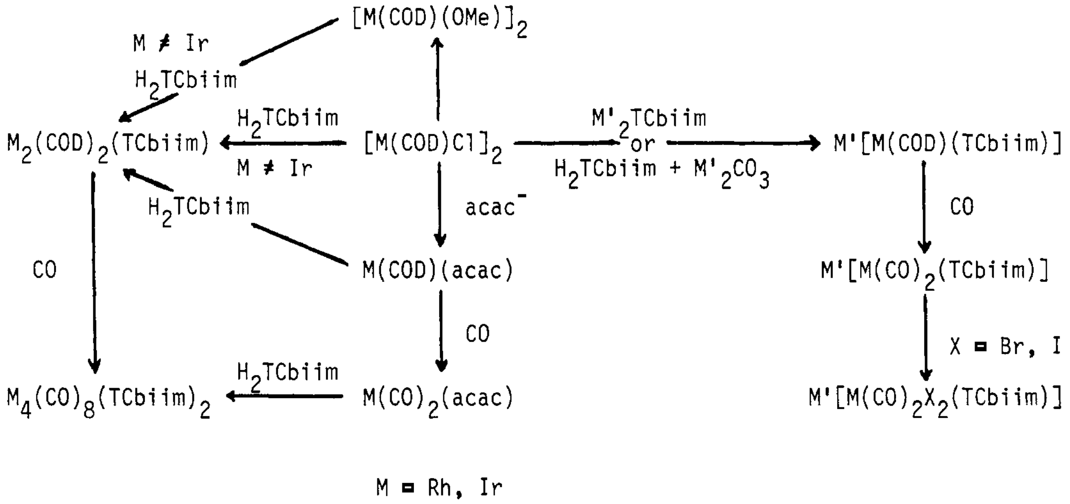
Scheme I



calculations[10] on the $Tcbiim^{2-}$ give charge distributions in accord with the expectation of strong electron withdrawal by the nitriles through the π system. Cyclic voltammetry on bis(tetraethylammonium)Tcbiim in acetonitrile shows two reversible one-electron oxidation waves at 0.94 and 1.32 V vs. NHE, confirming the stability of the π-electron system of the anion.

As expected from its acidity, complexes of $H_2Tcbiim$ are invariably in the dianionic form. Starting from aqueous $K_2M(CN)_4$, M = Ni, Pd, Pt, treatment with $H_2Tcbiim$ gives white $K_2[M(CN)_2(Tcbiim)]$ although in the case of platinum the yield is low.[11] Susceptibility measurements on the nickel compound confirmed its diamagnetism, indicative of square-planar geometry.

The structure of these complexes is also apparent from the infrared spectra, which show absorptions typical of cis ionic cyanides with splittings of 5–20 cm^{-1} ($\sim$2140 cm^{-1}) and barely resolvable splitting of $\leq$7 cm^{-1} due to the inequivalent Tcbiim nitriles ($\sim$2225 cm^{-1}).

Preliminary analysis of these results suggested that $Tcbiim^{2-}$ is a ligand of very low σ-donor strength and a strong π acceptor. These tendencies have been verified by the preparation of a series of complexes of Rh(I) and Ir(I). One useful starting material for synthesis of these complexes is M(COD)(AcAc)[12] (COD = 1,5 cyclooctadiene, AcAc = acetylacetone anion, M = Rh, Ir). Treatment of this material with 0.5 equiv of $H_2Tcbiim$ affords dimers, similar to those formed by H_2biim but with greater tendency to solvate.

The COD is readily displaced in these compounds by CO, yielding tetramers of formula $M_4(CO)_8(Tcbiim)_2$, which again appear to mimic the complicated structures found for the H_2biim.[1-3] The reactions and interconversions that we have observed are summarized in Scheme I. The series of composition $M'[Ir(CO)_2(Tcbiim)]$, $M' = K^+, Na^+, Li^+, N(Et)_4^+$, are all yellow in dilute solution but show a variety of colors in the solid state, ranging from red with $N(Et_4)^+$ to dark blue with Li^+. These color changes suggested intermolecular interactions of the sort necessary for developing highly anisotropic properties. Accordingly we have attempted a number of oxidation experiments on these salts. Cyclic voltammetry in acetonitrile on $N(Et)_4[Ir(CO)_2(Tcbiim)]$ gives a reversible two-electron oxidation wave at 0.84 V. Bulk electrochemical oxidation of this salt yields a solid whose structure is still under investigation but that does not resemble the highly conducting anistropic materials. Oxidation by bromine or iodine yields several isomers of the expected oxidative addition products. These products do not react with the univalent iridium precursors to produce intermediate valence states.

The IR bands due to CO are typically shifted 5–25 cm^{-1} higher in $H_2Tcbiim$ compounds compared to those of H_2biim compounds. Clearly, $H_2Tcbiim$ is a ligand of strong π-accepting properties. Its synthetic versatility will allow the formation of a wide variety of compounds especially in combination with metals in low oxidation states. Although $H_2Tcbiim$ has not thus far led us to highly conducting species, structural and synthetic studies are continuing.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

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[10] Calculations were carried out by using the ICON 8 program with weighted H_{ij} formula. Ammeter, J. H.; Bürgi, H. B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

[11] We used initially the prolonged reflux method of Kiernan and Ludi (Kiernan, P.; Ludi, A. *J. Chem. Soc., Dalton Trans.* **1978**, 1127). An improved but somewhat more elaborate procedure will be published elsewhere.

[12] Robinson, S. D.; Shaw, B. L. *J. Chem. Soc.* **1965**, 4997.

Facile Preparation of 2,3-Benzo-1,4-diphenyl-7-silanorbornadiene Derivatives and the First Clear Evidence of Silylene to Disilene Thermal Rearrangement[1]

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Received June 7, 1982

This paper describes the synthesis of the so far elusive[2,3] 2,3-benzo-1,4-diphenyl-7-silanorbornadiene derivatives (**1**), which undergo thermal extrusion of variously substituted silylenes. The first definitive evidence for the silylene–disilene rearrangement is also reported.

To a dichloromethane (40 mL) solution of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (**3a**, 525 mg, 2.0 mmol; eq 1) and 1-aminobenzotriazole (**4**) (402 mg, 3.0 mmol) was added a dichloromethane (15 mL) solution of lead tetraacetate (90%, 1.48 g, 3.0 mmol) dropwise during 10 min at 0 °C. The mixture was subjected to flash chromatography through a short column (3 cm × 5 cm) packed with silica gel. Benzene was used as an eluent. Removal of the solvent gave a yellow viscous oil, from which 257 mg (38%) of colorless crystalline 2,3-benzo-7,7-dimethyl-1,4-diphenyl-7-silanorbornadiene (**1a**, mp 108–109 °C) was obtained by addition of hexane followed by standing overnight in a re-

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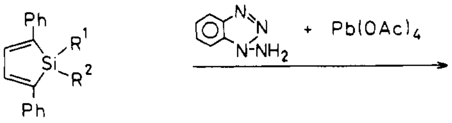
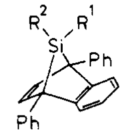
[1] Chemistry of Organosilicon Compounds, 164.

[2] Gilman, H.; Cottis, S. G.; Atwell, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 1596. These authors have prepared stable 2,3-benzo-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silanorbornadiene (**2**).

[3] **1** was presumed as a useful silylene generator but was recorded as thermally extremely unstable. See inter alia: (a) Maruca, R. *J. Org. Chem.* **1971**, *36*, 1626. (b) Barton, T. J.; Nelson, A. J.; Clardy, J. *Ibid.* **1972**, *37*, 895. (c) Maruca, R.; Fischer, R.; Roseman, L.; Gehring, A. *J. Organomet. Chem.* **1973**, *49*, 139. (d) Mayer, B.; Neumann, W. P. *Tetrahedron Lett.* **1980**, *21*, 4887. (e) Barton, T. J.; Goure, W. F.; Witiak, J. L.; Wulff, W. D. *J. Organomet. Chem.* **1982**, *225*, 87.



3a, $R^1 = R^2 = Me$
b, $R^1 = Me$; $R^2 = SiMe_3$
c, $R^1 = Me$; $R^2 = SiMe_2Ph$
d, $R^1 = Me$; $R^2 = Si_2Me_5$
e, $R^1 = R^2 = SiMe_3$

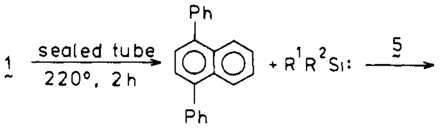


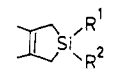
(1)

1a, $R^1 = R^2 = Me$; mp 108-109 °C (38%)
b, $R^1 = Me$, $R^2 = SiMe_3$; mp 113-115 °C (63%)
c, $R^1 = Me$, $R^2 = SiMe_2Ph$; mp 138-139 °C (30%)
d, $R^1 = Me$, $R^2 = Si_2Me_5$; mp 115-116 °C (79%)
e, $R^1 = R^2 = SiMe_3$; mp 153-154 °C (39%)

frigerator. Since **1a** is unstable on silica gel, it is essential to minimize the contact time with chromatographic materials. The use of excess **4** and lead tetraacetate (1.5-2 equiv added to **3**) is also important. Several silicon-substituted 7-silanorbornadiene derivatives were prepared by the same method.[4]

These new compounds are fairly thermally stable. For example, no reaction occurred in the thermolysis of **1a** in the presence of 2,3-dimethylbutadiene (**5**) at 180 °C for 7.5 h. However, **1a** decomposed completely at 220 °C to give 1,2,4,4-tetramethyl-4-silacyclopentene (**6a**, 40%)[5] and 1,4-diphenylnaphthalene[6] (eq 2).





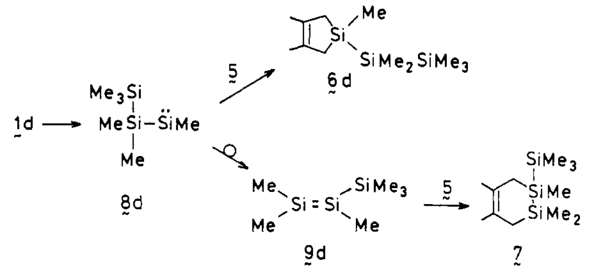
(2)

6a, $R^1 = R^2 = Me$ (40%)
b, $R^1 = Me$; $R^2 = SiMe_3$ (40%)[7]
c, $R^1 = Me$; $R^2 = SiMe_2Ph$ (44%)[8]
e, $R^1 = R^2 = SiMe_3$ (50%)[7]

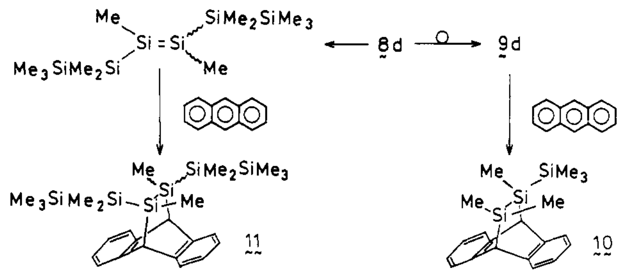
Other 7-silanorbornadienes, **1b,c,e**, undergo similar reactions to afford the corresponding silacyclopentenes. Therefore, these are convenient reagents for silylene generation.

A remarkable product 1,2,4,5,5-pentamethyl-4-(trimethylsilyl)-4,5-disilacyclohexene (**7** Scheme I)[9,10] was obtained from cothermolysis of **1d** and **5** in addition to the expected 1,2,4-trimethyl-4-(pentamethyldisilanyl)-4-silacyclopentene (**6d**).[11]

Scheme I



Scheme II



The most economical mechanistic rationalization for the formation of **7** is 1,2-trimethylsilyl migration of the silylene **8d** (Scheme I) to form a disilene **9d**, which undergoes the Diels-Alder reaction with **5**. Yields of **6d** and **7** depend upon the relative amount of **1d** to **5**. At a higher ratio of **5**/**1d** (10/1), **6d** (27%) was formed in a yield comparable with **7** (24%), but at a lower ratio of **5**/**1d** (1.2/1.0), the yield of **6d** (7%) was far lower than that of **7** (20%). This fact indicates that **6d** and **7** form competitively with each other and that the silylene to disilene rearrangement is a rapid process. The silylene-silene isomerization has been reported recently in both photochemical[12] and thermal[13] reactions, but the present finding represents the first clear example of a silylene to disilene rearrangement.[14]

Both trimethylsilyl and methyl shifts from **8d** can give the disilene **9d**, but the fact that no rearrangement product was obtained in the reaction of **1b** and **1e** excludes the methyl-shift mechanism. Phenyl shift also did not occur in the reaction of $PhMe_2SiMeSi$: (**8c**) generated from **1c**.

In a previous paper, we have reported efficient dimerization of silylene to disilene, the latter being trapped by anthracene.[7] However, cothermolysis of **1d** (46 mg, 0.10 mmol) and anthracene (21 mg, 0.12 mmol)[15,16] dissolved in 0.4 mL of benzene in a sealed tube at 220 °C for 2 h gave 2,3,5,6-dibenzo-7,7,8-trimethyl-8-(trimethylsilyl)-7,8-disilabicyclo[2.2.2]octa-2,5-diene (**10**, 45%)[17] as a main product. Only a trace amount of the anthracene adduct (**11**) of the disilene, formed by dimerization of the silylene **8d**, was detected by mass spectroscopy.

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[4] Among two possible isomers in the reaction of **3b,c,d**, only single isomers were obtained. Structures of **1b,c,d** have been assigned as indicated by judging from NMR data and steric requirements. Satisfactory ^1H, ^{13}C, and ^{29}Si NMR and mass spectral and C,H analyses were obtained. It is worthwhile mentioning that ^{29}Si chemical shifts of 7-Si appear at a much lower field. ^{29}Si chemical shifts relative to Me_4Si in $CDCl_3$ were as follows (ppm): **1a**, 76.9; **1b**, −19.3, 82.5; **1c**, −22.1, 80.2; **1d**, −47.6, −15.5, 85.7; **1e**, −18.7, −17.5, 97.7; **2**, 67.7.

[5] Atwell, W. H.; Weyenberg, D. R. *J. Am. Chem. Soc.* **1968**, *90*, 3438.

[6] Bavin, P. M. G. *J. Chem. Soc.* **1964**, 5484.

[7] Nakadaira, Y.; Kobayashi, T.; Otsuka, T.; Sakurai, H. *J. Am. Chem. Soc.* **1979**, *101*, 486.

[8] **6c** (an oil); ^1H NMR(C_6D_6) δ 0.21 (3 H, s, SiMe), 0.40 (6 H, s, $SiMe_2$), 1.46 (2 H, d, J = 16 Hz, SiCH), 1.67 (2 H, d, J = 16 Hz, SiCH), 1.73 (6 H, br s, CCH_3), 7.10–7.35 (5 H, m, ArH); MS, *m/e* M^+ 260 (78), 135 (100); high-resolution MS found 260.1423, calcd for $C_{15}H_{24}Si_2$ 260.1417.

[9] **7** (an oil): ^1H NMR (C_6D_6) δ 0.249 (3 H, s, SiMe), 0.253 (3 H, s, SiMe), 0.300 (3 H, s, $SiMe_3$), 0.327 (3 H, s, SiMe), 1.575 (2 H, br s, $SiCH_2$), 1.638 (1 H, d, J = 14 Hz, SiCH), 1.701 (1 H, d, J = 14 Hz, SiCH), 1.898 (6 H, br s, CCH_3); ^{13}C NMR(C_6D_6) δ −8.4 (q), −3.5 (q), −2.0 (q), −0.9 (q), 21.0 (t), 22.3 (q), 25.4 (t), 124.1 (s), 124.5 (s); ^{29}Si NMR(C_6D_6) δ −50.7, −16.1, −14.4; MS, *m/e* M^+ 256 (43), 183 (94), 174 (52), 73 (100); high-resolution MS, found 256.1499, calcd for $C_{12}H_{28}Si_3$ 256.1499.

[10] Mazerolles, P.; Joanny, M.; Tourrou, G. *J. Organomet. Chem.* **1973**, *60*, C3. These authors reported the formation of **7** by another reaction. We thank Dr. Mazerolles for sending GC–MS data of **7** to us.

[11] **6d** (an oil): ^1H NMR(C_6D_6) δ 0.180 (9 H, s, $SiMe_3$), 0.217 (6 H, s, $SiMe_2$), 0.271 (3 H, s, SiMe), 1.491 (2 H, d, J = 16 Hz, SiCH), 1.701 (2 H, d, J = 16 Hz, SiCH), 1.788 (6 H, br s, CCH_3); ^{13}C NMR(C_6D_6) δ −6.6 (q), −3.1 (q), −1.4 (q), 19.5 (q), 25.3 (t), 131.0 (s); ^{29}Si NMR (C_6D_6) δ −48.7, −15.9, −8.0; *m/e* M^+ 256 (42), 183 (83), 125 (34), 73 (100); high-resolution MS found 256.1501, calcd for $C_{12}H_{28}Si_3$ 256.1499.

[12] Drahnak, T. J.; Michl, J.; West, R. *J. Am. Chem. Soc.* **1981**, *103*, 1845.

[13] Barton, T. J.; Burns, G. T.; Goure, W. F.; Wulff, W. D. *J. A. Chem. Soc.* **1982**, *104*, 1149.

[14] Wulff, W. D.; Goure, W. F.; Barton, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 6236.

[15] Dimerization of silylene is far slower than the reaction with **5**.[16] Only a very small amount of a product corresponding to the adduct of **5** with $Me_3SiMe_2SiMeSi{=}SiMeSiMe_2SiMe_3$ (M_r 430) was detected by GC–MS.

[16] Kobayashi, T. Ph.D. Thesis, Tohoku University, 1978.

[17] **10** (an oil): ^1H NMR (CCl_4) δ −0.20 (3 H, s, SiMe), −0.12 (3 H, s, SiMe), −0.10 (9 H, s, $SiMe_3$), 0.03 (3 H, s, SiMe), 3.81 (1 H, s, CH), 4.01 (1 H, s, CH), 6.86–7.05 (8 H, m, Ar H); MS, *m/e* M^+ 352 (24), 178 (50), 174 (100), 73 (38); high-resolution MS found 352.1504, calcd for $C_{20}H_{28}Si_3$ 352.1499.

These results demonstrate clearly that the silylene–disilene rearrangement by the silyl shift is an efficient process and opens a new way to disilene.

Acknowledgment. We thank Toshiba Silicone Co., Ltd., for a gift of chlorosilanes. The work was supported by a grant-in-aid (Scientific Research No. 543007) from the Ministry of Education, Science, and Culture.

Synthesis and Structure of the $\{[(C_7H_8)Rh]_5(cis\text{-}Nb_2W_4O_{19})_2\}^{3-}$ Anion

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Received August 2, 1982

The metal tricarbonyl and rhodium pentamethylcyclopentadienyl complexes $[(OC)_3Mn(Nb_2W_4O_{19})]^{3-}$,[1] $[(C_5H_5)Ti(Mo_5O_{18})Mn(CO)_3]^{2-}$,[2] $[(OC)_3Re(Nb_2W_4O_{19})]^{3-}$,[1] and $\{[(CH_3)_5C_5]Rh(Nb_2W_4O_{19})\}^{2-}$ [3] all contain polyoxohexametallate ions bound to organometallic units with a triangle of three contiguous bridging oxygen atoms. In order to extend this family of 18-electron organometallic complexes to more reactive species, we had hoped to prepare the norbornadiene Rh^I complex $[(C_7H_8)Rh(Nb_2W_4O_{19})]^{3-}$. Much to our surprise, however, we have been unable to isolate this complex from the reaction of $[(C_7H_8)Rh(NCCH_3)_2][PF_6]$[4] with equimolar $(cis\text{-}Nb_2W_4O_{19})[(n\text{-}C_4H_9)_4N]_4$.[1] We have isolated instead the $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$ anion, a structurally unique complex in which each of two $cis\text{-}Nb_2W_4O_{19}{}^{4-}$ ions, by utilizing both terminal and bridging oxygens, behaves as a pentadentate, bridging ligand.

Addition of 2.5 equiv of $[(C_7H_8)Rh(NCCH_3)_2](PF_6)$ to 4.0 g of $(cis\text{-}Nb_2W_4O_{19})[n\text{-}C_4H_9)_4N]_4$ in CH_3CN followed by addition of $(C_2H_5)_2O$, filtration of the resulting precipitate, washing with CH_2Cl_2 and $(C_2H_5)_2O$, and drying in vacuo yields 3.6 g of a yellow-orange powder. This powder is crystallized to pure $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}[(n\text{-}C_4H_9)_4N]_3$,[5] **1**, by cooling a saturated, boiling CH_3CN solution to room temperature. Single crystals marginally suitable for X-ray diffraction studies were obtained only after repeated recrystallization attempts from CH_3CN.

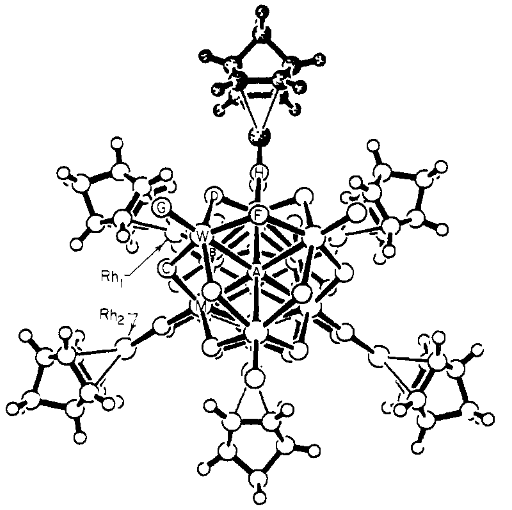

Figure 1. SCHAKAL[7] drawing of the crystallographically disordered $\{[(C_7H_8)Rh]_5(cis\text{-}Nb_2W_4O_{19})_2\}^{3-}$ anion, viewed approximately along a crystallographic C_3 axis. Atoms in the norbornadiene (C_7H_8) units are not labeled. In the remainder of the C_{3h} structure, one member from each set of symmetry-equivalent metal atoms (M, W, Rh$_1$, Rh$_2$) and oxygen atoms (A–D, F–H) are labeled. All non-hydrogen atoms were located X-ray crystallographically; hydrogen atom positions were generated by using idealized sp^2 and sp^3 hybridization and a C–H bond length of 0.96 Å. An ordered structure is obtained by removing a Rh$_2$ norbornadiene unit, one of which is shaded.

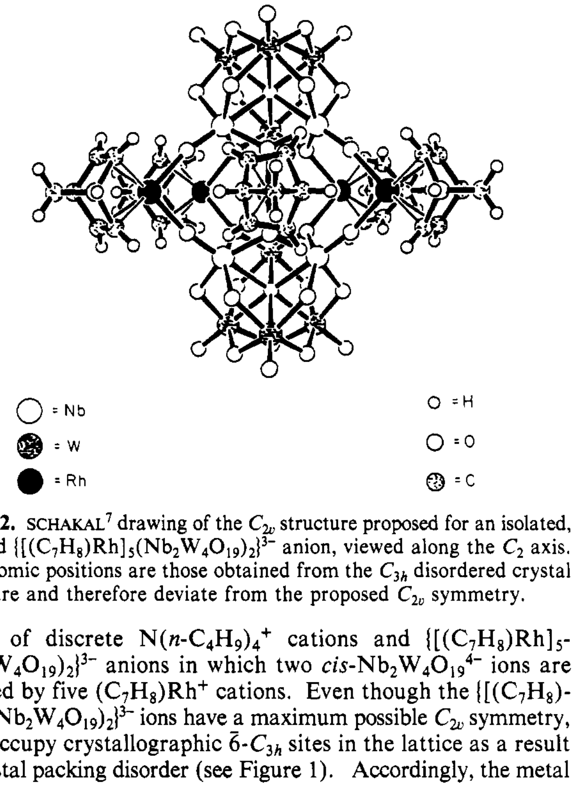

Figure 2. SCHAKAL[7] drawing of the C_{2v} structure proposed for an isolated, ordered $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$ anion, viewed along the C_2 axis. The atomic positions are those obtained from the C_{3h} disordered crystal structure and therefore deviate from the proposed C_{2v} symmetry.

X-ray structural analysis[6] revealed that crystals of **1** are composed of discrete $N(n\text{-}C_4H_9)_4{}^+$ cations and $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$ anions in which two $cis\text{-}Nb_2W_4O_{19}{}^{4-}$ ions are bridged by five $(C_7H_8)Rh^+$ cations. Even though the $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}^{3-}$ ions have a maximum possible C_{2v} symmetry, they occupy crystallographic $\bar{6}\text{-}C_{3h}$ sites in the lattice as a result of crystal packing disorder (see Figure 1). Accordingly, the metal

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(1) Besecker, C. J.; Klemperer, W. G. *J. Am. Chem. Soc.* **1980**, *102*, 7598.

(2) Day, V. W.; Fredrick, M. F.; Thompson, M. R.; Klemperer, W. G.; Liu, R.-S.; Shum, W. *J. Am. Chem. Soc.* **1981**, *103*, 3597.

(3) Day, V. W.; Thompson, M. R.; Besecker, C. J.; Klemperer, W. G., to be submitted for publication.

(4) Green, M.; Kuc, T. A.; Taylor, S. H. *J. Chem. Soc. A* **1971**, 2334.

(5) Anal. Calcd for $C_{83}H_{148}N_3Nb_4O_{38}Rh_5W_8$: C, 24.00; H, 3.59; N, 1.01; Nb, 8.95, Rh, 12.39; W, 35.42. Found: C, 23.97; H, 3.68; N, 0.99; Nb, 8.97; Rh, 12.32; W, 35.53. $^{13}C\{^1H\}$ NMR (CD_3NO_2, Me_4Si = 0.0, 75.47 MHz, 298 K) δ 61.4, 61.0, 60.7 (d, $^3J_{C-Rh} \approx 6$ Hz, CH_2), 60.0 (s, NCH_2), 52.0–50.6 (CH and olefinic), 24.9 (s, NCH_2CH_2), 20.8 (s, CH_2CH_3), 14.1 (s, CH_3).

(6) Crystals of **1** are hexagonal, space group $P\bar{6}2C\text{-}D_{3h}{}^4$ (No. 190) with $a = 16.833$ (8) Å, $c = 27.610$ (13) Å, and $Z = 2$ ($d_{calcd} = 2.02$ g/cm^3; μ_a (Mo K$\bar{\alpha}$) = 8.10 mm^{-1}). Three-dimensional diffraction data (a total of 2600 independent reflections having $2\theta_{Mo\,K\bar{\alpha}} < 55°$) were collected on a computer-controlled Nicolet P$\bar{1}$ autodiffractometer using graphite-monochromated Mo K$\bar{\alpha}$ radiation and full 1° wide ω scans. The structural parameters have been refined to convergence [R (unweighted, based on F) = 0.063 for 932 independent absorption corrected reflections having $2\theta_{Mo\,K\bar{\alpha}} < 55°$ and $I > 3\sigma(I)$] in cycles of empirically weighted full-matrix least-squares refinement that employed anisotropic thermal parameters for W, Nb, and Rh atoms and isotropic thermal parameters for the remaining non-hydrogen atoms. See paragraph at end of paper regarding supplementary material.

(7) A FORTRAN program for the graphical representation of molecular models written by Dr. Egbert Keller. We are grateful to Dr. Keller for providing a copy of his program.

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