Table 1. Motifs of mutual adjunction, interatomic distances [pm], and coordination numbers (C.N.).

	F(1)	F(2)	F(3)	F(4)	F(5)	F(6)	C.N.
Ag^{2+}	–	–	–	2/1	2/1	2/1	4+2
d(Ag-F)	–	–	–	2×236.7(7)	2×206.7(7)	2×203.0(6)	
Ta^{5+}	1/1	1/1	1/1	1/1	1/1	1/1	6
d(Ta-F)	181.7(7)	186.5(7)	183.4(6)	191.0(7)	197.6(6)	200.0(6)	
C.N.(F^-)	1	1	1	2	2	2	

The structure of $Ag[TaF_6]_2$ is best described in terms of a layer structure (Fig. 1):[6] Three $[AgF_6]$-octahedra are each coupled alternately "above and below" the (100) plane by three *cis* F^- forming a triangular face of a markedly distorted $[TaF_6]$-octahedron; cf. motifs of mutual adjunction[7] in Table 1.

No further coupling via cations takes place between these (two-dimensional) "layer packets".

$$[Ag(\overset{4}{F}_{t/2})_2\,(\overset{5}{F}_{t/2})_2\,(\overset{6}{F}_{t/2})_2]\,[\overset{4}{F}_{t/2}\,\overset{5}{F}_{t/2}\,\overset{6}{F}_{t/2}\,Ta\,\overset{1}{F}_{t/1}\,\overset{2}{F}_{t/1}\,\overset{3}{F}_{t/1}]_{\infty/3}$$

As follows from the interatomic distances (Table 1), Ag^{2+} in this type of compound shows the expected and favored elongated octahedral coordination for d^9-configurated cations. This, as mentioned at the outset, is certainly not the rule but rather an exception in the case of divalent silver. According to the crystal data ($a=906.1$, $b=560.7$, $c=520.7$ pm, $\alpha=118.7$, $\beta=91.61$, $\gamma=102.3°$) (four-circle diffractomer measurement) $Ag[NbF_6]_2$ is isotypic.

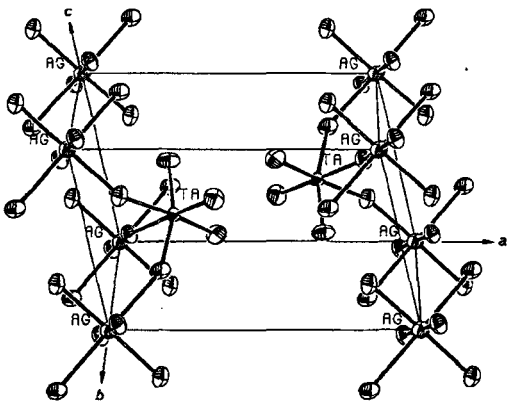

Fig. 1. Crystal structure of $Ag[TaF_6]_2$.

$Ag[TaF_6]_2$ is paramagnetic, the Curie or Curie-Weiss law is obeyed down to ca. 13 K ($\mu_{eff}(251\,K)=1.95$ B.M.; $\mu_{eff}(13\,K)=1.90$ B.M., $\theta_{calc}=3.1$ (±1.1) K). This finding is understandable, because the AgF_6 octahedra are isolated from each other and consequently a magnetic interaction via F^- bridges is not possible.

Experimental

About 200–300 mg of an equimolar amount of Ag_2O (Merck p.a.) and M_2O_5 (pure, Merck) was transferred to an open Monel cylinder and inserted into a stainless-steel autoclave furnished with a Monel inlet. The autoclave (total volume: ca. 6 mL) was then cooled (with $(N_2)_{liq}$) to −196°C and filled with ca. 4.5 mL $(F_2)_{liq}$ (the fluorine was taken from a steel bomb (Kali Chemie), passed over NaF to remove HF, condensed into a calibrated cold finger (Duran glass), and finally distilled into the autoclave). The (still) cold autoclave was placed in a furnace preheated to ca. 300°C; the furnace was then brought to 380–400°C ($p_{F_2}=3.4$ kbar) and kept at this temperature for 5–6 weeks (formation of single crystals). After slow cooling to room temperature the F_2/O_2 mixture still remaining was removed by distillation at −196°C and the autoclave (again at room temperature and still under residual fluorine) finally opened. The samples were transferred into carefully baked out glass vessels under dry argon and worked up or stored at −20°C in a refrigerator.

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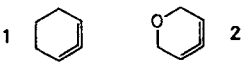
[2] B. G. Müller, *J. Fluorine Chem.* 17 (1981) 317/329.
[3] B. G. Müller, *Z. Anorg. Allg. Chem.*, in press.
[4] B. G. Müller, *J. Fluorine Chem.* 29 (1985) 22.
[5] B. Standke, M. Jansen, *Angew. Chem.* 97 (1985) 114; *Angew. Chem. Int. Ed. Engl.* 24 (1985) 118.
[6] $P\bar{1}$; $a=904.4(4)$, $b=559.6(2)$, $c=519.8(2)$ pm; $\alpha=118.76(2)$, $\beta=91.53(3)$, $\gamma=102.42(3)°$. Siemens AED2 four-circle diffractometer; $Mo_{K\alpha}$; 1260 independent reflections; $R=0.073$, $R_w=0.038$. Further details of the crystal structure investigation are available from the Fachinformationszentrum Energie, Physik, Chemie GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-52382, the name of the author, and the journal citation.
[7] R. Hoppe, *Angew. Chem.* 92 (1980) 106; *Angew. Chem. Int. Ed. Engl.* 19 (1980) 110.

Generation and Interception of 1-Oxa-3,4-cyclohexadiene**

By *Michael Schreck* and *Manfred Christl**

The short-lived 1,2-cyclohexadiene **1**, the most highly strained of the previously known monocyclic allenes, is regarded as well characterized.[1] Very little is known, however, about hetero derivatives of this reactive intermediate; we therefore searched for an access to the title compound **2**. Allene **1** is best generated by treatment of 6,6-dibromobicyclo[3.1.0]hexane with methyllithium.[2] Hence, 6,6-dichloro- **3a**[3] and 6,6-dibromo-3-oxabicyclo[3.1.0]hexane **3b**[3a, 4] are potential precursors for **2**. The reactions of **3a**[5] and **3b**[4] with *n*-butyllithium have already been investigated, but products derived from **2** were neither sought for nor found.[6] Utilizing well-established reaction partners[7] of **1** as solvents, we have now repeated such experiments at −40 to −20°C and obtained trapping products of **2**.



The results of the reactions with activated acyclic alkenes and the yields obtained are shown in Scheme 1. Styrene yielded a 10 : 1 mixture of the *exo*- and *endo*-8-phenyl-

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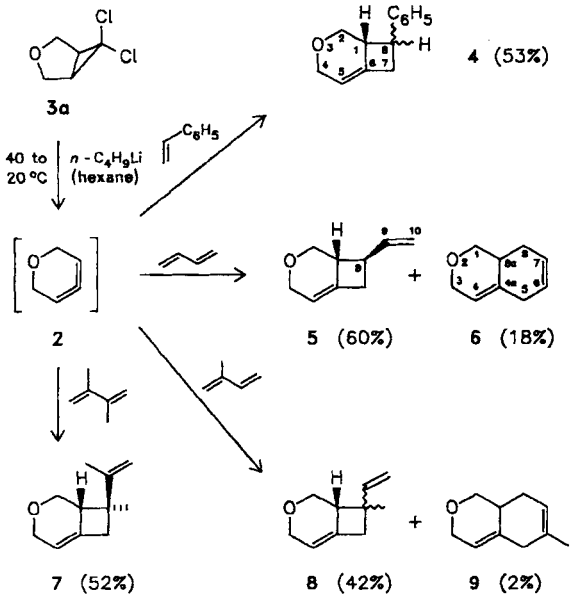
3-oxabicyclo[4.2.0]oct-5-enes **4**. 1,3-Butadiene gave rise to the [2+2]-cycloadduct **5** and the [4+2]-cycloadduct **6**. Isoprene afforded a 10:1 mixture of the diastereomeric [2+2]-cycloadducts **8** and a small amount of the [4+2]-cycloadduct **9**, while 2,3-dimethyl-1,3-butadiene furnished only the [2+2]-cycloadduct **7** (for selected physical data see Table 1).



Scheme 1. [8]

Table 1. Selected physical data of **4**–**6**, **11**, **12**, and **14**; IR (CCl_4; cm^{-1}), NMR ($CDCl_3$; δ values, coupling constants in Hz).

exo-**4**: ^{1}H-NMR: 3.02 and 3.08 (each br. dd, $J_{7,7}=13.0$, $J_{7,8}=7.8$; 7-H_2), 3.17 (q, $J_{1,8}=7.8$; 8-H), 3.19 (t, $J_{1,2endo}=J_{2,2}=9.5$; 2-H_{endo}), 3.24 (m; 1-H), 4.13 and 4.26 (each br. d, $J_{4,4}=16.2$; 4-H_2), 4.17 (dd, $J_{1,2exo}=5.5$; 2-H_{exo}), 5.38 (m; 5-H), 7.14–7.32 (m; C_6H_5).—^{13}C-NMR: 40.05 (t, C-7), 43.46 (d, C-8), 48.56 (d, C-1), 65.37 (t, C-4), 67.97 (t, C-2), 112.44 (d, C-5), 126.27 (d, *p*-C), 126.39 (d, *o*-C), 128.39 (d; *m*-C), 135.49 (s, C-6), 143.46 (s, *ipso*-C)

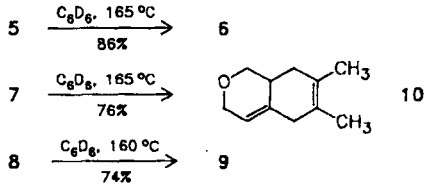
5: ^{1}H-NMR: 2.61 (≈br. quint, $J_{1,8}=J_{7endo,8}=J_{7exo,8}=7.8$, $J_{8,9}=6.5$; 8-H), 2.75 and 2.84 (each br. dd, $J_{7,7}=12.5$; 7-H_2), 2.99 (m; 1-H), 3.09 (t, $J_{1,2endo}=J_{2,2}=9.6$; 2-H_{endo}), 4.08 (dd, $J_{1,2exo}=6.4$; 2-H_{exo}), 4.10 and 4.23 (each br. d, $J_{4,4}=16.2$; 4-H_2), 4.98 (br. d, $J_{9,10trans}=10.3$; 10-H_{trans}), 5.02 (br. d, $J_{9,10cis}=16.7$; 10-H_{cis}), 5.32 (br. s; 5-H), 5.95 (ddd; 9-H).—^{13}C-NMR: 38.67 (t, C-7), 42.07 (d; C-8), 47.16 (d, C-1), 65.36 (t, C-4), 67.58 (t, C-2), 112.04 (d, C-5), 113.74 (t, C-10), 136.00 (s, C-6), 140.59 (d, C-9)

6: ^{1}H-NMR: 2.05 (ddm, $J_{8,8}=17.0$, $J_{8,8a}=11.0$) and 2.14 (br. dt, $J_{7,8}=J_{8,8a}=5.2$) (8-H_2), 2.36 (m; 8a-H), 2.63 (dt, $J_{5,5}=19.4$, $J=2.9$) and 2.88 (dm) (5-H_2), 3.49 and 3.91 (each dd, $J_{1,1}=11.4$, $J_{1,8a}=4.9$; 1-H_2), 4.08 and 4.12 (each dq, $J_{3,3}=15.6$, $J\approx2.8$; 3-H_2), 5.53 (quint, $J=2.5$; 4-H), 5.64 and 5.69 (each dm, $J_{6,7}\approx10.0$; 6-H, 7-H).—^{13}C-NMR: 30.21 (t, C-8), 33.03 (t, C-5), 33.63 (d, C-8a), 65.97 (t, C-3), 69.70 (t, C-1), 118.50 (d, C-4), 125.95 (double intensity, d, C-6, C-7), 135.09 (s, C-4a)

11: IR: 3620, 3480 (broad), 3400 (broad) (OH).—^{1}H-NMR: 0.92 (t, $J_{3',4'}=7.2$; 4'-H_3), 1.33 (m; 3'-H_2), 1.45 (m; 2'-H_2), 1.89 (br. s; OH), 2.21 (br. t, $J_{1',2'}=7.6$; 1'-H_2), 4.29 (d, $J_{1,2}=7.0$; 1-H_2), 5.17 (dt, $J_{2,5trans}=J_{5,5}=1.4$, $J_{4,5trans}=11.0$; 5-H_{trans}), 5.30 (br. d, $J_{4,5cis}=17.5$; 5-H_{cis}), 5.56 (br. t; 2-H), 6.61 (ddd, $J_{2,4}=0.7$; 4-H).—^{13}C-NMR: 13.85 (q, C-4'), 22.56 (t, C-3'), 30.77 (t, C-2'), 32.90 (t, C-1'), 58.47 (t, C-1), 115.16 (t, C-5), 127.74 (d, C-2), 132.27 (d, C-4), 139.69 (s, C-3)

12: B.p. 60–80 °C (bath)/0.2 torr.—^{1}H-NMR: 2.34 (t, $J_{1,1}=J_{1endo,8a}=10.0$; 1-$H_{endo}$), 2.64 (≈dtq, $J_{1exo,8a}=4.8$, $J_{8,8a}=4.3$, $J_{4,8a}=3.1$; 8a-H), 3.94 (dt, $J_{3,3}=16.5$, $J_{3,4}=J_{3,8a}=3.1$) and 4.28 (dt, $J_{3,4}=J_{3,8a}=2.1$) (3-H_2), 4.18 (dd; 1-H_{exo}), 5.06 (dm; 8-H), 5.18 (m; 5-H), 5.62 (m; 4-H), 6.02 and 6.38 (each dd, $J_{6,7}=5.7$, $J_{5,6}=J_{7,8}=1.7$; 6-H, 7-H).—^{13}C-NMR: 39.43 (d, C-8a), 64.60 (t, C-3), 67.57 (t, C-1), 79.50 and 79.70 (each d, C-5, C-8), 115.77 (d, C-4), 128.82 (d, C-7), 136.01 (d, C-6), 137.16 (s, C-4a)

14: IR: 3600, 3400 (broad) (OH).—^{1}H-NMR: 3.49 (br. s; OH), 4.26 (dd, $J_{1,2}=6.5$, $J_{1,3}=1.6$; 1-H_2), 5.76 (dtd, $J_{2,3}=11.2$, $J_{2,4}=1.1$; 2-H), 6.23 (tt, $J_{3,4}=11.3$; 3-H), 6.71 (dd; 4-H).—^{13}C-NMR: 58.96 (t, C-1), 123.90, 124.14, and 132.97 (each d, C-2, C-3, C-4), 124.89 (s, C-5)

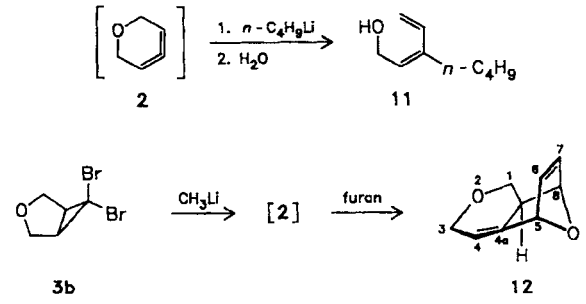


Scheme 2. [8]

As shown in Scheme 2, the 8-vinyl-3-oxabicyclo[4.2.0]-oct-5-enes **5**, **7**, and **8** could be converted into the 3,5,8,8a-tetrahydro-1*H*-2-benzopyrans **6**, **10**, and **9**, respectively, in good yields by heating at 160–165 °C. With regard to the mechanisms of all these processes, the same concepts may be applied which have been outlined for the formation of the corresponding adducts of **1**[7,9] and their rearrangement.[7c]

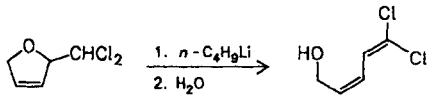
The reaction of *n*-butyllithium with **3a** in furan, which counts among the less reactive trapping agents for **1**,[7b] did not produce an adduct of the heteroarene but gave the butylpentadienol **11**[8] in 49% yield[6] (Scheme 3). We also obtained **11** when using petroleum ether as solvent. *n*-Butyllithium probably attacks the central C-atom of the allene moiety of **2** and initiates ring-opening in an S_N2' reaction, in which the oxygen atom, possibly complexed by a lithium ion, serves as leaving group. Since furan is obviously not reactive enough to compete with *n*-butyllithium for **2** we generated **2** from **3b**[3] in furan by the less nucleophilic methyllithium and isolated the [4+2]-cycloadduct **12**[8] in 21% yield (Scheme 3).

Because of the smaller covalent radius of the oxygen atom, the oxa derivative **2** should have a more bent allene moiety in comparison to 1,2-cyclohexadiene **1** and, as a consequence, should exhibit a higher strain energy. Despite this, **2** can be generated in an analogous way as **1**, and cycloaddition products with activated alkenes are formed in similar yields as in the case of **1**. A specific feature of **2** is the addition of the nucleophile *n*-butyllithium to give **11**.



Scheme 3.

The majority of the above reactions of **3a** were not carried out with the pure substance but in the presence of the insertion product **13** of dichlorocarbene and 2,5-dihydrofuran which is also formed in the synthesis of **3a**.[3] *n*-Bu-



13 14

tyllithium converts **13** by ring-opening β-elimination into (*Z*)-5,5-dichlorpenta-2,4-dienol **14**,[10] which could, however, be readily separated from the cycloadducts.

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[1] R. P. Johnson in J. F. Liebman, A. Greenberg (Eds.): *Molecular Structure and Energetics, Vol. 3*. p. 85, VCH Publishers, Deerfield Beach, FL, USA 1986.
[2] W. R. Moore, W. R. Moser, *J. Am. Chem. Soc. 92* (1970) 5469.
[3] a) J. C. Anderson, D. G. Lindsay, C. B. Reese, *J. Chem. Soc. 1964*, 4874; b) E. V. Dehmlow, K. Franke, *Liebigs Ann. Chem. 1979*, 1456.
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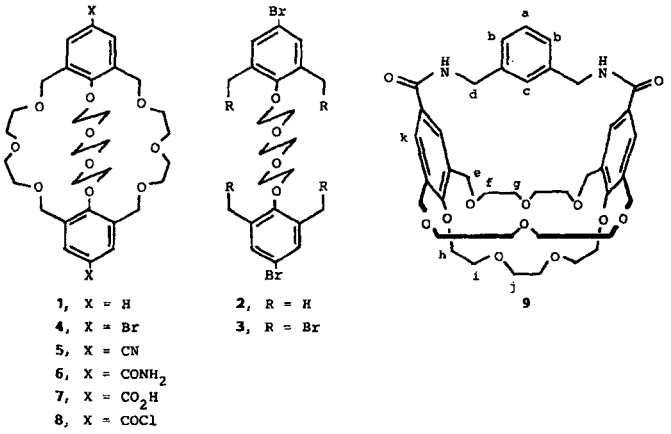
[6] In ref. [5], "butyl-containing products" are mentioned without any further information. Presumably the product in question was **11**.
[7] a) Styrene: W. R. Moore, W. R. Moser, *J. Org. Chem. 35* (1970) 908; b) 2,3-dimethyl-1,3-butadiene: A. T. Bottini, L. L. Hilton, J. Plott, *Tetrahedron 31* (1975) 1997; c) 1,3-butadiene and isoprene: M. Christl, M. Schreck, *Angew. Chem. 99* (1987) 474; *Angew. Chem. Int. Ed. Engl. 26* (1987) 449.
[8] The products of Schemes 1 and 2 and the compounds **11** and **14** were isolated by preparative gas chromatography (1.5m-column, 20% EGA on Chromosorb, 110–150°C), the diastereomeric pairs **4** and **8** as mixtures. Compound **12** was purified by distillation. All the compounds gave correct elemental analyses (except **12**) and were characterized by ^{1}H-NMR, ^{13}C-NMR and mass spectra.
[9] a) S. Harnos, S. Tivakornpannarai, E. E. Waali, *Tetrahedron Lett. 27* (1986) 3701; b) M. Christl, M. Schreck, *Chem. Ber. 120* (1987) 915.
[10] A compound of the structure **14** is described, but the data do not allow any conclusions to be drawn about the configuration: M. Julia, J. Bouchaudon, *C. R. Acad. Sci. 253* (1961) 1111.

Second Sphere Coordination of Tetraammineplatinum(II) by a Macropolycyclic Crown Ether Bisamide Receptor**

By *David R. Alston, Alexandra M. Z. Slawin, J. Fraser Stoddart,* David J. Williams*, and *Ryszard Zarzycki*

In our quest to find a molecular receptor more highly designed than [18]crown-6 (18C6)[1] for the antitumour drug cisplatin, [*cis*-$Pt(NH_3)_2Cl_2$], we decided to modify chemically those macrobicyclic polyethers with the demonstrated ability[2] to form adducts with cationic *cis*-diamminerhodium complexes. Since preliminary experiments indicated that **1** does not form adducts in a variety of organic solvents with cisplatin, it was decided, in view of our observation[1] of the inter-adduct hydrogen bonding interactions (a) between ammine and chlorine ligands and (b) between ammine ligands and solvating dimethylacetamide (dma) molecules in [{*cis*-$[Pt(NH_3)_2Cl_2]\cdot dma\}_2$-18C6], to incorporate between the two trisubstituted benzene rings a fourth chain containing two amide linkages as potential hydrogen bonding donors to the chlorine ligands. Here, we describe the preparation[3] in eight steps (→**2**→**3**→**4**→**5**→**6**→**7**→**8**→**9**) of the macropolycyclic bisamide **9** starting from 4-bromo-2,6-dimethylphenol and the X-ray crystal structures[4] of both the free receptor and its 2:1 adduct with $[Pt(NH_3)_4][PF_6]_2$.



1, X = H
4, X = Br
5, X = CN
6, X = $CONH_2$
7, X = CO_2H
8, X = COCl

2, R = H
3, R = Br

The structure (Fig. 1, top) of **9**, when viewed from **A**[5] shows (Fig. 1, bottom) the existence of a shallow elongated cavity bounded at the bottom by the bisamide bridge, at the top by the three adjacently-located polyether chains and, on either side, by the two slightly inclined (33° between their mean planes) tetrasubstituted benzene rings (centroid-centroid distance, 4.9 Å). Of particular note is the directing of the two amide N–H bonds towards mouth **A** of the receptor cleft.

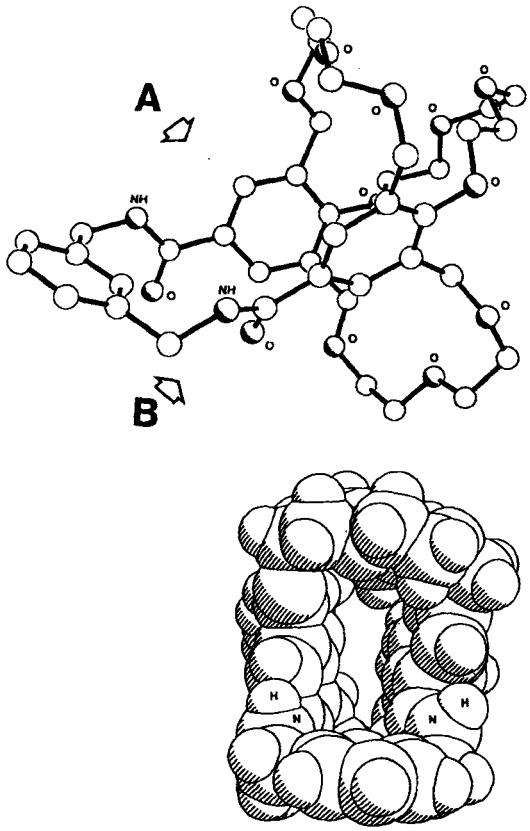


Fig. 1. Top: Structure of **9** in the crystal with the **A** and **B** mouths indicated. Bottom: Space-filling representation of the structure of **9** viewed from the **A** mouth.

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