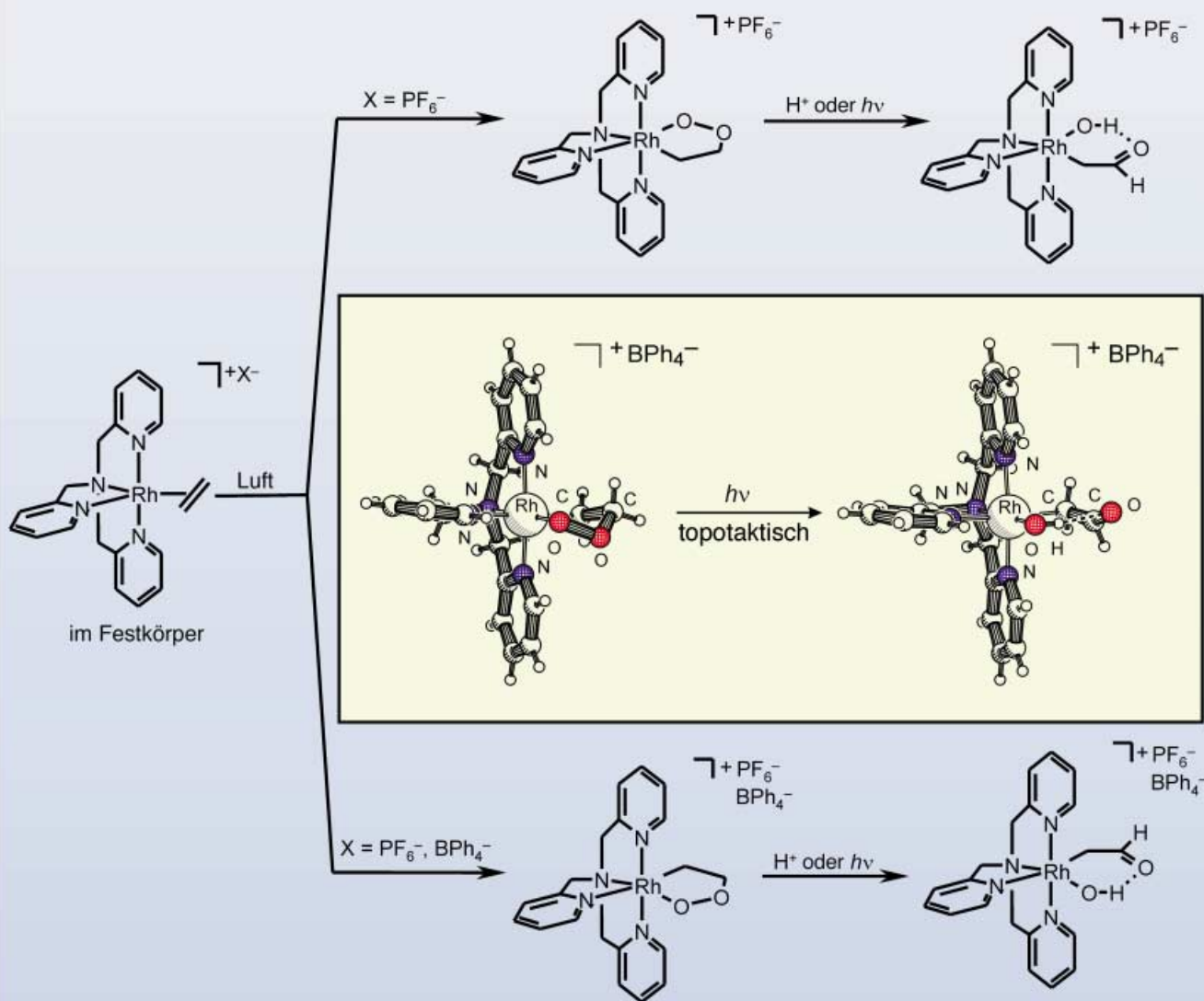


Aktivierung von Disauerstoff

Disauerstoff reagiert mit Ethenkomplexen zu 3-Rhoda-1,2-dioxolanen, woran sich eine Spaltung der O-O-Bindung anschließen kann.



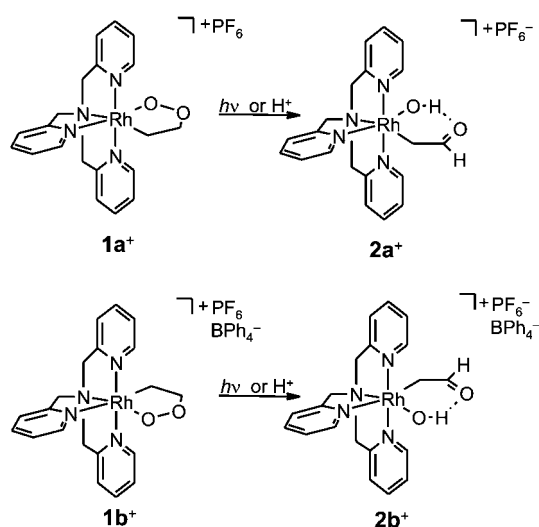
Unter Einwirkung von Licht erfolgt z. B. bei einem Einkristall eines solchen Rhodadioxolans eine topotaktische Umwandlung in einen Rhodium-Formylmethyl-Hydroxy-Komplex.

Auf den folgenden Seiten erfahren Sie mehr über diese Umlagerung, die im Widerspruch zu früheren Vorhersagen zu Umwandlungen von 3-Metalla-1,2-dioxolanen steht.

Rearrangement of 3-Rhoda-1,2-dioxolanes to Rhodium Formylmethyl Hydroxy Complexes**

Monique Krom, Ruud G. E. Coumans, Jan M. M. Smits, and Anton W. Gal*

3-Metalla-1,2-dioxolanes have been proposed as intermediates in catalytic oxidation of olefins by metals of Groups 6 and 8–10.^[1] We previously reported the formation of the stable 3-rhoda-1,2-dioxolanes **1a**⁺ and **1b**⁺ (Scheme 1) by reaction of solid rhodium ethene complexes of the N₄ ligand tris-(2-pyridylmethyl)amine (tpa) with air.^[2] We now report their rearrangement to rhodium formylmethyl hydroxy complexes upon exposure to light or protons.



Scheme 1. Rearrangement of 3-rhoda-1,2-dioxolanes to rhodium formylmethyl hydroxy complexes.

Exposure of microcrystalline **1b**-BPh₄ to glass-filtered daylight under N₂ resulted in selective conversion to the corresponding rhodium formylmethyl hydroxy complex **2b**-BPh₄ over several weeks (Scheme 1). Similarly, exposure of a solution of **1b**-BPh₄ in CD₃CN to the glass-filtered light from a high-pressure mercury lamp at –30 °C resulted in conversion to **2b**-BPh₄. The ¹H NMR spectrum of the resulting solution indicated that an optimum yield of 90 % **2b**-BPh₄ was obtained after 90 min of illumination.

The ESI-MS spectrum of **2b**⁺ is the same as that of **1b**⁺,^[2] with the exception of a peak at *m/z* = 435, which corresponds to loss of water from the parent cation. Such loss of water in

the gas phase was observed earlier for the transient formylmethyl hydroxy complex [(MeCN)(κ³-Bzbp)Rh(κ¹-CH₂CHO)(OH)]BPh₄, the only formylmethyl hydroxy complex reported thus far.^[3,4]

The ¹H NMR and ¹³C NMR spectra of **2b**-BPh₄ reveal the presence of a formylmethyl fragment [¹H NMR: δ = 2.69 (dd, ³*J*(H,H) = 5.1, ²*J*(H,Rh) = 2.9 Hz, RhCH₂CHO) and 9.26 (t, ³*J*(H,H) = 5.1 Hz, RhCH₂CHO); ¹³C NMR: δ = 26.9 (d, ¹*J*(C,Rh) = 21.0 Hz, RhCH₂CHO) and 209.0 (RhCH₂CHO)]. The ¹H NMR signals for the formylmethyl group of **2b**⁺ are comparable to those of [(MeCN)(κ³-Bzbp)Rh(κ¹-CH₂CHO)(OH)]BPh₄ [δ = 3.37 (dd, ³*J*(H,H) = 5.3, ²*J*(H,Rh) = 2.9 Hz, RhCH₂CHO) and 10.3 (t, ³*J*(H,H) = 5.3 Hz, RhCH₂CHO)].^[4] Formylmethyl hydroxy complex **2b**⁺ shows a strong IR absorption for a carbonyl group at 1655 cm^{–1}.

After repeated attempts to obtain X-ray quality crystals of **2b**-BPh₄ had failed, an attempt was made to photochemically convert a single crystal of **1b**-BPh₄ to a single crystal of **2b**-BPh₄. The crystal that was used for X-ray structure determination of **1b**-BPh₄^[2] was exposed to glass-filtered daylight for one week, and its crystal structure was re-determined.^[5] It was found that **1b**⁺ had been fully converted to **2b**⁺ in a topotactic transformation that left the crystal packing virtually unchanged.^[6] The crystal structure of **2b**⁺ shows that the hydroxy group forms a hydrogen bond with the formyl fragment in a puckered six-membered ring (Figure 1). The bridging hydrogen atom H1 was localized at an O1–H1 distance of 0.80(5) Å (Rh–O1–H1 99(4)°) and an H1–O2 distance of 1.92(5) Å (O1–H1–O2 168(5)°), well within the range of hydrogen bonding. The puckering of the six-membered ring results from rotation of the formyl group around the C1–C2 bond (torsion angle Rh–C1–C2–O2 = 72(3)°).

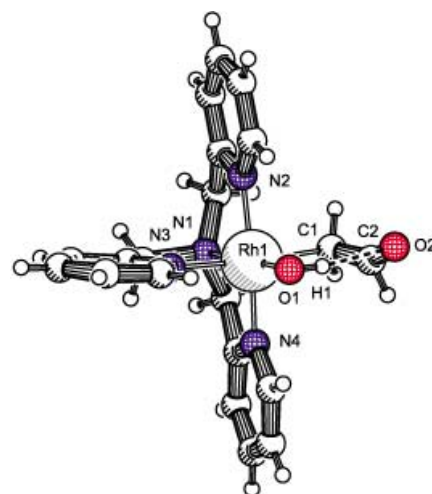


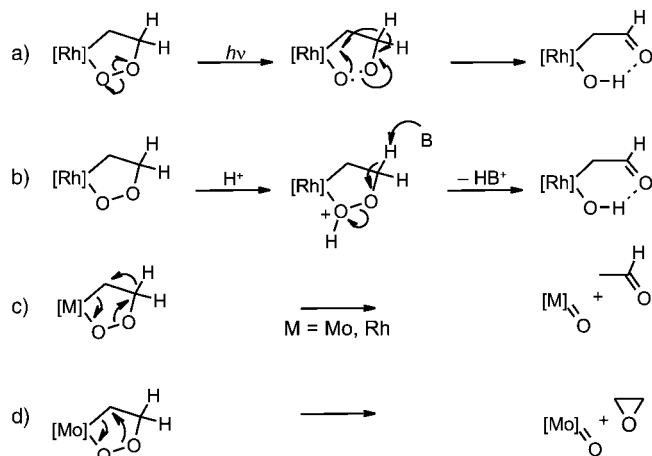
Figure 1. X-Ray structure of rhodium formylmethyl hydroxy complex **2b**⁺. Selected bond lengths [Å]: Rh1–N1 2.040(3), Rh1–N2 2.018(4), Rh1–N3 2.102(3), Rh1–N4 2.033(4), Rh1–C1 2.085(4), Rh1–O1 2.014(3), O2–C2 1.103(11), C1–C2 1.245(12), H1–O2 1.92(5), O1–H1 0.80(5).

We propose that the photochemical rearrangement of **1b**⁺ to **2b**⁺ involves photolysis of the O–O bond followed by abstraction of a β-hydrogen atom from CH₂CH₂O• by O• (Scheme 2a). This β-hydrogen abstraction is probably facili-

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Supporting information for this article is available on the WWW under <http://www.angewandte.com> or from the author.

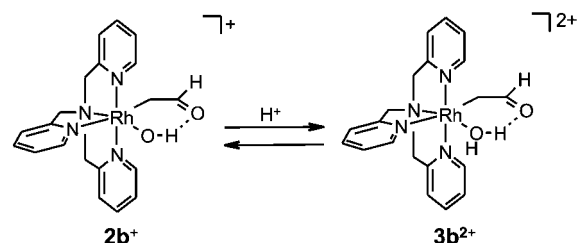


Scheme 2. Mechanisms for rearrangement of a 3-metalla-1,2-dioxolane: a) photochemically to a formylmethyl hydroxy complex, b) proton-assisted to a formylmethyl hydroxy complex, c) directly to an oxo complex and acetaldehyde,^[1a,d] and d) directly to an oxo complex and ethylene oxide.^[1f]

tated by the envelope structure of the 3-rhoda-1,2-dioxolane moiety,^[2] which positions one β -hydrogen atom close to O1.

Analogous to microcrystalline 3-rhoda-1,2-dioxolane **1b**-BPh₄, the microcrystalline mixture of the isomeric 3-rhoda-1,2-dioxolanes **1a**-PF₆ and **1b**-PF₆ (**1a**-PF₆/**1b**-PF₆) rearranged photochemically to a mixture of the isomeric formylmethyl hydroxy complexes **2a**-PF₆ and **2b**-PF₆ (**2a**-PF₆/**2b**-PF₆; Scheme 1). However, **1b**-BPh₄ and **1a**-PF₆/**1b**-PF₆ reacted differently upon exposure to an N₂ atmosphere saturated with H₂O; whereas **1b**-BPh₄ proved stable, **1a**-PF₆/**1b**-PF₆ rearranged to **2a**-PF₆/**2b**-PF₆. Since **1b**-BPh₄ and **1a**-PF₆/**1b**-PF₆ both proved stable under dry N₂, this reactivity must have been triggered by the presence of H₂O. It may result from protonation of the rhodadioxolane by traces of HF, formed by hydrolysis of PF₆⁻.

As the ³¹P NMR spectrum (120 MHz) of the mixture of formylmethyl hydroxy complexes did not reveal signals of the hydrolysis product PF₂O₂⁻, we decided to investigate proton-assisted ring opening in solution. Therefore, 0.1 equiv of the noncoordinating acid [H(OEt₂)₂]B[C₆H₃(CF₃)₂]₄ (HBAr₄^F) was added to a solution of **1b**-BPh₄ in CD₃CN. ¹H NMR spectroscopy showed that **1b**⁺ is converted within 1 h to formylmethyl hydroxy complex **2b**⁺ in approximately 70% yield. Likewise, addition of 1.1 equiv of HBAr₄^F to a solution of **1b**-BPh₄ gave formylmethyl aqua complex **3b**²⁺ (that is, protonated **2b**⁺) in approximately 85% yield within 10 min (Scheme 3).^[7] In the latter case any **2b**⁺ formed is apparently directly protonated. This protonation results in a downfield



Scheme 3. Protonation of rhodium formylmethyl hydroxy complex **2b**⁺ to rhodium formylmethyl aqua complex **3b**²⁺.

shift of the RhCH₂CHO and RhCH₂CHO ¹H NMR signals from $\delta = 2.69$ to $\delta = 3.05$ and from $\delta = 9.26$ to $\delta = 9.51$, respectively. The base peak in the ESI-MS spectrum of the obtained solution has the correct isotope distribution pattern and m/z value (227) for **3b**²⁺. As evidenced by its formylmethyl ¹H NMR signals, a trace of **3b**²⁺ also forms in the conversion of solid **1a**-PF₆/**1b**-PF₆ to **2a**-PF₆/**2b**-PF₆ under N₂ saturated with H₂O. This seems to confirm our hypothesis of HF-catalyzed ring opening.

A possible mechanism for the acid catalyzed ring opening is shown in Scheme 2b. Protonation of **1b**⁺ at O_a induces heterolytic splitting of the O–O bond, followed by formation of a carbonyl double bond and deprotonation at C _{β} by an external base.

The isomeric 3-rhodadioxolanes **1a**⁺ and **1b**⁺ clearly differ in their photoreactivity: upon exposure of a CD₃CN solution of **1a**⁺ and **1b**⁺ to glass-filtered daylight at room temperature, the relative intensities of the 2-peroxyethyl ¹H NMR signals show that the initial reaction rate of **1a**⁺ is three times higher than that of **1b**⁺ (Figure 2).

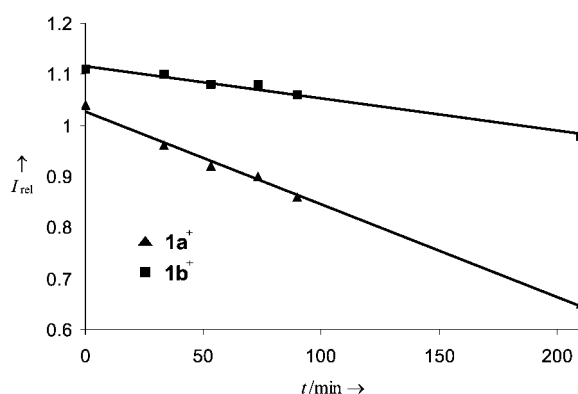


Figure 2. Relative intensities of the 2-peroxyethyl ¹H NMR signals of **1a**⁺ and **1b**⁺ on exposure to glass-filtered daylight.

The observed rearrangement of 3-rhoda-1,2-dioxolanes to formylmethyl hydroxy complexes is in marked contrast to the direct rearrangement of a 3-metalla-1,2-dioxolane to a metal oxo complex and acetaldehyde (as proposed for 3-rhoda-1,2-dioxolanes and calculated for 3-molybdena-1,2-dioxolanes; Scheme 2c)^[1a, 8] or to a metal oxo complex and ethylene oxide (as proposed for 3-molybdena-1,2-dioxolanes).^[1f] The reactivity of the rhodium formylmethyl hydroxy and formylmethyl aqua complexes is currently being investigated.

Experimental Section

The NMR spectra were recorded on Bruker DPX200 and AM500 spectrometers. Shifts are reported relative to CD₃CN: $\delta(^1H) = 1.94$, $\delta(^{13}C) = 118.1$. ESI-MS spectra were recorded on Finnigan TSQ 7000 and MAT 900S mass spectrometers. Infrared spectra were recorded on a Perkin-Elmer 1720X spectrometer.

Compounds [(CH₂CH₂)₂RhCl]₂,^[9] tpa,^[10] [(tpa)Rh($\kappa^2C^1O^2$ -OOCH₂CH₂)]-BPh₄/PF₆,^[2] and [H(OEt₂)₂]B[C₆H₃(CF₃)₂]₄ (HBAr₄^F)^[11] were prepared according to literature procedures.

2a-PF₆/**2b**-PF₆: Solid **1a**-PF₆/**1b**-PF₆ was exposed to an N₂ atmosphere saturated with H₂O for 3 d at room temperature. A mixture of **2a**-PF₆ and **2b**-PF₆ was obtained in an approximate ratio of 1:1. **2a**-PF₆: ¹H NMR (500 MHz, CD₃CN, 243 K): $\delta = 9.98$ (t, 1H, ³J(H,H) = 4.9 Hz,

RhCH₂CHO), 8.68 (d, 2H, ³J(H,H)=5.5 Hz, Py_b-H6), 8.53 (d, 1H, ³J(H,H)=5.5 Hz, Py_a-H6), 7.84 (m, 2H, Py_b-H4), 7.66 (dt, 1H, ³J(H,H)=7.7, ⁴J(H,H)=1.5 Hz, Py_a-H4), 7.48 (d, 2H, ³J(H,H)=8.2 Hz, Py_b-H3), 7.36 (t, 2H, ³J(H,H)=6.6 Hz, Py_b-H5), 7.28 (t, 1H, ³J(H,H)=6.6 Hz, Py_a-H5), 7.17 (d, 1H, ³J(H,H)=8.8 Hz, Py_a-H3), 5.39 (d(AB), 2H, ²J(H,H)=15.0 Hz, NCH₂Py_b), 4.88 (s, 2H, NCH₂Py_a), 4.76 (d(AB), 2H, ²J(H,H)=15.0 Hz, NCH₂Py_b), 3.47 (dd, 2H, ³J(H,H)=4.8, ²J(H,Rh)=2.9 Hz, RhCH₂CHO); ¹³C{¹H} NMR (125 MHz, CD₃CN, 243 K): δ = 210.8 (d, ²J(C,Rh)=9.6 Hz, RhCH₂CHO), 165.0 (Py_b-C2), 163.5 (Py_a-C2), 151.5 (Py_b-C6), 150.2 (Py_a-C6), 139.6 (Py_b-C4), 138.8 (Py_a-C4), 125.4 (Py_b-C5/C3), 125.1 (Py_a-C5/C3), 124.4 (Py_b-C5/C3), 122.1 (Py_a-C5/C3), 66.4 (NCH₂Py_b), 66.2 (NCH₂Py_a), 34.5 (d, ¹J(C,Rh)=25.0 Hz, RhCH₂CHO); ESI-MS (CH₃CN): 453 [M – PF₆]⁺.

2b-BPh₄: Method A: A stirred solution of **1b-BPh₄** in CD₃CN under nitrogen was exposed to the glass-filtered light from a high-pressure mercury vapor lamp^[12] for 90 min at –30 °C. **2b-BPh₄** was obtained in >90 % yield, as determined by ¹H NMR spectroscopy. Method B: HBAR₄^F (5.5 mg, 5.4 μmol) was added to a solution of **1b-BPh₄** (41.8 mg, 54 μmol) in CD₃CN (1 mL) under N₂. **2b-BPh₄** was obtained in approximately 70 % yield after about 1 h, as determined by ¹H NMR spectroscopy. ¹H NMR (200 MHz, CD₃CN, 300 K): δ = 9.26 (t, 1H, ³J(H,H)=5.0 Hz, RhCH₂CHO), 9.21 (brd, 1H, ³J(H,H)=6.0 Hz, Py_a-H6), 8.62 (brd, 2H, ³J(H,H)=5.6 Hz, Py_b-H6), 7.84 (dt, 2H, ³J(H,H)=7.8, ⁴J(H,H)=1.6 Hz, Py_b-H4), 7.73 (dt, 1H, ³J(H,H)=7.8, ⁴J(H,H)=1.6 Hz, Py_a-H4), 7.32 (m, 6H, Py_b-H3, Py_b-H5), 7.27 (m, 8H, BAR-H2), 6.99 (t, 8H, ³J(H,H)=7.4 Hz, BAR-H3), 6.83 (t, 4H, ³J(H,H)=7.2 Hz, BAR-H4), 5.01 (d(AB), 2H, ²J(H,H)=15.9 Hz, NCH₂Py_b), 4.71 (d(AB), 2H, ²J(H,H)=14.9 Hz, NCH₂Py_b), 4.67 (s, 2H, NCH₂Py_a), 2.69 (dd, 2H, ³J(H,H)=5.1, ²J(H,Rh)=2.9 Hz, RhCH₂CHO); ¹³C{¹H} NMR (125 MHz, CD₃CN, 243 K): δ = 209.0 (RhCH₂CHO), 163.9 (q, ¹J(C,B)=49.2 Hz, BAR-C1), 162.4 (Py_b-C2), 159.0 (Py_a-C2), 149.9 (Py_b-C6), 147.2 (Py_a-C6), 139.3 (Py_b-C4), 139.2 (Py_a-C4), 135.7 (BAR-C2), 126.1 (q, ³J(C,B)=2.7 Hz, BAR-C3), 125.4 (Py_b-C5/C3), 124.9 (Py_a-C5/C3), 124.4 (Py_b-C5/C3), 122.1 (BAR-C4), 121.2 (Py_a-C5/C3), 70.7 (NCH₂Py_a), 68.3 (NCH₂Py_b), 26.9 (d, ¹J(C,Rh)=21.0 Hz, RhCH₂CHO); ESI-MS (CD₃CN): 453 [M – BPh₄]⁺, 435 [M – H₂O – BPh₄]⁺, 425 [M – C₂H₄ – BPh₄]⁺, 409 [M – C₂H₄O – BPh₄]⁺, 393 [M – C₂H₄O₂ – BPh₄]⁺, 391 [M – C₂H₄O₂ – H₂ – BPh₄]⁺; IR (KBr): 1655 cm^{–1}.

3b-BPh₄/BAR₄^F: HBAR₄^F (57 mg, 0.11 mmol) was added to a solution of **1b-BPh₄** (40 mg, 0.1 mmol) in CD₃CN (1.0 mL) under N₂. **3b-BPh₄/BAR₄^F** was obtained in approximately 85 % yield as determined by ¹H NMR spectroscopy. ¹H NMR (200 MHz, CD₃CN, 300 K): δ = 9.51 (t, 1H, ³J(H,H)=4.8 Hz, RhCH₂CHO), 8.96 (d, 1H, ³J(H,H)=5.5 Hz, Py_a-H6), 8.52 (d, 2H, ³J(H,H)=5.7 Hz, Py_b-H6), 7.95 (dt, ³J(H,H)=7.8, ⁴J(H,H)=1.6 Hz, Py_b-H4), 7.81 (dt, ³J(H,H)=7.8 Hz, ⁴J(H,H)=1.6 Hz, Py_a-H4), 7.73 (m, 8H, BAR₄^F-H2), 7.68 (s, 4H, BAR₄^F-H4), 7.6–7.4 (m, 5H, Py_b-H3, Py_b-H5, Py_a-H3/5), 7.33 (m, 8H, BAR-H2), 7.21 (m, 1H, Py_a-H3/5), 7.01 (t, 8H, ³J(H,H)=7.4 Hz, BAR-H3), 6.85 (t, 4H, ³J(H,H)=6.9 Hz, BAR-H4), 5.15 (d(AB), 2H, ²J(H,H)=16.4 Hz, NCH₂Py_b), 4.82 (s, 2H, NCH₂Py_a), 4.69 (d(AB), 2H, ²J(H,H)=16.6 Hz, NCH₂Py_b), 3.05 (dd, 2H, ³J(H,H)=4.9, ²J(H,Rh)=2.7 Hz, RhCH₂CHO); ¹³C{¹H} NMR (125 MHz, CD₃CN, 243 K): δ = 206.7 (d, ²J(C,Rh)=1.9 Hz, RhCH₂CHO), 164.0 (q, ¹J(C,B)=49.2 Hz, BAR-C1), 161.9 (q, ¹J(C,B)=49.8 Hz, BAR^F-C1), 161.6 (Py_b-C2), 158.0 (Py_a-C2), 151.5 (Py_b-C6), 148.7 (Py_a-C6), 140.9 (Py_b-C4), 140.4 (Py_a-C4), 135.8 (BAR-C2), 134.9 (BAR^F-C2), 129.0 (qq, ²J(C,F)=31.4 Hz, ³J(C,B)=2.9 Hz, BAR^F-C3), 126.4 (Py_b-C5/C3), 126.2 (q, ³J(C,B)=2.6 Hz, BAR-C3), 125.8 (Py_a-C5/C3), 125.4 (Py_b-C5/C3), 124.6 (q, ¹J(C,F)=271.9 Hz, BAR^F-CF₃), 122.3 (BAR-C4), 122.1 (Py_a-C5/C3), 73.5 (NCH₂Py_a), 69.6 (NCH₂Py_b), 27.8 (d, ¹J(C,Rh)=20.4 Hz, RhCH₂CHO). The signal for BAR^F-C4 is obscured by one of the solvent signals. ESI-MS (CH₃CN): 227 [M – BPh₄ – BAR₄^F]²⁺, 218 [M – H₂O – BPh₄ – BAR₄^F]²⁺.

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- [5] A transparent yellow crystal of **2b-BPh₄** was obtained by exposure of a crystal of **1b-BPh₄** (obtained by slow diffusion of diethyl ether into a 1,2-dichloroethane/acetonitrile solution^[2]) to glass-filtered daylight for one week. The X-ray diffraction data were collected at 150(2) K on an Enraf-Nonius CAD4 diffractometer with rotating anode and CCD area detector with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å). The structure was solved by the PATTY^[13] option of the DIRDIF^[14] program package. Crystal data: C₄₈H_{50.50}BCIN_{4.50}O_{2.50}Rh, *M_r* = 879.60, monoclinic, space group C2/c, *a* = 36.0362(2), *b* = 10.77600(10), *c* = 24.2975(2) Å, β = 116.3883(4)°, *V* = 8452.21(11) Å³, *Z* = 8, ρ_{calcd} = 1.382 Mg m^{–3}. All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms, except H1, were placed at calculated positions and refined isotropically in riding mode. H1 was clearly observed in a difference Fourier map, and its position was subsequently determined automatically. Its positional and thermal parameters were refined freely, and this refinement proved to be stable. The position of H1 is well outside the regions influenced by the SQUEEZE procedure described below. From the anisotropic thermal displacement parameters for C2 and O2 it is clear that these atoms show a large positional disorder. Although it is possible to use several partially occupied positions for these atoms, no physically reasonable models result from these parameters, and none is any better than the model presented here. Splitting these atoms serves no other purpose than to lower the *R* value. The calculated hydrogen positions on C2 are therefore merely indications of possible positions. Calculations (PLATON, Spek 1995)^[15] showed two distinct voids, one of 239 Å³ containing 58 electrons around a twofold axis (position 4e, 0, *y*, 1/4; *y* = –0.041), and one of 152 Å³ containing 39 electrons around an inversion center (position 4b: 1/2, 0, 0). Based on the synthetic route and evidence from NMR spectroscopy it is assumed that these electron densities possibly represent one molecule of diethyl ether (C₄H₁₀O, 42 electrons) plus one molecule acetonitrile (CH₃CN, 22 electrons) in the first void (64 electrons, 29.9 Å³/non-hydrogen atom), and one molecule of dichloroethane (C₂H₄Cl₂, 50 electrons) in the second (38.0 Å³/non-hydrogen atom). These assumptions are in accordance with the earlier crystal structure determination of the original crystal of **1b-BPh₄** before its exposure to glass-filtered daylight^[2] and account for the calculated physical molecular properties as reported in this paper. It was not possible to assign any physically meaningful parameters to the electron densities found in the difference Fourier map. Therefore the SQUEEZE procedure was applied to account for these electron densities. CCDC-170096 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
- [6] Space group before and after transformation: C2/c. Cell dimensions before transformation: *a* = 35.8688(5) Å, *b* = 10.7328(2) Å, *c* = 24.2609(4) Å, β = 116.666(1)°, *V* = 8346.4(3) Å³. Cell dimensions after transformation: *a* = 36.0362(2) Å, *b* = 10.7760(1) Å, *c* = 24.2975(2) Å, β = 116.3883(4)°, *V* = 8452.2(2) Å³.
- [7] The longer reaction time and lower yield upon addition of 0.1 equiv HBAR₄^F can be explained by the lower acidity of the solution and slow decomposition of **2b**⁺. The absence of the aqua complex **3b**²⁺ in the resulting reaction mixture can be explained by its slow conversion to **2b**⁺ through proton abstraction by BPh₄[–]. Acid decomposition of BPh₄[–] to BPh₃ and benzene is described in H. Nishida, N. Takada, M. Yoshimura, T. Sonoda, H. Kobayashi, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600, and references therein.
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Paramagnetic Keplerate “Necklaces” Synthesized by a Novel Room-Temperature Solid-State Reaction: Controlled Linking of Metal-Oxide-Based Nanoparticles**

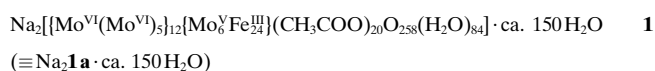
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Dedicated to Professor C. N. R. Rao on the occasion of the Silver Jubilee of his Solid State and Structural Chemistry Unit

The search for extended structures based on linked nano-sized stable building blocks especially with well-defined electronic and magnetic properties is an extremely worthy task because such multidimensional networks could result in new types of functionalized materials.^[1] In this context we are involved in the synthesis of ever larger well-defined metal-oxide-based nanoparticles with unique host properties and their linking through M–O–M- or M–O–M'-type bonds to obtain a wide range of architectures.^[2] For instance, spherical metal-oxide-based Keplerate-type clusters with icosahedral symmetry, which exhibit an internal cavity (diameter) large

enough to even encapsulate Keggin-type clusters—thus leading to remarkable composites—can be generated in a facile synthesis.^[3] The Keplerate-type clusters also display interesting topologies.^[4] So far there has been no report on the linking of such large spherical objects to form a chain structure (for very interesting fullerene-type systems see ref. [5]). Here we report the synthesis and structure of an unusual mixed-valence compound^[6] containing discrete {Mo^{VI}(Mo^{VI})₅}₁₂{Mo^VFe^{III}}_{24}-type Keplerate clusters and their one-dimensional linking by a novel type of solid-state reaction at room temperature to form chains. We also present a theoretical model based on a modification of a {Mo^{VI}(Mo^{VI})₅}₁₂{Fe^{III}}_{30} prototype^[7] that helps to explain the measured magnetic properties of the chain compound.

If a strongly acidified aqueous solution of sodium molybdate is treated with ferrous chloride in the presence of air and a rather high concentration of acetic acid, black crystals of **1** containing {Mo^{VI}(Mo^{VI})₅}₁₂{Mo^VFe^{III}}_{24}-type anionic clusters precipitate, which upon drying at room temperature get linked to chains, yielding (the black) compound **2** (see also Experimental Section).



During the formation process, the Fe^{II} ions partly reduce the Mo^{VI} centers though most of the Fe^{II} cations are oxidized by air to Fe^{III}. In any case the presence of Fe^{II} is necessary, as beginning the synthesis with Fe^{III} as starting material in the presence of a reducing agent leads immediately to a non-crystalline precipitate.

Whereas compound **2** was characterized to a full extent by elemental analysis, thermogravimetry (to determine the crystal water content), bond valence sum (BVS) calculations,^[8] spectroscopic methods (IR, resonance Raman, VIS-NIR, ⁵⁷Fe Mössbauer) as well as magnetic measurements and single-crystal structure analysis,^[9] compound **1**, which contains discrete spherical clusters, could only be identified by single-crystal X-ray structure analysis of the non-dried crystals. These crystals were cooled immediately to liquid nitrogen temperature to block any further release of water and subsequent condensation reactions which would lead to the formation of **2**.^[9]

Both the spherical cluster anion **1a** and the spherical building blocks of the anion chain **2a** comprise 12 pentagonal fragments of the type {Mo^{VI}(Mo^VO)₂₁} (containing a central pentagonal MoO₇ bipyramid edge-sharing with five {MoO₆} octahedra) which are connected by 24 {Fe^{III}(H₂O)₂}³⁺¹⁰ and six {Mo^VO(H₂O)}³⁺ linkers (the six Mo(4d) electrons are also partially delocalized over the Mo positions of the pentagonal {Mo(Mo₅)} building groups, cf. ref. [11]) statistically distributed over the 30 vertices of an icosidodecahedron. The acetate ligands are located inside the sphere and are coordinated in a bidentate fashion to the metal centers, preferentially bridging Fe and Mo sites. In crystals of **2** the icosahedral spherical building blocks, that is {Mo(Mo)₅}₁₂{Mo₆Fe}_{24}-type spheres,

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