Silyl ether **19a** (150 mg, 0.28 mmol), ethyl iodoacetate (0.042 mL, 0.35 mmol), and $Bu_3SnSnBu_3$ (0.017 mL, 0.028 mmol) were dissolved under argon in benzene (1.1 mL). Irradiation for 16 hours and removal of the solvent afforded the crude product, which was purified by flash column chromatography (SiO_2, Et_2O/pentane 1/20) to give **21** (110 mg, 87%) as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 0.86$ (t, $J = 7.1$, 3H, CH_3), 1.06 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 1.59–1.67 (m, 1H), 1.77–1.83 (m, 1H), 2.19 (t, $J = 7.4$, 2H), 2.49–2.54 (m, 1H, SiCH), 3.03 (d, $J = 13.3$, 1H, PhCH), 3.78–3.89 (m, 2H, CH_2O), 7.06–7.10 (m, 1H, aromat.), 7.11–7.28 (m. 10H, aromat.), 7.81–7.84 (m, 2H, aromat.), 7.91–7.94 (m, 2H, aromat.); ^{13}C NMR (125 MHz, $CDCl_3$): 14.19 (CH_3), 24.75 (CH_2), 25.53 (CH_3), 28.74 (CH), 30.08 (CH_3), 35.09 (CH_2), 59.99 (CH_2), 62.66 (CH), 82.14 (C), 127.10 (CH), 127.94 (CH), 128.29 (CH), 128,39 (CH), 128.42 (CH), 130.47 (CH), 130.53 (CH), 134.03 (C), 135.24 (CH), 135.66 (CH), 135.93 (C), 140.47 (C), 172.46 (C). EI-MS: m/z (%): 444.2 (3, M^+), 388.2 (9), 386.2 (100), 295.1 (12), 227.1 (81), 199.1 (63), 183.1 (53). C,H analysis calcd for $C_{28}H_{32}O_3Si$ (444.6): C 75.64, H 7.25, O 10.79, Si 6.32; found: C 75.41, H 7.34.

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[10] Silyl ether **1** was prepared according to known procedures[11] from 2-bromobenzyl alcohol and 1-chloro-2,2-dimethyl-1,1,2-triphenyldisilane (78% yield). Compound **2** was obtained from the corresponding chlorosilane (imidazole, DMF, 87%). Stannylated silyl ether **3** was synthesized from (diphenylsilyl)trimethyl tin chloride[12] and 2-iodobenzyl alcohol (85%).

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[18] So far the origin of the reduction product is not clear. When the UMCT reaction was conducted under higher dilution (0.01M) no reduction product **11** was observed; however, unidentified side products were formed.

[19] Since no authentic sample of the desired cyclization product was available, it was not possible to determine by NMR analyis whether the UMCT product was formed in small quantities. Initiation of the UMCT reaction with Bu_3SnH did not provide better results.

[20] Interestingly, the presence of the reduction product in analogy to the formation of **11** could not be observed.

[21] The mediocre yield is due to partial decomposition of the products during chromatography.

[22] The diastereoisomers could not be separated. We could not determine which isomer was formed in excess.

[23] The relative configuration was assigned by NOE experiments.

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The Weak-Link Approach to the Synthesis of Inorganic Macrocycles[**]

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Inorganic and organometallic macrocycles have been topics of intense study with implications for host–guest chemistry, modeling of biological systems, catalysis, and even molecular electronics.[1] These structures can vary in size, shape (rings, squares, rectangles, and cylinders), and the number of metal centers that comprise the macrocycle.[2] One of the most popular synthetic strategies for macrocycles is the "molecular box, square, or rectangle strategy", which was pioneered by Fujita et al.[3] and has now been utilized by many;[4] this strategy uses conformationally rigid ligands bound to metal centers in a *cis* fashion to form tetranuclear complexes in exceptionally high yields. Although this strategy works well for rigid ligands, it will undoubtedly fail with flexible ones because of competing oligimerization and polymerization reactions.

Herein we report a new, general, high-yield (>95%) strategy for synthesizing homobimetallic macrocycles with chemically tailorable cavity properties from flexible ligands (Scheme 1). We refer to this strategy as the "weak-link approach" to the synthesis of inorganic macrocycles. In 1996 Steel and co-workers showed that the reaction between Ag^I and an aromatic ligand with multiple ligating sites resulted in the formation of dimetallocyclophanes.[5] These solid-state structures, which do not remain intact in solution, have ether

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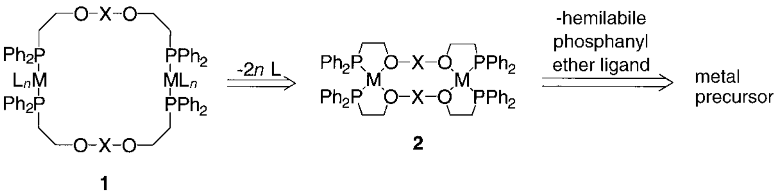


Scheme 1. Retrosynthetic outline of the weak-link strategy for the synthesis of inorganic macrocycles. M = late transition metal, X = aromatic group.

oxygen atoms weakly coordinated to the Ag^{I} ions and exhibit arene–arene π-stacking interactions. Our strategy as presented in Scheme 1 takes advantage of 1) Steel's observation that 1,4-aryl diethers can bind weakly to late transition metals to form bimetallic compounds,[5] 2) hemilabile ligands,[6] and 3) $\pi-\pi$ interactions between two aromatic groups that have been strategically incorporated into the ligands.

With this strategy, a target macrocyclic structure **1** is condensed in a retrosynthetic fashion to form the polycyclic compound **2**, which is made up of a series of fused thermodynamically stable rings with several strong (Rh–P) and weak (Rh–O, $\pi-\pi$ interactions) chemical links (Scheme 1). This latter structure can be prepared with the appropriate hemilabile ligand and a metal compound, and once generated it can be opened into a series of structurally different macrocycles by adding a variety of ligands that can break its weak links. To demonstrate the viability of this strategy, we prepared the new hemilabile phosphanyl alkyl ether ligand **3** (1,4-bis[2-(diphenylphosphanyl)ethoxy]-2,3,5,6-tetramethylbenzene). It is synthesized by allowing dihydroxydurene[7] to react with two equivalents of 2-chloroethyl *p*-toluenesulfonate to form 1,4-bis[2-chloroethoxy]-2,3,5,6-tetramethylbenzene, followed by displacement of the chlorine atoms by -PPh$_2$ with KPPh$_2$ (overall yield 72 %). Spectroscopic data for solutions of **3** are completely consistent with its proposed structure.[8] Significantly, ligand **3** reacts in a 1:1 stoichiometric ratio with a Rh^{I} precursor (formed by the reaction between [{RhCl(cot)$_2$}$_2$] (cot = cyclooctene) and AgBF$_4$ in CH$_2$Cl$_2$) to provide the new, fused polycycle **4**[9] in almost quantitative yield (> 95 %, Scheme 2). Consistent with this structural formulation, the ^{31}P NMR spectrum of **4** exhibits a resonance at $\delta = 61$ ($J_{\mathrm{Rh,P}} = 213$ Hz), which is characteristic of a Rh^{I} complex with a square-planar, *cis*-phosphane, *cis*-ether coordination geometry.[10] Mass spectrometry and ^{1}H NMR spectroscopy also support this structural formulation.[9] In addition, the solid-state structure of **4**, as determined by a single-crystal X-ray diffraction study, is consistent with its assigned solution structure (Figure 1).[11] Complex **4** is made up of a series of fused, thermodynamically favorable five-membered rings.[12] The two durenylene moieties in **4** are coplanar and separated by only 3.32 Å, which is similar to the separation between carbon layers in graphite (3.35 Å)[12] and implies that π-stacking interactions play a role in stabilizing its structure. The Rh$\cdots$Rh distance of 8.36 Å in **4** is clearly nonbonding.

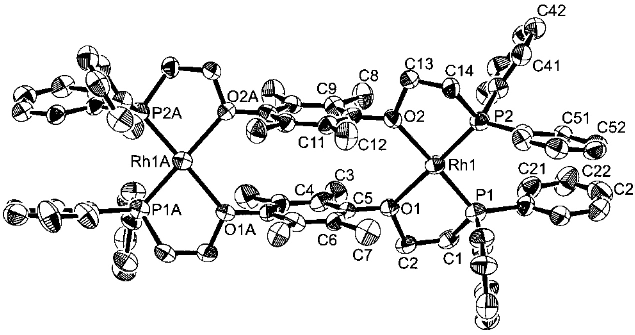
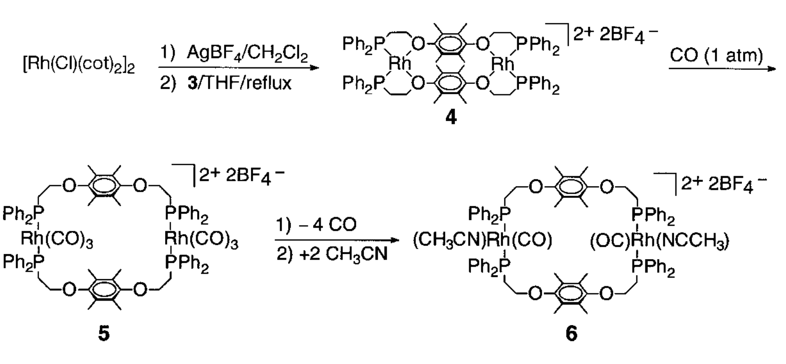


Figure 1. ORTEP drawing of complex **4** with thermal ellipsoids drawn at the 30 % probability level. Hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Rh(1)–Rh(1a) 8.362(10), Rh(1)–P(1) 2.169(3), Rh(1)–P(2) 2.172(3), Rh(1)–O(1) 2.247(7), Rh(1)–O(2) 2.217(7); P(1)-Rh(1)-P(2) 98.35(12), P(1)-Rh(1)-O(1) 81.3(2), P(1)-Rh(1)-O(2) 174.8(2), P(2)-Rh(1)-O(1) 173.9(2), P(2)-Rh(1)-O(2) 82.3(2), O(1)-Rh(1)-O(2) 98.7(2).

The weak Rh–O links in **4** can be broken with the more strongly coordinating ligand CO (1 atm) in CH$_2$Cl$_2$ to form the 26-membered macrocycle **5** (Scheme 2). Compound **5** was characterized in CD$_2$Cl$_2$ by ^{1}H and ^{31}P NMR spectroscopy.[13] The latter, which exhibits a doublet at $\delta = 21$ ($J_{\mathrm{Rh,P}} = 88$ Hz), is highly diagnostic of a complex with trigonal-bipyramidal Rh^{I}.[14] Macrocycle **5** can be synthesized in one pot without isolating or purifying macrocycle **4** due to the high yields of all the synthetic steps involved.

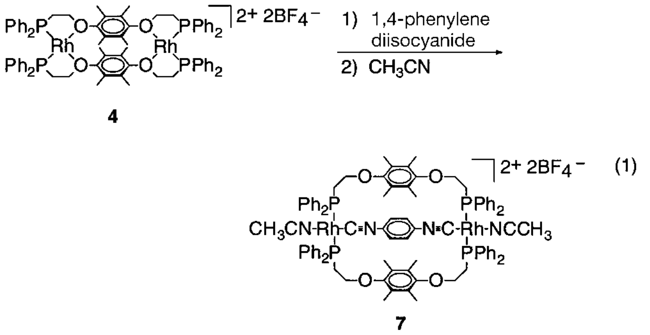
Removal of solvent and CO from **5** under vacuum and dissolution of the product in acetonitrile results in the formation of the CH$_3$CN adduct **6**. This compound was spectroscopically characterized,[15] and all data are consistent with the formulated structure. For example, the IR spectrum of **6** in CH$_2$Cl$_2$ exhibits two ν_{CO} bands at 2008 (s) and 1971 cm^{-1} (w), and its ^{1}H NMR spectrum in CD$_2$Cl$_2$ shows a resonance at $\delta = 1.62$ for the coordinated CH$_3$CN ligands. The ^{31}P NMR spectrum of **6** in CD$_2$Cl$_2$ displays a single resonance at $\delta = 20.5$ (d) with a coupling constant ($J_{\mathrm{Rh,P}} = 117$ Hz) that compares well with that reported for the analogous mononuclear compound [Rh(PPh$_3$)$_2$(CO)(CH$_3$CN)][HC(SO$_2$CF$_3$)$_2$] ($J_{\mathrm{Rh,P}} = 119$ Hz).[16]

Interestingly, exposure of **4** to one equivalent of 1,4-phenylene diisocyanide in CD$_2$Cl$_2$ leads to the immediate formation of an uncharacterized or-



Scheme 2. Synthesis of compounds **4**–**6**.

ange precipitate, which is presumably an oligomer or polymer cross-linked by the bifunctional 1,4-phenylene diisocyanide. Introduction of ten equivalents of CH_3CN to a suspension of the precipitate results in the quantitative formation of **7** [Eq. (1)].[17] Compound **7** was characterized by ^1H, ^{31}P, and NOE difference NMR spectroscopy. The proton resonances of the bound 1,4-phenylene diisocyanide have shifted 1.4 ppm upfield from those for the metal-free compound, which is indicative of π–π interactions between the aromatic groups of the macrocycle and the complexed molecule.[18] The NOE difference spectrum shows an interaction between the protons of the complexed 1,4-phenylene diisocyanide and the methyl protons of the macrocycle. This NOE interaction clearly indicates that the 1,4-phenylene diisocyanide is bound inside the macromolecular cage. Furthermore, the solid-state structure of **7**, which was determined by a single-crystal X-ray diffraction study, is consistent with our structural formulation of **7** in solution (Figure 2).[19] In the solid state, the aromatic groups in **7** are uniformly separated by a distance of 4.24 Å, and the angles between the planes of the arenes are within 3.1° of being coplanar. The 1,4-phenylene diisocyanide is clearly situated inside the cage and bound to each Rh^I center.



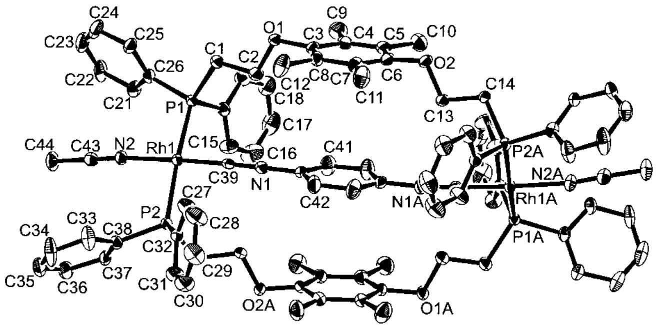


Figure 2. ORTEP drawing of complex **7** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Rh(1)–Rh(1a) 11.598(13), Rh(1)–P(1) 2.343(6), Rh(1)–P(2) 2.326(6), Rh(1)–N(2) 2.06(2), Rh(1)–C(39) 1.85(2); P(1)-Rh(1)-P(2) 170.1(2), C(39)-Rh(1)-N(2) 177.4(10), N(2)-Rh(1)-P(2) 90.1(6), N(2)-Rh(1)-P(1) 89.8(6), C(39)-Rh(1)-P(2) 88.8(7), C(39)-Rh(1)-P(1) 91.0(7).

We have demonstrated the utility of this new synthetic strategy for the preparation of a novel class of homobimetallic macrocycles from flexible ligands in high yields and in one pot. These macrocycles contain Rh^I centers with steric and electronic environments that can be controlled through choice of ancillary ligands. Furthermore, we have taken advantage of the size of the macrocycle and the reactivity of the metal centers to demonstrate how such complexes can be used to direct the sequestration of bifunctional molecules.

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[8] Compound **3**: ^1H NMR (CD_2Cl_2): $\delta = 7.46$ (m, 8H, PPh_2), 7.34 (m, 12H, PPh_2), 3.68 (q, 4H, OCH_2), 2.66 (t, 4H, PCH_2), 2.33 (s, 12H, CH_3); $^{31}P\{H\}$ NMR (CD_2Cl_2): $\delta = -22$ (s); MS (EI) m/z: 590.2 (M^+).

[9] Compound **4**: ^1H NMR (CD_2Cl_2): $\delta = 7.51$ (m, 16H, PPh_2), 7.39 (t, 8H, PPh_2), 7.30 (t, 16H, PPh_2), 3.62 (m, 8H, OCH_2) 2.66 (m, 8H, PCH_2), 2.34 (s, 24H, CH_3); MS (FAB$^+$): m/z: 1473 ($M^+ - BF_4^-$).

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[11] a) Crystal structure data for **4** ($C_{76}H_{80}B_2F_8O_4P_4Rh_2$): trigonal, $P31c$, $a = 22.39145(5)$, $c = 26.4671(9)$ Å, $V = 12035.3(6)$ Å^3, $Z = 6$, $T = 218(2)$ K, $\rho_{calcd} = 1.292$ g cm^{-1}, $R(F) = 9.99\%$ for 8529 observed independent reflections ($3° \leq 2\theta \leq 56°$). b) Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666 (Frau S. Höhler-Schlimm); e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD- 380141 (**4**) and -380142 (**7**).

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[15] Compound **6**: ^1H NMR (CD_2Cl_2): $\delta = 7.72$ (m, 16H, PPh_2), 7.49 (m, 24H, PPh_2), 4.03 (m, 8H, PCH_2), 3.17 (m, 8H, OCH_2), 2.01 (s, 24H, CH_3), 1.62 (s, 6H, CH_3CN).

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[17] Compound **7**: ^1H NMR (CD_2Cl_2): $\delta = 7.70$ (m, 16H, PPh_2), 7.53 (m, 24H, PPh_2), 5.96 (s, 4H, 1,4-$(CN)_2C_6H_4$), 3.54 (m, 8H, OCH_2), 3.27 (m, 8H, PCH_2), 1.80 (s, 24H, CH_3), 0.99 (s, 6H, CH_3CN); $^{31}P\{H\}$ NMR (CD_2Cl_2): $\delta = 18$ (d, $J_{Rh,P} = 125.0$ Hz).

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[19] Crystal structure data for **7** ($C_{101}H_{122}B_2C_{12}F_8N_4O_7P_4Rh_2$): tetragonal, $P4_12_12$, $a = 16.6807(1)$, $c = 39.1582(1)$ Å, $V = 10895.6(1)$ Å^3, $Z = 4$, $T = 223(2)$ K, $\rho_{calcd} = 1.266$ g cm^{-1}, $R(F) = 7.33\%$ for 9088 observed independent reflections ($3° \leq 2\theta \leq 56°$).