have excellent indirect evidence (knowing without seeing, wonderful stuff!). Elsewhere, Emily Grosholz and I have written of this incredible process, and the way that the chemists' necessity to move simultaneously in macroscopic and microscopic worlds forces chemists to use a mixture of symbolic and iconic representation of compounds/molecules (Grosholz and Hoffmann, 2000).

Making molecule **3** is the necessary preparation—the remainder of this excellent paper uses **3** to do everything the authors set out claims to:

Diphosphane **3** seems to be an ideal scaffold on which to assemble *trans*-chelate complexes: for example it reacts with one equivalent of AgBF_4 to form complex **4**. The FAB mass spectrum of **4** exhibits an intense signal at m/z 1069.6 with the appropriate isotopic profile for the $(\mathbf{3}-\text{BF}_4)^+$ ion. NMR data collected for **4** show the molecule to possess C_2 symmetry, with the chemical shift found for the ^{31}P NMR signal being exactly as expected for the assigned structure.[9]

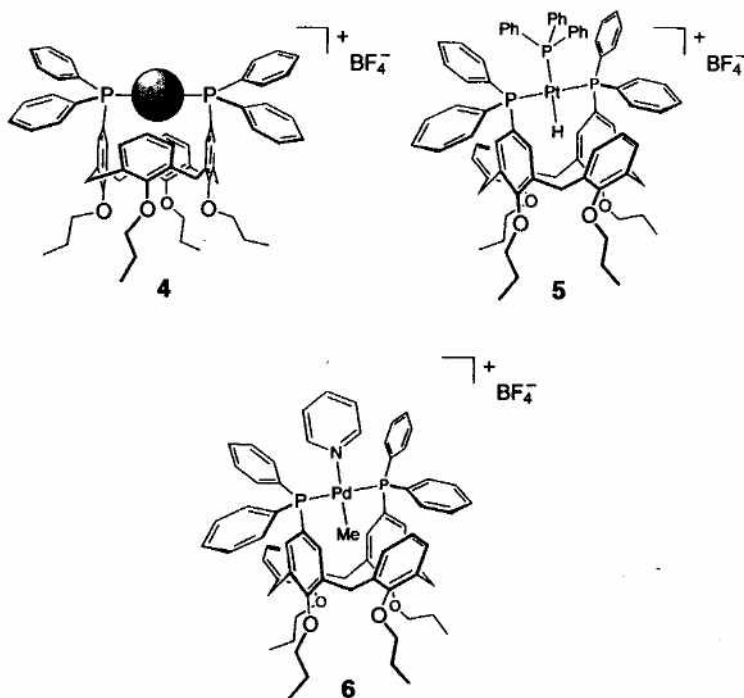
As Wieser-Jeunesse, Matt, and De Cian say in the first sentence, the “diphosphane” is designed to, and does, clasp pretty much any metal ion, and silver in particular. This is shown in their molecular structure **4**, reproduced in Figure 11.

The next part of the paper is interesting, for it begins with a sentence that for a chemical paper is relatively uncommon:

The above studies serve to indicate, not unsurprisingly, that the phosphane groups remain readily accessible for complexation with Ag^+ ions; more challenging targets were then sought.

2. It is chemical custom to refer to molecular structures by boldface numbers. This is done both by the authors of the paper studied and by me, using the same numbers. The structures are defined in the figures.

FIGURE 11



This says: "that was easy; let's try for something harder." Do you think they will fail?

Let me next sketch in sparse detail the subsequent neat chemistry Wieser-Jeunesse, Matt, and De Cian carried out. Using instead of a silver compound a platinum one, they get a platinum-containing unit bound in between the phosphoruses. But now that platinum unit is not "naked," like the silver was, but carries a hydrogen poking into the cavity of the chalice—which doesn't have all that much room for extra atoms. The hydrogen senses the constrained environment; signals from within tell us it is there and nowhere else. That's the NMR (nuclear magnetic resonance) spectroscopy referred to in the paper; in a fit of creative euphemism our fearful society has renamed the technique in its medical incarnation as MRI.

The alternative, given the desire of the platinum to have a square-planar environment, would have been to poke the much bigger PPh_3 (Ph is an abbreviation for phenyl, or a C_6H_5 benzene) group inside.

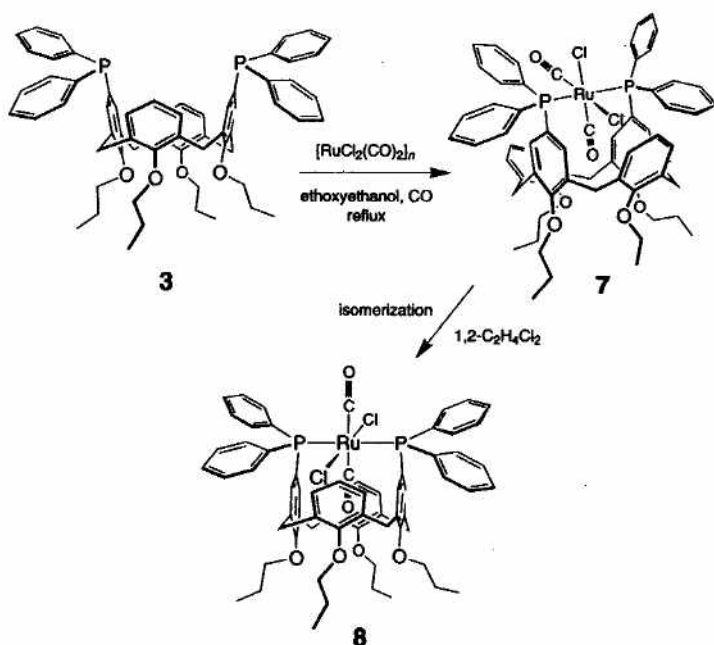
Incidentally, "Given the desire . . ." refers to my *métier*, for as a theoretical chemist I would like to think of myself as a delineator of desire. Of course, the desire (to be in one geometry or another) is there,

whether I am there or not. What I do is teach people, by telling plausible stories, why a molecule takes on one shape and not another. Politician, priest, storyteller, arbiter of molecular desire—that's what I am. At least one day a week.

Wieser-Jeunesse, Matt, and De Cian then tuck in a palladium, with a still bulkier "Me" (that is a piece of colloquial notation for the CH_3 grouping of atoms) group on the inside, **6** (see Fig. 11). It is only contemplating my imminent departure for Lacoste, Provence, to live, perchance to write, for a month in the shadow of the ancestral château of the Marquis de Sade, which leads me to muse about the fact that Wieser-Jeunesse, Matt, and De Cian don't stop there. They want to test the limits, ring the changes, see how much that constrained chalice space will take. All the ways of its bonding . . .

In their Scheme 2 (Fig. 12 here) you see the realized plan: even a locally octahedral ruthenium atom can be lured to bind in the cavity of the calixarene (the structure, determined with X-ray crystallography, is shown in their article).

FIGURE 12



Scheme 2. Positioning of octahedral ruthenium units at the mouth of calixarene **3**.

One carbon monoxide "ligand" on the ruthenium, the one poking into the cavity, is much affected. Wieser-Jeunesse, Matt, and De Cian claim bonding; I actually would disagree, for theoretical reasons. This is my only disagreement with their lovely work.

On this note the paper ends, quite abruptly. I might add that this excellent research caught not only my eye, but that of the editors of the periodical, who feature its climactic synthesis in a separate graphic (Fig. 13) on the cover of that issue of *Angewandte Chemie*.

THE WAY IT IS TOLD

You open an issue of a modern chemical periodical, and you see more of what I have shown you. Riches upon riches: reports of new discoveries, marvelous molecules, unmakeable, unthinkable yesterday—made today, reproducibly, with ease. The chemist reads of the incredible properties of novel high temperature superconductors, organic ferromagnets, and supercritical solvents. New techniques of measurement, quickly equipped with acronyms—EXAFS, INEPT, COCONOESY—allow you to puzzle out the structure of what you make more expeditiously. Information just flows. It's chemistry—communicated, exciting, alive.

I have shown to you an article reporting excellent chemistry, and a well written one. I assure you that it is given to me and my colleagues to read much that is palpably worse. How tired I am of seeing articles that begin with "The structure, bonding, and spectroscopy of molecules of type X have been subjects of intense interest.²²"! In the vast majority of the chemical literature I see a ritual product, at times stultifying in its sameness. There is general use of the third person and the passive voice. Few overtly expressed personal motivations, and few accounts of historical development, are to be found. Here and there in the neutered language one glimpses stated claims of achievement or priority—"a novel metabolite," "the first synthesis," "a general strategy," "parameter-free calculations." But these are more in the service of hype than elegance. On studying many papers one finds a mind-deadening similarity. In this land of the new! Nevertheless, one also sees here and there style—a distinctive, connected scientific/written/graphic way of looking at the chemical universe.

There is much more to say, both about the history of the journal article, and the essentially chemical nature of the process of representation of molecules (Hoffmann and Laszlo, 1991) The rhetorical structure of the chemical article is also fascinating—elsewhere, I have argued that much more goes on in that article than one imagines at first sight; that what goes on is a kind of dialectical struggle between what a chemist imagines

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FIGURE 13

should be said (the paradigm, the normative) and what he or she must say to convince others of his argument or achievement. That struggle endows the most innocent-looking article with a lot of suppressed tension (see chapters 17 and 18 in Hoffmann, 1995).

WHAT IS TO BE DONE?

I love this complex molecular science. I know that its richness was created by human beings. So I'm unhappy to see their humanity suppressed in the way they express themselves in print. The periodical article system of transmitting new knowledge has worked remarkably well for two centuries or more. But I think there are real dangers implicit in its current canonical form.

One danger, specific to the scientific article, is that by dehumanizing our mode of communication, by removing emotion, motivation, the occasionally irrational, we may in fact have done much more than chase away the Naturphilosophen of the early nineteenth century. One hundred and fifty years down the line what we have created is a mechanical, ritualized product that 5×10^5 times per year propagates the notion that scientists are dry and insensitive, that they respond only to wiggles in a spectrum. The public at large types us by the nature of our product. How can it do otherwise, when we do not make a sufficient effort to explain to the public what it is that we really do in our jargon-barricaded world?

What is to be done? I would argue for a general humanization of the publication process. The community should relax those strictures, editorial or self-imposed, on portraying in words, in a primary scientific paper, motivation, whether personal and scientific, emotion, historicity, even some of the irrational. So what if it takes a little more space? As it is, we can keep up with the chemical literature, and tell the mass of hack work from what is truly innovative, without much trouble. And we recognize hype ever so easily. The humanizing words will not mislead; they may actually encourage us to read more carefully the substance of what is said. I would plead for a valuation and teaching of style, in the written and spoken language of one's own country, as well as in English. I think chemistry has much to gain from reviving the personal, the emotional, the stylistic core of the struggle to discover and create the molecular world.

FOLLOW YOUR OWN ADVICE

Nice words in that plea for humanizing the scientific article—who could argue with them? Well, the young assistant professor trying to carve out a

career niche, anxious to have people see and value his or her research as it is published in the literature—is he or she likely to follow this advice? And risk losing it at the gate, so to speak, as conservative editors and reviewers, intent to find something moderately intelligent to say, look askance at modernities of style, colloquialisms, not to speak of worse deviances from the ossified standard?

It would take a very, very courageous young colleague to do so. He or she should turn the question around and ask me: “Do you, Roald, even as you are in a much more privileged position than I am (he doesn’t realize that my papers are for various reasons criticized more vehemently than his), do you follow your preaching?”

Yes, and no; sadly, mostly no. I write papers that generally look like the ones you’ve seen (well, maybe a little prettier); Figure 14 shows a page from a recent paper (Merschrod, Tang, and Hoffmann, 1998). Note the blend of graphic and text, the desperate aspiration to a *Gesamtkunstwerk*. I do cultivate a certain style with cognitive and literary features; the components of that style on the chemical, cognitive side are:

- (a) an in-depth examination of many compounds, attention to the literature;
- (b) lots of carefully designed drawings, of molecules and orbitals;
- (c) a suppression of results produced by the computer in favor of qualitative explanations; and
- (d) a mixture of rationalization and prediction.

As literary devices, I use

- (a) a generally discursive style, with occasional repetitions and rehearsals, and lots of those drawings, too; and
- (b) colloquial language where I can, trying to have the paper read the way a seminar sounds. This is a device whose purpose is to make the reader feel comfortable with inherently complex material.

All these devices—the pedagogic style, repetition, colloquial language—are guaranteed to cause trouble with reviewers and editors. So I struggle, to this day, 450 papers down the line. Here is an example of a recent (1997) review of one of my papers, reacting to style more than content:

The theoretical data in this paper is of value and definitely deserves publication. But the paper, which is extremely well-written and beautifully presented, is far too long as a vehicle to transmit the essential data which it includes. The elegant diagrams and discursive style are highly desirable at the

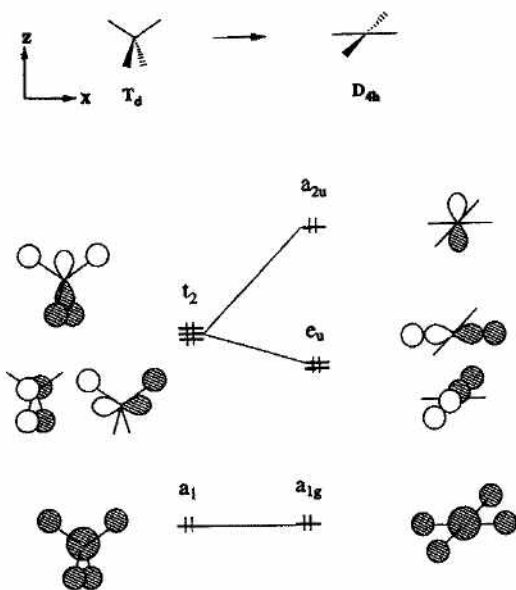
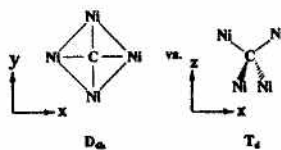


Fig. 4. Schematic orbital correlation diagram for the occupied molecular orbitals of CH_4 in T_d (left) and D_{4h} (right) geometries.

planar counterpart. The origin of the stability difference may be seen for CH_4 in Fig. 4. In a tetrahedral geometry, the t_2 orbitals form three C-H σ bonds, while in the square-planar conformation, the t_2 orbitals split into a bonding e_u set of orbitals and a high-lying a_{2u} orbital.

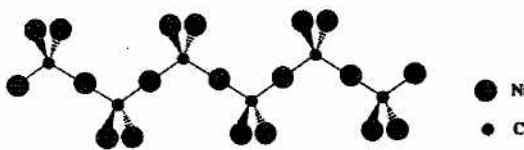
The latter is non-bonding, while the strength of the C-H bonding in the e_u orbitals of the D_{4h} geometry is almost a third smaller than that in the t_2 orbitals in the T_d geometry (as measured by computed overlap populations). The result is a net loss of C-H bonding in the planar geometry as compared to the tetrahedral one. We decided to look at a tetrahedral alternative for the $(\text{Ni}_4\text{C})^{4-}$ molecular cluster, to see whether there was any factor discriminating against it. On going from a square planar $(\text{Ni}_4\text{C})^{4-}$ model to a tetrahedral one (5, keeping Ni-C bond lengths constant; the computational details are not shown here), the three highest occupied orbitals in Fig. 1 become a totally bonding t_2 set. The Ni-C bonds are strengthened in the tetrahedral geometry of Ni_4C^{4-} , just as they are in the case of CH_4 . Tetrahedral Ni_4C^{4-} is computed as 1.15 eV more stable than the D_{4h} form. There appears to be nothing wrong with this structure, though one loses

some Ni-Ni bonding in departing from the square planar structure.



5

A similar situation should also arise in the extended structure. Using the tetrahedral building block shown at the right of 5, we can construct a one-dimensional extended structure 6 (one of many possibilities). In hypothetical structure 6, we keep the Ni-C bond lengths the same as in 2. The resulting Ni-Ni separation is 3.04 Å.



6

How do the energetics of the tetrahedral alternative compare to those of the planar geometry in the extended systems? The unit cell of 6 is $[\text{Ni}_6\text{C}_2]^{8-}$, containing twice as many atoms as in 2. The extended Hückel calculation indicates that hypothet-

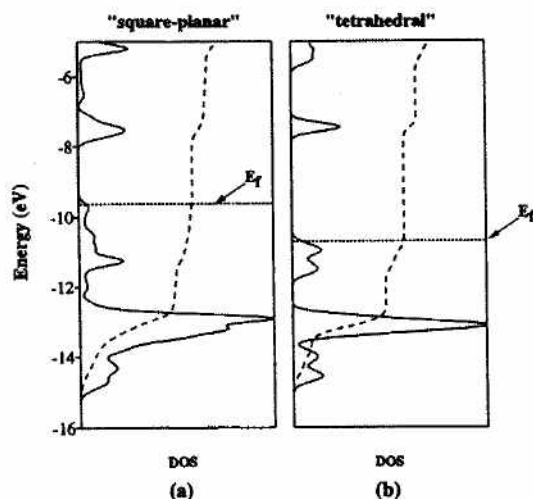


Fig. 5. Total DOS plots of (a) the "square-planar" structure (2) and (b) the "tetrahedral" one (6). The horizontal dotted line denotes the Fermi level.

level of a postgraduate thesis, but for publication in the open literature the manuscript needs to be greatly condensed, in particular to meet the current standards of the journal.

The editor, a friend, commenting on my remonstrance says:

Roald, I believe referee D was not criticizing your paper because it is pedagogical. He was complimenting it. I think he was trying to say that in his opinion, although the paper is very well written, it is suitable for a more specialized journal.

The paper was rejected, and found a home in another journal.

Basta!

Often I and my coworkers write papers the way the system wants us to write them. Here's an example from the beginning of one (Landrum, Hoffmann, Evers, and Boysen, 1998):

The TiNiSi (or Co₂Si) structure type (space group Pnma, Pearson symbol oP12) is a lower symmetry relative of the CeCu₂ structure (space group Imma). In a previous publication, we presented a detailed analysis of the bonding in the CeCu₂ structure type.^[1] While CeCu₂ is quite a common structure, with 81 known examples as of 1991,^[2] the TiNiSi structure type is even more versatile; 495 manifestations are reported in the same publication. There are strong similarities between the two structure types. Both TiNiSi and CeCu₂ have three-dimensional four-connected (3D₄C) anionic networks with cations sitting in large channels. Both networks can be viewed as being composed of two-dimensional sheets of edge sharing six-membered rings similar to those in black phosphorus running perpendicular. . . .

Sometimes, my students and I manage to do better (Landrum and Hoffmann, 1998). Here is an example:

The more crystal structures we know, the clearer it becomes that in the solid state there are many contacts in the range between a bond and a van der Waals interaction. N. W. Alcock introduced the useful term "secondary bonding" for these, and formulated a set of rules for their occurrence and directionality.^[1]

For electron-rich main-group systems there are two popular ways to address in a qualitative way the electronic structure of secondary bonded species—either as a manifestation of hypervalence (electron-rich three-center or multicenter bonding^[2]) or as directional donor-acceptor bonding.^[3] We feel these approaches are in fact equivalent, though we doubt that

the number of energetic electrons expended on the demerits of one or the other chemical views is exhausted.

More of my papers are of the first variety, I must admit.

There is another reason why I do not write in a radically different style. As a theoretician I am in the business of shaping (in a very minor way) a worldview of chemistry. I am after the mind of the chemist. Not the mind of my fellow theoreticians; they're too smart, and besides they have their own spiritual wares to peddle. Not my older experimentalist colleagues, for they are often set in ways of thinking that work perfectly well for them. My audience is very clearly in sight—I write for the senior graduate student, for the young assistant professor. Their minds are open; if it is useful, they will take up a new way of thinking.

For my audience, writing in an entirely offbeat way, inventing batteries of neologisms, claiming that the patently derivative is entirely new by . . . rephrasing the problem—all of these are doomed strategies. The way to introduce the new is in small steps, in a sequence of minor seductions of ever-thirsty mind. So, on stylistic matters, or inventing new words, I go easy. I use familiar concepts, comfortable phrases to introduce a new way of looking at the world. Just here and there I sneak in a word, a phrase that shocks the reader into the realization that he or she is empowered to see things in a different light.

I write, I draw, chemistry . . . so as to teach.

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