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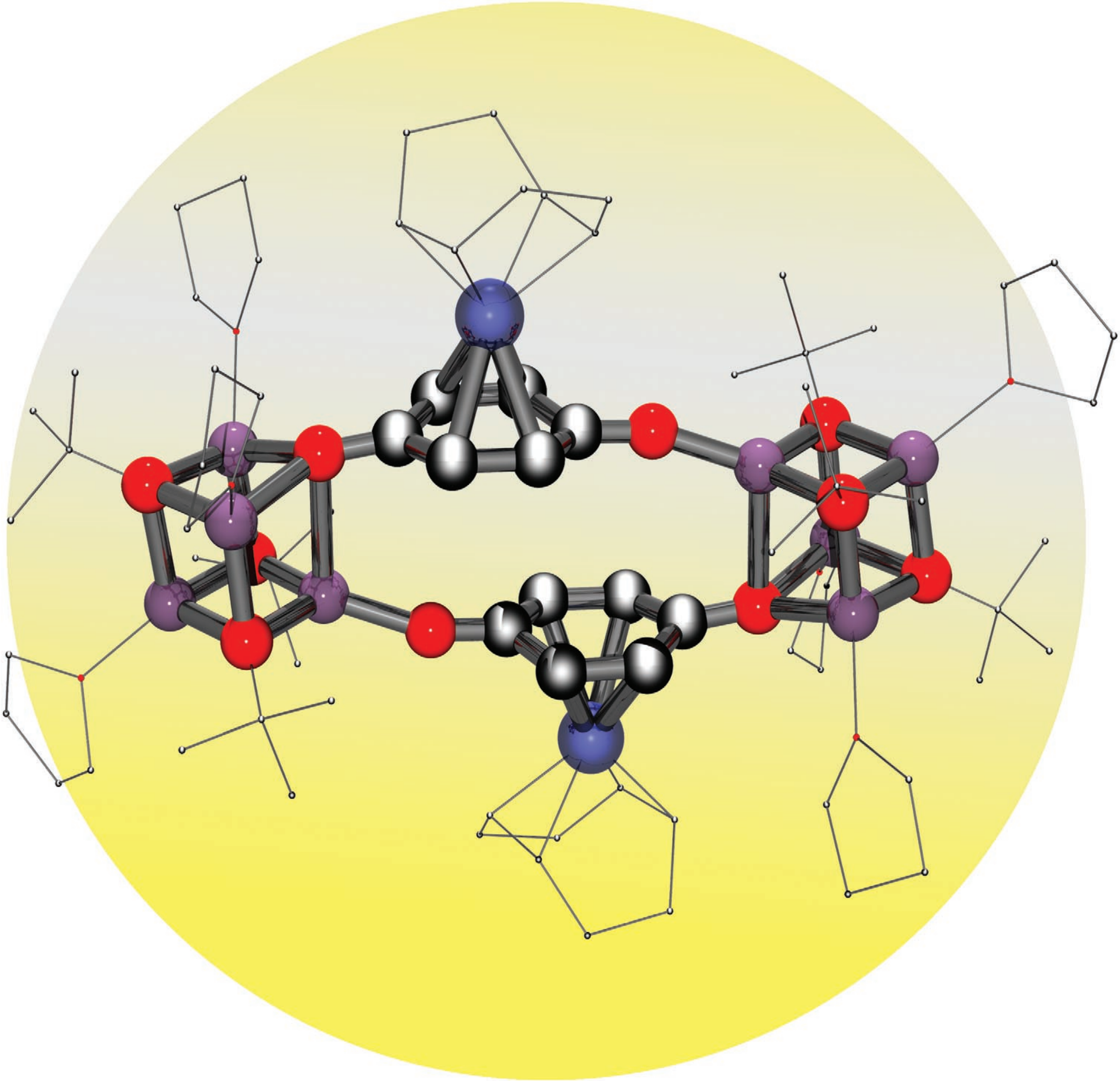

Übergangsmetallkomplexe können bei der Verknüpfung von $\{Li_4O_4\}$-Cuban-Einheiten helfen. Mit dem Organometallkomplex $[(\eta^4\text{-chinon})Rh(cod)]^-$ wurde ein einzigartiger doppelt verbrückter Komplex aufgebaut, bei dem jede Cubaneinheit an einer Ecke ein Chinon-Sauerstoffatom enthält. Details beschreiben D. A. Sweigart et al. auf den folgenden Seiten.

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Lithium Alkoxide $\{Li_4O_4\}$ Cubanes Bridged by Rhodium–Quinonoid Organometalloligands**

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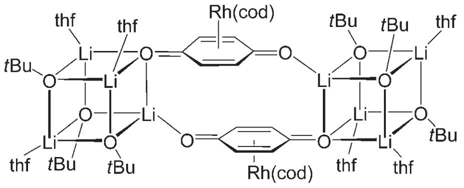
Organolithium reagents with alkoxide and similar oxygen-donor ligands frequently aggregate in aprotic solvents into rectangular $\{Li_2O_2\}$ and cubic $\{Li_4O_4\}$ fragments.[1–3] Lithium $\{Li_4O_4\}$ cubane species are especially prevalent and have been extensively investigated because of the great importance of organolithium reagents in organic synthesis.[1–2] Herein, we report the synthesis and characterization of the novel lithium cubane aggregate **1**, which possesses two unprecedented features: 1) $\{Li_4O_4\}$ units that incorporate a quinone oxygen-donor atom at one of the corners and 2) $\{Li_4O_4\}$ units bridged by two rhodium $[(\eta^4\text{-benzoquinone})Rh(cod)]^-$ (cod = cyclooctadiene) organometalloligands.



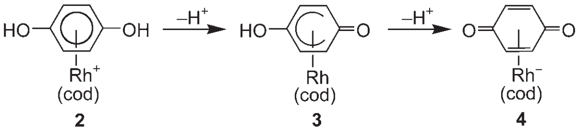
$[Li_4(OtBu)_3(thf)_3(\eta^4\text{-benzoquinone})Rh(cod)]_2$

1

It is known that Li_4O_4 cubanes can be linked or bridged by sharing a corner oxygen-donor atom. Bridged structures are also known in which the organic moiety attached to a cubane corner oxygen atom either covalently links to an oxygen atom in a second cubane or provides a donor atom that coordinates to a lithium corner in a second cubane. Examples of bridging units in these categories include carbonate and benzamide aza enolates.[4] Cubane fragments can also be linked together by "external" multifunctional donors that coordinate to two or more lithium corners.[4c,5] In these cases, the cubanes function as so-called secondary building units (SBUs) that self-assemble in the presence of multifunctional ligands or spacers to generate main-group metal-coordination networks. Spacers utilized in this manner include chloride, tetramethylethylenediamine (TMEDA), and *p*-dioxane.

Compound **1** reported herein is unique in that the bifunctional ligand that connects the cubane units is a transition-metal complex. As discussed below, it is likely that supramolecular structures analogous to **1** are accessible with a variety of transition-metal fragments.

The starting materials for the synthesis of **1** consisted of LiO*t*Bu in THF and the recently reported quinonoid complex $[(\eta^6\text{-hydroquinone})Rh(cod)]^+$ (**2**).[6] π-Coordination of a metal center to hydroquinone is known to greatly facilitate deprotonation, which is accompanied by electron transfer to the metal center and changes in the hapticity of the quinonoid ring.[6,7] In the case of **2**, neutral η^5-semiquinone and anionic η^4-quinone complexes **3** and **4**, respectively, are formed as shown in Scheme 1. π-Bonded quinone complexes analogous to **4** have already found significant applications in the catalysis of aldehyde arylation (rhodium as the metal) and in the formation of metal–organometallic coordination networks (manganese as the metal).[6,8] Herein, it is shown that the rhodium–quinone complex **4** reacts with LiO*t*Bu in THF to afford a novel structural motif in which a quinone oxygen atom functions as a pseudo butoxide ligand in a $\{Li_4O_4\}$ cubane unit, while the other quinone oxygen atom links to a lithium atom in a second companion cubane unit.



Scheme 1. Deprotonation of a π-bonded rhodium–hydroquinone complex.

Deprotonation of **2** in THF at room temperature with a fivefold excess of LiO*t*Bu led to a homogeneous yellow solution that slowly deposited crystals of **1** when stored at −15 °C for a period of weeks. The X-ray structure of **1** is shown in Figure 1. Each of the two $\{Li_4O_4\}$ cubanes contains three butoxide oxygen atoms and one quinone oxygen atom. Three thf ligands and an "external" quinone oxygen atom complete the pseudo tetrahedral coordination at each cubane lithium center. The quinonoid ring in **1** adopts a boat conformation with the phenolic carbon atoms C1 and C4 bent out of the C2-C3-C5-C6 diene plane away from the rhodium center by 10 and 13°, respectively. As a consequence, the {Rh(cod)} fragment is only weakly bonded to C1 and C4, and the overall structure is perhaps best described as an η^4-quinone. The relatively short C1−O1 and C4−O2 bond lengths of 1.29 and 1.26 Å support this interpretation.

The Li−O bond lengths in **1** are all in the typical 1.8–2.0 Å range, except for Li1−O1 which is much larger at 2.36(2) Å.

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

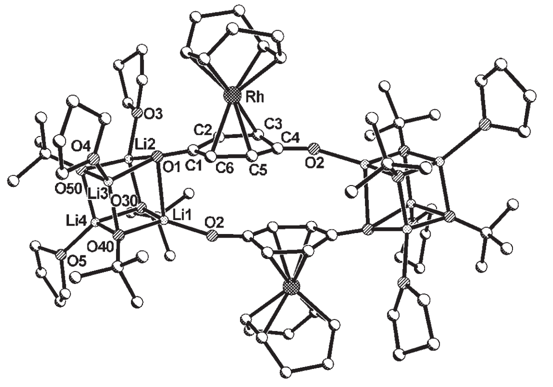

Figure 1. Crystal structure of **1** (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh-C1 2.44(1), Rh-C2 2.30(1), Rh-C3 1.22(1), Rh-C4 2.41(1), Rh-C5 2.27(1), Rh-C6 2.28(1), C1-O1 1.29(1), C4-O2 1.26(1), Li1-O1 2.36(2), Li1-O2 1.84(2), Li1-O30 1.86(2), Li1-O40 1.95(2), Li2-O1 1.97(2), Li2-O3 1.98(2), Li2-O30 1.92(2), Li2-O50 1.88(2), Li3-O1 2.03(2), Li3-O4 1.99(2), Li3-O40 1.92(2), Li3-O50 1.93(2), Li4-O5 1.99(2), Li4-O30 1.95, Li4-O40 1.95(2), Li4-O50 1.99(2); Li2-O1-Li3 83(1), Li2-O50-Li3 88(1), O1-Li2-O50 95(1), O1-Li3-O50 92(1), Li1-O30-Li4 83(1), Li1-O40-Li4 81(1), O30-Li1-O40 99(1), O30-Li4-O40 96(1), C1-O1-Li1 97(1), O1-Li1-O2 107(1).

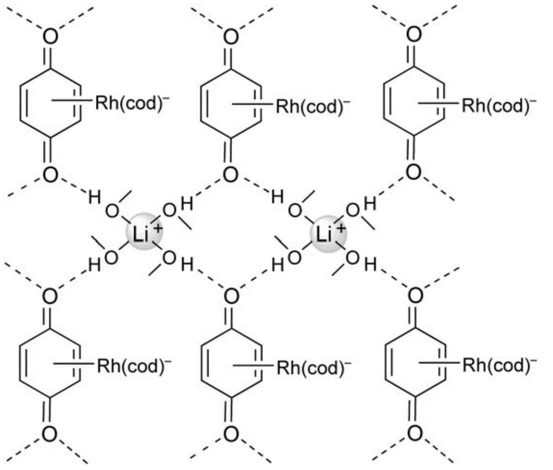

Figure 2. Hydrogen-bonding network in **5**.

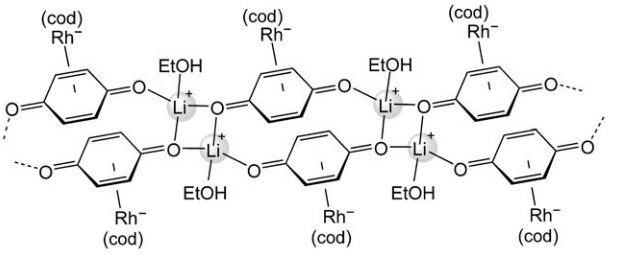

Figure 3. One-dimensional metal–organometallic coordination network **6**.

The consequence of the long Li1–O1 bond is that the O1 corner of the cubanes bends out of the O1-Li2-O50-Li3 face with a dihedral angle of 13°. The opposite face of the cubane, Li1-O30-Li4-O40, is planar to within 1°. The 13° bending of the cubane O1 corners effectively increases the separation of the two bridges from each other, which is probably the reason for the approximate 0.4-Å elongation of the Li1–O1 bond beyond that typically found in $\{Li_4O_4\}$ structures. The C1–O2 separation in **1** is just 3.1 Å, and the quinone rings partially eclipse, with a 3.2-Å ring-to-ring separation which indicates fairly strong π–π stacking interactions.[8,9] If the Li1–O1 bond length was similar to the others (ca. an average of 1.95 Å), the bridge-to-bridge separation would be greatly decreased, thus necessitating significantly different angles from those observed to avoid repulsive interactions between the bridges. In terms of the thermodynamic driving force, it is apparent that having a long Li1–O1 bond is the preferred compromise in the generation of the observed doubly bridged assembly.

To explore possible chemical processes relevant to the formation of **1**, a solution of complex **2** in THF with a fivefold excess of LiO*t*Bu was evaporated before any cubane dimer **1** had formed (one hour after mixing). The residue was washed with diethyl ether and THF. A portion of the residue dissolved in methanol afforded the salt $[Li(MeOH)_4][(\eta^4\text{-quinone})Rh(cod)]$ (**5**). The X-ray structure of **5** shows that it consists of the two-dimensional hydrogen-bonded network illustrated in Figure 2. The hydrogen bonds between the quinone oxygen atoms and the methanol ligands have average O···O distances of 2.63 Å.

The fundamentally different product **6** (Figure 3) was afforded by dissolution of the residue in ethanol instead of methanol. Complex **6** is a one-dimensional metal–organometallic coordination network (MOMN) containing rectangular $\{Li_2O_2\}$ units linked by anionic $[(\eta^4\text{-quinone})Rh(cod)]^-$ organometalloligand. Each lithium ion is bonded to three quinone oxygen atoms and one ethanol molecule. One quinone oxygen atom from each spacer molecule is bidentate and forms part of the $\{Li_2O_2\}$ ring, whereas the other oxygen atom is unidentate and propagates the network by coordinating "externally" to a lithium ion.

The X-ray structure of **6** shows that the $\{Li_2O_2\}$ rings are nearly square (internal angles: 84 and 96°) and the Li–O bond lengths average 1.94 Å, which is in the range found for most of the Li–O bonds in the cubane units in **1** (other than Li1–O1). The coordinated ethanol ligand in **6** is not hydrogen bonded. The addition of one equivalent of 1,1-bis(4-hydroxyphenyl)-methane to **6** in ethanol resulted in displacement of the quinone monodentate oxygen atom from the lithium ion and afforded the new two-dimensional network **7**, in which polymeric one-dimensional $\{Li_2O_2\}$ chains are linked through hydrogen-bonding interactions (Figure 4). The X-ray structures of **6** and **7** are given in the Supporting Information.

Having established the viability of $\{Li_4O_4\}$ and $\{Li_2O_2\}$ aggregates that incorporate a rhodium–η^4-quinone organometalloligand at a vertex, we next used NMR spectroscopy to probe any dynamic behavior that may occur. A solution of the slightly soluble cubane **1** in $[D_8]$THF gave no evidence for dynamic processes on the NMR timescale at room temperature. However, a solution of hydroquinone complex **2** in THF with ten equivalents of LiO*t*Bu, from which the **1** evolves over a period of days/weeks (see below), shows site exchange of the quinone hydrogen atoms in the deprotonated

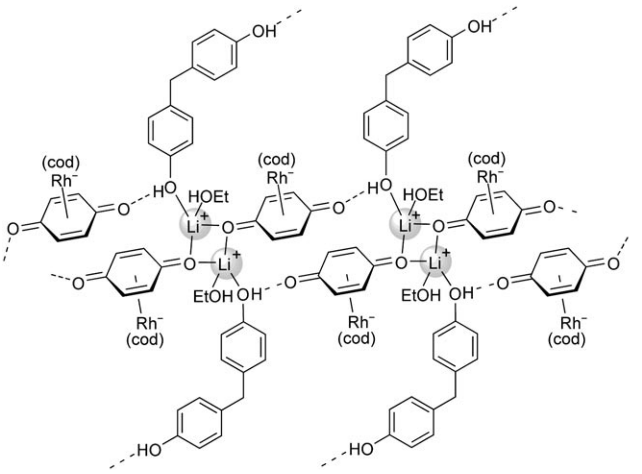

Figure 4. Two-dimensional metal–organometallic coordination network **7**.

complex $[(\eta^4\text{-benzoquinone})\mathrm{Rh(cod)}]^-$, which is rapidly formed in situ according to Scheme 1. The NMR spectra of the quinone hydrogen atoms is illustrated in Figure 5 for the temperature range 10 to −30 °C. Simulations[10] of the observed two-site exchange process gave a very good fit to the Eyring equation, with the following activation parameters: $\Delta H^{\neq} = 84\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S^{\neq} = 110\,\mathrm{J\,K^{-1}\,mol^{-1}}$. The process that occurs almost certainly involves differential lithium coordination to the quinone oxygen atoms, possibly as depicted in Figure 6. The ligands (L) likely include thf, although the butoxide groups may also be involved.

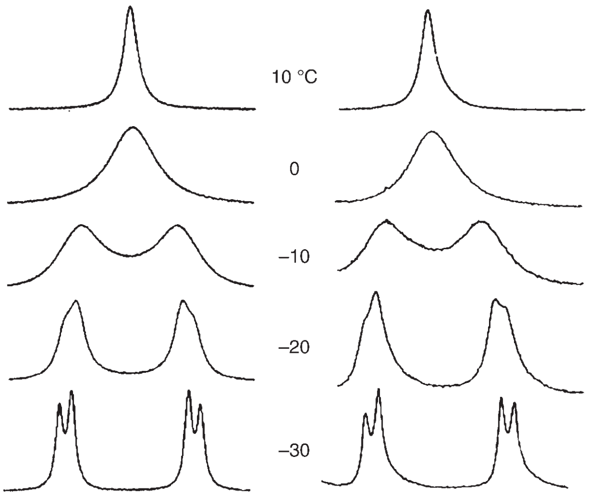

Figure 5. Simulated (left) and observed (right) ^{1}H NMR spectra of the quinone hydrogen atoms in a solution of $[(\eta^4\text{-benzoquinone})\mathrm{Rh(cod)}]$ in $[\mathrm{D_8}]$THF with excess LiO*t*Bu.

The actual exchange may be more complex than that illustrated, for example, species with a $\{\mathrm{Li_2O_2}\}$ core may be present. The highly positive entropy of activation is suggestive of solvent loss in the transition state to give an activated complex such as that illustrated in Figure 6. Whatever the specific details, the NMR behavior demonstrates that the quinone oxygen atoms can rapidly change their mode of coordination to the lithium centers in the species that exists prior to the formation of the cubane aggregate **1**.

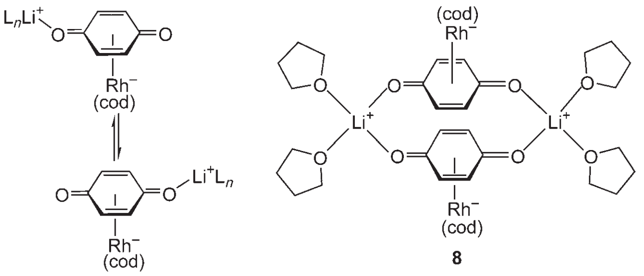

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Figure 6. Dynamic coordination of the quinone oxygen atoms to lithium in a solution of THF, possibly via activated complex **8**.

In conclusion, it has been demonstrated that lithium alkoxide aggregates[11] can be synthesized that have two $\{\mathrm{Li_4O_4}\}$ cubane units bridged by a quinone organometalloligand. The key to the construction of this discrete species, as well as related polymeric $\{\mathrm{Li_2O_2}\}$ species, is the ability of the quinone oxygen atoms in $[(\eta^4\text{-quinone})\mathrm{Rh(cod)}]^-$ to function as ligands, both as part of and external to the cubane aggregate itself. The methodology described herein should be readily extendable to anionic π-bonded quinone complexes of a variety of transition metals.

Experimental Section

All reactions were carried out under $\mathrm{N_2}$ in flame-dried glassware. THF and diethyl ether solvents were HPLC grade. $[\{\mathrm{RhCl(cod)}\}_2]$ was purchased from Strem Chemicals, Inc. The ^{1}H NMR spectra were recorded on a 300 MHz Bruker spectrometer. Elemental analyses were performed by Quantitative Technologies Inc. (New Jersey, USA).

$[\{\mathrm{Li_4}(t\mathrm{OBu})_3(\mathrm{thf})_3(\eta^4\text{-benzoquinone})\mathrm{Rh(cod)}\}_2]$ (**1**): $[(\eta^6\text{-hydroquinone})\mathrm{Rh(cod)}]\mathrm{BF_4}$ (**2**; 0.10 g, 0.25 mmol) in HPLC-grade THF (7 mL) was placed in a flame-dried 50-mL Schlenk flask and LiO*t*Bu (0.10 g, 1.25 mmol) was added with stirring at room temperature. A yellow precipitate of the neutral $[(\eta^5\text{-semiquinone})\mathrm{Rh(cod)}]$ formed initially, but dissolved after addition of the base was complete. The homogeneous yellow solution was stirred for 1 h and placed in a refrigerator at −15 °C for several weeks, during which time yellow crystals of **1** formed in 68 % yield of the isolated product (0.096 g, 0.085 mmol). ^{1}H NMR ($[\mathrm{D_8}]$THF): $\delta = 5.64$ (d, $J = 7.0$ Hz, benzoquinone, 4 H), 4.53 (d, $J = 6.9$ Hz, benzoquinone, 4 H), 4.27 (br, cod, 8 H), 2.25 (m, cod, 8 H), 2.01 (m, cod, 8 H), 1.15 ppm (s, *t*BuO, 54 H). Washing **1** with THF and drying under vacuum produced **5**, which was characterized by NMR (see below) and elemental analysis ((%) calcd for $\mathrm{C_{14}O_2H_{16}Rh_1Li_1}$: C 51.56, H 4.95; found: C 51.55, H 4.93).

Preliminaries for the synthesis of complexes **5**–**7**: **2** and LiO*t*Bu were combined as described above at room temperature, stirred for 1 h, and the solvent removed with a rotary evaporator. The residue was vacuum dried for 30 min, washed with diethyl ether, washed with THF, and dried again under vacuum. The residue, which contained an equivalent of $\mathrm{LiBF_4}$, was obtained in 56 % yield (0.057 g, 0.14 "mmol"). ^{1}H NMR ($[\mathrm{D_6}]$DMSO): $\delta = 4.96$ (s, benzoquinone, 4 H), 3.51 (br, cod, 4 H), 2.20 (m, cod, 4 H), 1.98 ppm (m, cod, 4 H); elemental analysis (%) calcd for $\mathrm{C_{14}O_2H_{16}Rh_1Li_2B_1F_4}$: C 40.05, H 3.84; found: C 40.04, H 4.17.

$[\mathrm{Li(MeOH)_4}][\mathrm{Rh}(\eta^4\text{-benzoquinone})(\mathrm{cod})]$ (**5**): The residue described above (20 mg) was dissolved in methanol (1 mL), filtered through a celite pad, and transferred to a 5-mL vial. THF (3 mL) was carefully added to this solution as a layer, and the solution placed in a refrigerator (−15 °C) for three weeks. The yellow crystals formed in a yield of 55 % (0.011 g). ^{1}H NMR (CD_3OD): $\delta = 5.61$ (s, benzoquinone ring, 4 H), 3.94 (br, cod, 4 H), 2.33 (m, cod, 4 H), 2.08 ppm (m, cod, 4 H); elemental analysis (%) after drying under vacuum calcd for $C_{14}O_2H_{16}Rh_1Li_1$: C 51.56, H 4.95; found: C 51.50, H 4.60.

[Li(EtOH)(η^4-benzoquinone)Rh(cod)] (**6**): The residue described above (25 mg) was dissolved in ethanol (2 mL), filtered through a celite pad, and transferred to a 5-mL vial. After standing for two weeks at room temperature, yellow crystals had formed and were collected in a yield of 90 % (0.023 g). ^{1}H NMR(CD_3OD): $\delta = 5.61$ (s, benzoquinone, 4 H), 3.94 (br, cod, 4 H), 3.59 (q, $J = 5.2$ Hz, EtOH, 2 H), 2.33 (m, cod, 4 H), 2.08 (m, cod, 4 H), 1.16 ppm (t, $J = 5.2$ Hz, EtOH, 3 H); elemental analysis (%) after drying under vacuum calcd for $C_{14}O_2H_{16}Rh_1Li_1$: C 51.56, H 4.95; found: C 51.45, H 5.15.

[Li(EtOH)(1,1-bis(4-hydroxyphenyl)methane)(η^4-benzoquinone)Rh(cod)] (**7**): The residue described above (25 mg) and 1,1-bis(4-hydroxyphenyl)methane (18 mg) were dissolved in ethanol (2 mL), filtered through a celite pad, and transferred to a 5-mL vial. After standing for two weeks at room temperature, yellow crystals had formed and were collected in a yield of 64 % of the isolated product (0.026 g). After drying under vacuum (loss of EtOH): ^{1}H NMR ([D$_6$]DMSO): $\delta = 9.10$ (s, 2 H, phenolic OH, 2 H), 6.95 (d, J = 8.1 Hz, aryl ring, 4 H), 6.64 (d, J = 8.3 Hz, aryl ring, 4 H), 4.95 (s, benzoquinone, 4 H), 3.68 (s, CH_2, 2 H), 3.50 (br, cod, 4 H), 2.20 (m, cod, 4 H), 1.99 ppm (m, cod, 4 H); elemental analysis (%) calcd for $C_{27}O_4H_{28}Rh_1Li_1$: C 61.61, H 5.36; found: C 61.51, H 5.91.

Dynamic NMR study: **2** (5.0 mg, 0.012 mmol) was dissolved in [D$_8$]THF (1.5 mL) under N_2 in an NMR tube, and LiO*t*Bu (9.8 mg, 0.12 mmol) was added at room temperature. The NMR tube was shaken to generate a homogeneous yellow solution, which was then used to record NMR spectra over the temperature range −78–25 °C.

Crystallography: X-ray data collection was carried out using a Bruker single-crystal diffractometer equipped with an APEX CCD area detector and controlled by SMART version 5.0. Collection was done either at 100 K. Data reduction was performed by SAINT version 6.0 and absorption corrections were applied by SADABS version 2.0. The structures were typically determined by direct methods and refined on *F* squared by use of programs in SHELXTL version 5.0. Most hydrogen atoms appeared in a difference map, or they were generally inserted in ideal positions, riding on the atoms to which they are attached. CCDC-281279 (**1**), -281276 (**5**), -281277 (**6**), and -281278 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for **1**: $C_{38}H_{67}Li_4O_8Rh$, $M_r = 782.59$, triclinic, $P\bar{1}$, $a = 10.116(3)$, $b = 14.625(4)$, $c = 16.304(4)$ Å, $\alpha = 101.790(5)$, $\beta = 105.855(5)$, $\gamma = 107.430(4)°$, $V = 2103.3(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.236$ g cm^{-3}, $F_{000} = 832$, $\mu = 0.451$ mm^{-1}, $\theta = 1.54$–$21.04°$, reflections collected 13816, independent reflections 4499 ($R_{int} = 0.1682$), GOF = 1.008, $R_1 = 0.0752$, $wR_2 = 0.1633$, largest diffraction peak/hole 0.826/−0.879 Å^{-3}.

Crystal data for **5**: $C_{18}H_{32}LiO_6Rh$, $M_r = 454.29$, monoclinic, $P2/c$, $a = 11.5682(12)$, $b = 8.0923(8)$, $c = 12.2963(13)$ Å, $\beta = 105.855(5)°$, $V = 1032.97(18)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.461$ g cm^{-3}, $F_{000} = 472$, $\mu = 0.855$ mm^{-1}, $\theta = 1.96$–$26.42°$, reflections collected 9033, independent reflections 1956 ($R_{int} = 0.0876$), GOF = 0.961, $R_1 = 0.0420$, $wR_2 = 0.0889$, largest diffraction peak/hole 1.640/−0.726 Å^{-3}.

Crystal data for **6**: $C_{16}H_{22}LiO_3Rh$, $M_r = 372.19$, triclinic, $P\bar{1}$, $a = 6.962(2)$, $b = 7.876(3)$, $c = 14.236(5)$ Å, $\alpha = 75.933(7)$, $\beta = 85.810(8)$, $\gamma = 85.434(8)°$, $V = 753.5(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.640$ g cm^{-3}, $F_{000} = 380$, $\mu = 1.138$ mm^{-1}, $\theta = 2.67$–$23.23°$, reflections collected 2619, independent reflections 2619 ($R_{int} = 0.0000$), GOF = 0.950, $R_1 = 0.0932$, $wR_2 = 0.2161$, largest diffraction peak/hole 1.365/−1.148 Å^{-3}.

Crystal data for **7**: $C_{29}H_{34}LiO_5Rh$, $M_r = 572.41$, triclinic, $P\bar{1}$, $a = 9.6279(7)$, $b = 10.4545(7)$, $c = 14.0917(10)$ Å, $\alpha = 79.5920(10)$, $\beta = 85.1340(10)$, $\gamma = 65.3330(10)°$, $V = 1267.69(15)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.500$ g cm^{-3}, $F_{000} = 592$, $\mu = 0.711$ mm^{-1}, $\theta = 1.47$–$26.42°$, reflections collected 13673, independent reflections 10106 ($R_{int} = 0.0336$), GOF = 1.027, $R_1 = 0.0506$, $wR_2 = 0.1028$, largest diffraction peak/hole 1.005/−0.565 Å^{-3}.

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Keywords: cubanes · lithium · organometalloligands · quinones · rhodium

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