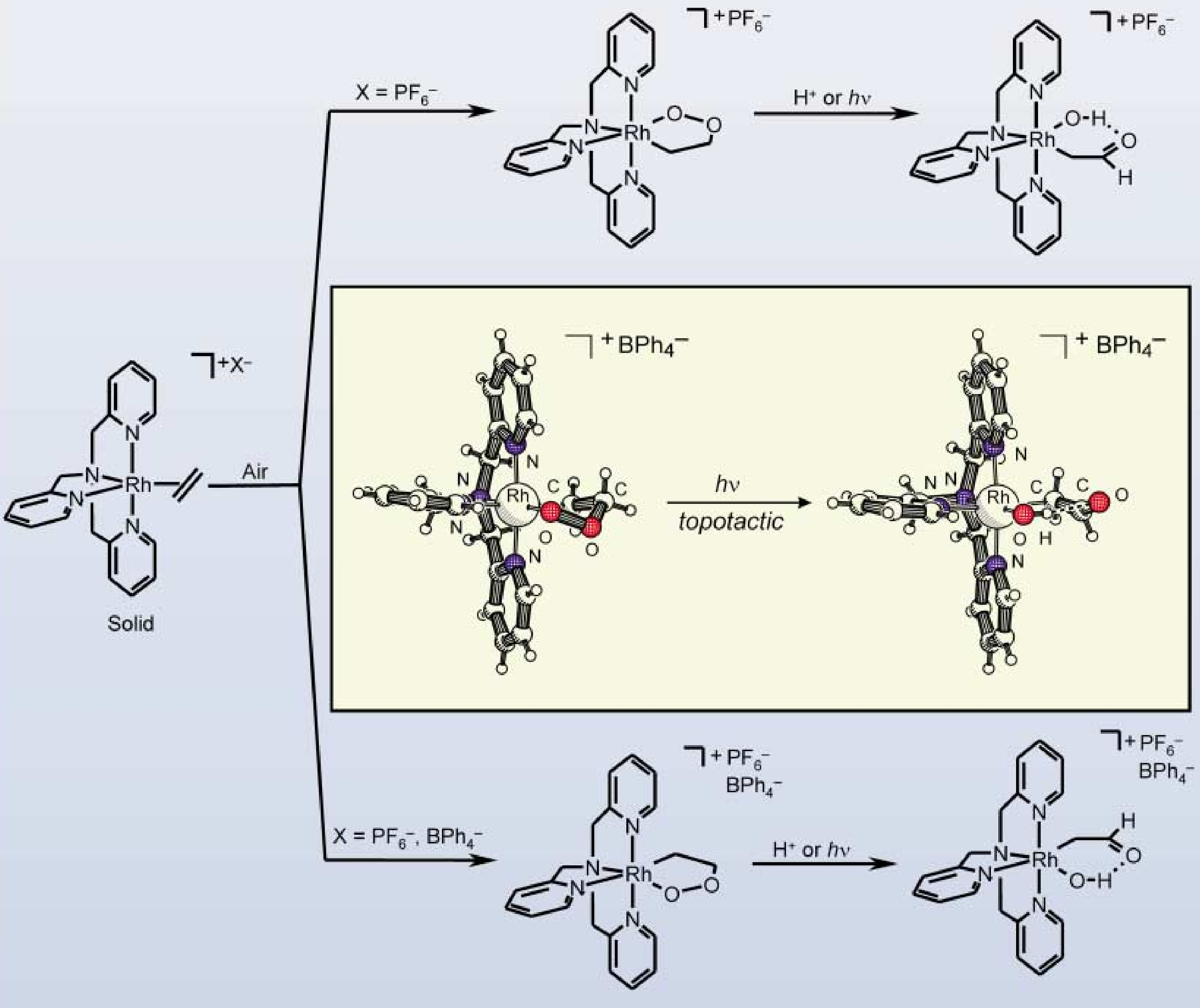
Dioxygen activation in progress

Dioxygen reacts with ethene complexes to 3-rhoda-1,2-dioxolanes and subsequently breaks its O–O bond.



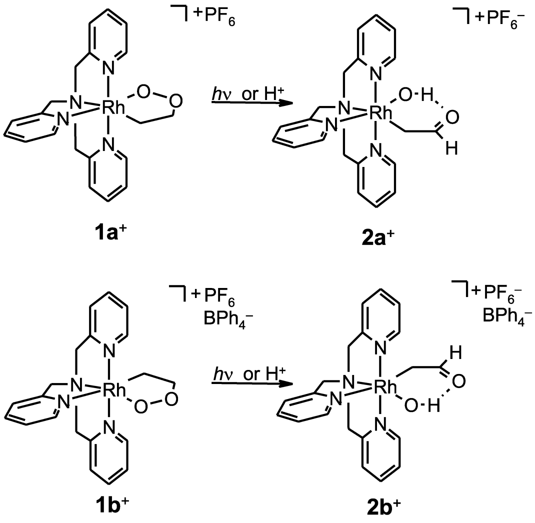
Exposure of a single crystal of a rhodadioxolane to light results in topotactic transformation to a rhodium formylmethyl hydroxy complex.

More about this rearrangement, which contradicts earlier proposed conversions of 3-metalla-1,2-dioxolanes, can be found on the following pages.

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 N_4 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**-BPh_4 to glass-filtered daylight under N_2 resulted in selective conversion to the corresponding rhodium formylmethyl hydroxy complex **2b**-BPh_4 over several weeks (Scheme 1). Similarly, exposure of a solution of **1b**-BPh_4 in CD_3CN to the glass-filtered light from a high-pressure mercury lamp at −30 °C resulted in conversion to **2b**-BPh_4. The ^1H NMR spectrum of the resulting solution indicated that an optimum yield of 90 % **2b**-BPh_4 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 $[(MeCN)(\kappa^3\text{-Bzbpa})Rh(\kappa^1\text{-}CH_2CHO)(OH)]BPh_4$, the only formylmethyl hydroxy complex reported thus far.[3, 4]

The ^1H NMR and ^{13}C NMR spectra of **2b**-BPh_4 reveal the presence of a formylmethyl fragment [^1H NMR: $\delta = 2.69$ (dd, $^3J(H,H) = 5.1$, $^2J(H,Rh) = 2.9$ Hz, $RhCH_2CHO$) and 9.26 (t, $^3J(H,H) = 5.1$ Hz, $RhCH_2CHO$); ^{13}C NMR: $\delta = 26.9$ (d, $^1J(C,Rh) = 21.0$ Hz, $RhCH_2CHO$) and 209.0 ($RhCH_2CHO$)]. The ^1H NMR signals for the formylmethyl group of **2b**$^+$ are comparable to those of $[(MeCN)(\kappa^3\text{-Bzbpa})Rh(\kappa^1\text{-}CH_2CHO)(OH)]BPh_4$ [$\delta = 3.37$ (dd, $^3J(H,H) = 5.3$, $^2J(H,Rh) = 2.9$ Hz, $RhCH_2CHO$) and 10.3 (t, $^3J(H,H) = 5.3$ Hz, $RhCH_2CHO$)].[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**-BPh_4 had failed, an attempt was made to photochemically convert a single crystal of **1b**-BPh_4 to a single crystal of **2b**-BPh_4. The crystal that was used for X-ray structure determination of **1b**-BPh_4[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)°).

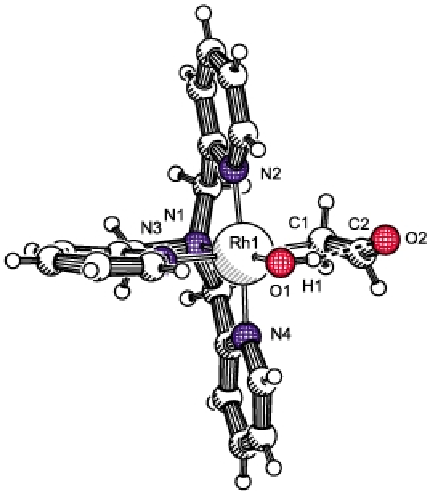


Figure 1. X-Ray structure of rhodium formylmethyl hydroxy complex **2b**$^+$. Selected bond lengths [Å]: Rh1-N1 2.040(3), Rh1-N2 2.018(4), Rh1-N3 2.102(3), Rh1-N4 2.033(4), Rh1-C1 2.085(4), Rh1-O1 2.014(3), O2-C2 1.103(11), C1-C2 1.245(12), H1-O2 1.92(5), O1-H1 0.80(5).

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 $CH_2CH_2O^\bullet$ by $O^\bullet$ (Scheme 2 a). 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.

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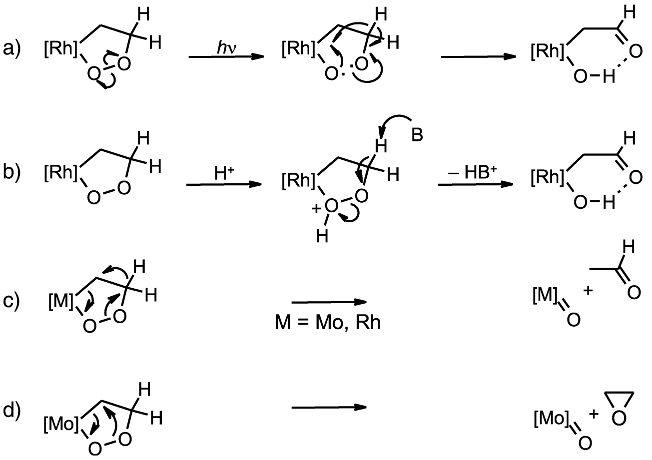
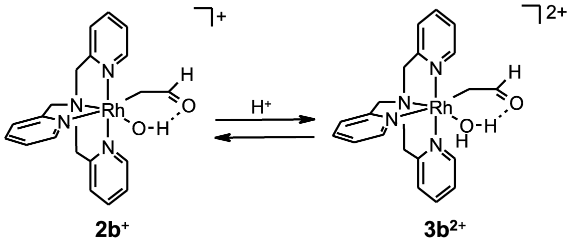


Scheme 2. Mechanisms for rearrangement of a 3-metalla-1,2-dioxolane: a) photochemically to a formylmethyl hydroxy complex, b) proton-assisted to a formylmethyl hydroxy complex, c) directly to an oxo complex and acetaldehyde,[1a, d] and d) directly to an oxo complex and ethylene oxide.[1f]

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**-BPh_4, the microcrystalline mixture of the isomeric 3-rhoda-1,2-dioxolanes **1a**-PF_6 and **1b**-PF_6[2] (**1a**-PF_6/**1b**-PF_6) rearranged photochemically to a mixture of the isomeric formylmethyl hydroxy complexes **2a**-PF_6 and **2b**-PF_6 (**2a**-PF_6/**2b**-PF_6; Scheme 1). However, **1b**-BPh_4 and **1a**-PF_6/**1b**-PF_6 reacted differently upon exposure to an N_2 atmosphere saturated with H_2O; whereas **1b**-BPh_4 proved stable, **1a**-PF_6/**1b**-PF_6 rearranged to **2a**-PF_6/**2b**-PF_6. Since **1b**-BPh_4 and **1a**-PF_6/**1b**-PF_6 both proved stable under dry N_2, this reactivity must have been triggered by the presence of H_2O. It may result from protonation of the rhodadioxolane by traces of HF, formed by hydrolysis of PF_6^-.

As the ^{31}P NMR spectrum (120 MHz) of the mixture of formylmethyl hydroxy complexes did not reveal signals of the hydrolysis product $PF_2O_2^-$, we decided to investigate proton-assisted ring opening in solution. Therefore, 0.1 equiv of the noncoordinating acid $[H(OEt_2)_2]B[C_6H_3(CF_3)_2]_4$ ($HBAr^F_4$) was added to a solution of **1b**-BPh_4 in CD_3CN. ^1H NMR spectroscopy showed that $\mathbf{1b}^+$ is converted within 1 h to formylmethyl hydroxy complex $\mathbf{2b}^+$ in approximately 70% yield. Likewise, addition of 1.1 equiv of $HBAr^F_4$ to a solution of **1b**-BPh_4 gave formylmethyl aqua complex $\mathbf{3b}^{2+}$ (that is, protonated $\mathbf{2b}^+$) in approximately 85% yield within 10 min (Scheme 3).[7] In the latter case any $\mathbf{2b}^+$ formed is apparently directly protonated. This protonation results in a downfield shift of the $RhCH_2CHO$ and $RhCH_2CHO$ ^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 $\mathbf{3b}^{2+}$. As evidenced by its formylmethyl ^1H NMR signals, a trace of $\mathbf{3b}^{2+}$ also forms in the conversion of solid **1a**-PF_6/**1b**-PF_6 to **2a**-PF_6/**2b**-PF_6 under N_2 saturated with H_2O. This seems to confirm our hypothesis of HF-catalyzed ring opening.



Scheme 3. Protonation of rhodium formylmethyl hydroxy complex $\mathbf{2b}^+$ to rhodium formylmethyl aqua complex $\mathbf{3b}^{2+}$.

A possible mechanism for the acid catalyzed ring opening is shown in Scheme 2b. Protonation of $\mathbf{1b}^+$ at O_α 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 $\mathbf{1a}^+$ and $\mathbf{1b}^+$ clearly differ in their photoreactivity: upon exposure of a CD_3CN solution of $\mathbf{1a}^+$ and $\mathbf{1b}^+$ to glass-filtered daylight at room temperature, the relative intensities of the 2-peroxyethyl ^1H NMR signals show that the initial reaction rate of $\mathbf{1a}^+$ is three times higher than that of $\mathbf{1b}^+$ (Figure 2).

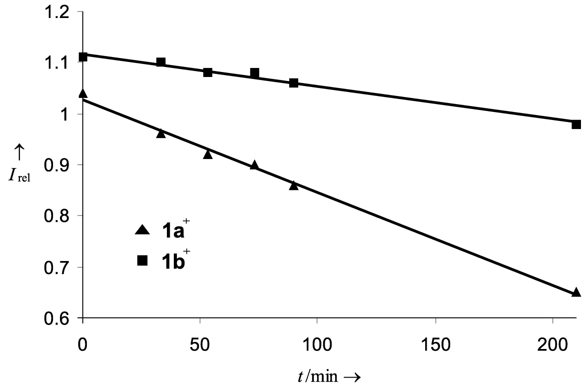


Figure 2. Relative intensities of the 2-peroxyethyl ^1H NMR signals of $\mathbf{1a}^+$ and $\mathbf{1b}^+$ on exposure to glass-filtered daylight.

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 CD_3CN: $\delta(^1H) = 1.94$, $\delta(^{13}C) = 118.1$. 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 $[\{(CH_2CH_2)_2RhCl\}_2]$,[9] tpa,[10] $[(tpa)Rh(\kappa^2C^1O^2\text{-}OOCH_2CH_2)]$-$BPh_4$/$PF_6$,[2] and $[H(OEt_2)_2]B[C_6H_3(CF_3)_2]_4$ ($HBAr^F_4$)[11] were prepared according to literature procedures.

2a-PF_6/**2b**-PF_6: Solid **1a**-PF_6/**1b**-PF_6 was exposed to an N_2 atmosphere saturated with H_2O for 3 d at room temperature. A mixture of **2a**-PF_6 and **2b**-PF_6 was obtained in an approximate ratio of 1:1. **2a**-PF_6: ^1H NMR (500 MHz, CD_3CN, 243 K): $\delta = 9.98$ (t, 1H, $^3J(H,H) = 4.9$ Hz, RhCH$_2$C*H*O), 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, NC*H*$_2$Py$_b$), 4.88 (s, 2H, NC*H*$_2$Py$_a$), 4.76 (d(AB), 2H, ^2J(H,H) = 15.0 Hz, NC*H*$_2$Py$_b$), 3.47 (dd, 2H, ^3J(H,H) = 4.8, ^2J(H,Rh) = 2.9 Hz, RhC*H*$_2$CHO); ^{13}C{^{1}H} NMR (125 MHz, CD$_3$CN, 243 K): δ = 210.8 (d, ^2J(C,Rh) = 9.6 Hz, RhCH$_2$*C*HO), 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 (N*C*H$_2$Py$_b$), 66.2 (N*C*H$_2$Py$_a$), 34.5 (d, ^1J(C,Rh) = 25.0 Hz, Rh*C*H$_2$CHO); ESI-MS (CH$_3$CN): 453 [*M* − PF$_6$]$^+$.

2b-BPh$_4$: Method A: A stirred solution of **1b**-BPh$_4$ in CD$_3$CN under nitrogen was exposed to the glass-filtered light from a high-pressure mercury vapor lamp[12] for 90 min at −30 °C. **2b**-BPh$_4$ was obtained in > 90 % yield, as determined by ^{1}H NMR spectroscopy. Method B: HBAr$^F_4$ (5.5 mg, 5.4 μmol) was added to a solution of **1b**-BPh$_4$ (41.8 mg, 54 μmol) in CD$_3$CN (1 mL) under N$_2$. **2b**-BPh$_4$ was obtained in approximately 70 % yield after about 1 h, as determined by ^{1}H NMR spectroscopy. ^{1}H NMR (200 MHz, CD$_3$CN, 300 K): δ = 9.26 (t, 1H, ^3J(H,H) = 5.0 Hz, RhCH$_2$C*H*O), 9.21 (br d, 1H, ^3J(H,H) = 6.0 Hz, Py$_a$-H6), 8.62 (br d, 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-H3, Py-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, NC*H*$_2$Py$_b$), 4.71 (d(AB), 2H, ^2J(H,H) = 14.9 Hz, NC*H*$_2$Py$_b$), 4.67 (s, 2H, NC*H*$_2$Py$_a$), 2.69 (dd, 2H, ^3J(H,H) = 5.1, ^2J(H,Rh) = 2.9 Hz, RhC*H*$_2$CHO); ^{13}C{^{1}H} NMR (125 MHz, CD$_3$CN, 243 K): δ = 209.0 (RhCH$_2$CHO), 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 (N*C*H$_2$Py$_a$), 68.3 (N*C*H$_2$Py$_b$), 26.9 (d, ^1J(C,Rh) = 21.0 Hz, Rh*C*H$_2$CHO); ESI-MS (CD$_3$CN): 453 [*M* − BPh$_4$]$^+$, 435 [*M* − H$_2$O − BPh$_4$]$^+$, 425 [*M* − C$_2$H$_4$ − BPh$_4$]$^+$, 409 [*M* − C$_2$H$_4$O − BPh$_4$]$^+$, 393 [*M* − C$_2$H$_4$O$_2$ − BPh$_4$]$^+$, 391 [*M* − C$_2$H$_4$O$_2$ − H$_2$ − BPh$_4$]$^+$; IR (KBr): 1655 cm^{-1}.

3b-BPh$_4$/BAr$^F_4$: HBAr$^F_4$ (57 mg, 0.11 mmol) was added to a solution of **1b**-BPh$_4$ (40 mg, 0.1 mmol) in CD$_3$CN (1.0 mL) under N$_2$. **3b**-BPh$_4$/BAr$^F_4$ was obtained in approximately 85 % yield as determined by ^{1}H NMR spectroscopy. ^{1}H NMR (200 MHz, CD$_3$CN, 300 K): δ = 9.51 (t, 1H, ^3J(H,H) = 4.8 Hz, RhCH$_2$C*H*O), 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, BAr$^F_4$-H2), 7.68 (s, 4H, BAr$^F_4$-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, NC*H*$_2$Py$_b$), 4.82 (s, 2H, NC*H*$_2$Py$_a$), 4.69 (d(AB), 2H, ^2J(H,H) = 16.6 Hz, NC*H*$_2$Py$_b$), 3.05 (dd, 2H, ^3J(H,H) = 4.9, ^2J(H,Rh) = 2.7 Hz, RhC*H*$_2$CHO); ^{13}C{^{1}H} NMR (125 MHz, CD$_3$CN, 243 K): δ = 206.7 (d, ^2J(C,Rh) = 1.9 Hz, RhCH$_2$*C*HO), 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-CF$_3$), 122.3 (BAr-C4), 122.1 (Py$_a$-C5/C3), 73.5 (N*C*H$_2$Py$_a$), 69.6 (N*C*H$_2$Py$_b$), 27.8 (d, ^1J(C,Rh) = 20.4 Hz, Rh*C*H$_2$CHO). The signal for BAr^F-C4 is obscured by one of the solvent signals. ESI-MS (CH$_3$CN): 227 [*M* − BPh$_4$ − BAr$^F_4$]$^{2+}$, 218 [*M* − H$_2$O − BPh$_4$ − BAr$^F_4$]$^{2+}$.

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[1] a) H. Mimoun, M. M. P. Machirant, I. Seree de Roch, *J. Am. Chem. Soc.* **1978**, *100*, 5437; b) G. Read, *J. Mol. Catal.* **1988**, *44*, 15; c) M. Bressan, F. Morandini, A. Morvillo, P. Rigo, *J. Organomet. Chem.* **1985**, *280*, 139; d) R. A. Sheldon, J. A. van Doorn, *J. Organomet. Chem.* **1975**, *94*, 115; e) H. Mimoun, *Angew. Chem.* **1982**, *21*, 734; *Angew. Chem. Int. Ed. Engl.* **1982**, *94*, 750; f) H. Mimoun, I. Seree de Roch, L. Sajus, *Tetrahedron* **1970**, *26*, 37.

[2] M. Krom, R. G. E. Coumans, J. M. M. Smits, A. W. Gal, *Angew. Chem.* **2001**, *113*, 2164; *Angew. Chem. Int. Ed.* **2001**, *40*, 2106.

[3] Bzbpa = *N*-benzyl-*N*,*N*-bis(2-pyridylmethyl)amine.

[4] B. de Bruin, J. A. W. Verhagen, C. H. J. Schouten, A. W. Gal, D. Feichtinger, D. A. Plattner, *Chem. Eur. J.* **2001**, *7*, 416.

[5] A transparent yellow crystal of **2b**-BPh$_4$ was obtained by exposure of a crystal of **1b**-BPh$_4$ (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 Mo$_{K\alpha}$ radiation (λ = 0.71073 Å). The structure was solved by the PATTY[13] option of the DIRDIF[14] program package. Crystal data: C$_{48}$H$_{50.50}$BClN$_{4.50}$O$_{2.50}$Rh, M_r = 879.60, monoclinic, space group *C*2/c, *a* = 36.0362(2), *b* = 10.77600(10), *c* = 24.2975(2) Å, β = 116.3883(4)°, *V* = 8452.21(11) Å^3, *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 Å^3 containing 58 electrons around a twofold axis (position 4e, 0, *y*, 1/4; *y* = −0.041), and one of 152 Å^3 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 (C$_4$H$_{10}$O, 42 electrons) plus one molecule acetonitrile (CH$_3$CN, 22 electrons) in the first void (64 electrons, 29.9 Å^3/non-hydrogen atom), and one molecule of dichloroethane (C$_2$H$_4$Cl$_2$, 50 electrons) in the second (38.0 Å^3/non-hydrogen atom). These assumptions are in accordance with the earlier crystal structure determination of the original crystal of **1b**-BPh$_4$ 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: *C*2/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) Å^3. 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) Å^3.

[7] The longer reaction time and lower yield upon addition of 0.1 equiv HBAr$^F_4$ 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 BPh$_4^-$. Acid decomposition of BPh$_4^-$ to BPh$_3$ 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.

[8] D. V. Deubel, J. Sundermeyer, G. Frenking, *J. Am. Chem. Soc.* **2000**, *122*, 10101.

[9] R. Cramer, *Inorg. Synth.* **1990**, *28*, 86.

[10] G. Anderegg, F. Wenk, *Helv. Chim. Acta* **1967**, *50*, 2330.

[11] M. Brookhart, B. Grant, A. F. Volpe, Jr., *Organometallics* **1992**, *11*, 3920.

[12] Immersion Lamp TQ 150 of Heraeus Noblelight GmbH; power consumption 150 W. The experimental setup is available as Supporting Information.

[13] P. T. Beurskens, G. Beurskens, M. Strumpel, C. E. Nordman in *Patterson and Pattersons* (Eds.: J. P. Glusker, B. K. Patterson, M. Rossi), Clarendon Press, Oxford, **1987**, p. 356.

[14] DIRDIF-96, a computer program system for crystal structure determination by Patterson methods and direct methods applied to difference structure factors: P. T. Beurskens, G. Beurskens, W. P. Bosman, R. de Gelder, S. García-Granda, R. O. Gould, R. Israël, J. M. M. Smits, Crystallography Laboratory, University of Nijmegen, The Netherlands, **1996**.

[15] PLATON-93, program for display and analysis of crystal and molecular structures: A. L. Spek, University of Utrecht, The Netherlands, **1995**.

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 nanosized 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 $\{Mo^{VI}(Mo^{VI})_5\}_{12}\{Mo^{V}_{6}Fe^{III}_{24}\}$-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 $\{Mo^{VI}(Mo^{VI})_5\}_{12}\{Mo^{V}_{6}Fe^{III}_{24}\}$-type anionic clusters precipitate, which upon drying at room temperature get linked to chains, yielding (the black) compound **2** (see also Experimental Section).

$Na_2[\{Mo^{VI}(Mo^{VI})_5\}_{12}\{Mo^{V}_{6}Fe^{III}_{24}\}(CH_3COO)_{20}O_{258}(H_2O)_{84}]\cdot$ ca. $150\,H_2O$ **1**
($\equiv Na_2$**1a** · ca. $150\,H_2O$)

$Na_2[\{Mo^{VI}(Mo^{VI})_5\}_{12}\{Mo^{V}_{6}Fe^{III}_{24}\}(CH_3COO)_{20}O_{258}(H_2O)_{82}]\cdot$ ca. $80\,H_2O$ **2**
($\equiv Na_2$**2a** · ca. $80\,H_2O$)

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 noncrystalline 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, ^{57}Fe 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 $\{Mo^{VI}(Mo^{VI}_{5}O_{21})\}$ (containing a central pentagonal MoO_7 bipyramid edge-sharing with five $\{MoO_6\}$ octahedra) which are connected by 24 $\{Fe^{III}(H_2O)_2\}^{3+}$[10] and six $\{Mo^{V}O(H_2O)\}^{3+}$ linkers (the six Mo(4d) electrons are also partially delocalized over the Mo positions of the pentagonal $\{Mo(Mo_5)\}$ 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 $\{Mo(Mo)_5\}_{12}\{Mo_6Fe_{24}\}$-type spheres,

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