Crown Ether-Substituted Indene and 3,4-Dimethylcyclopentadiene

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Several indene and cyclopentadiene derivatives have been synthesized, which are substituted with crown ethers, thereby creating ligands whose heterotopic faces have the ability to function as ligands in both organometallic and coordination chemistry. The syntheses of mono- and bis-*N*-3-indenylpropyl-substituted aza-12-crown-4 **4**, aza-15-crown-5 **5**, and diaza-18-crown-6 **6** ether compounds are described. However it was not possible to isolate stable η^5-bound metal complexes with **4**, **5**, or **6**. In an alternative approach 1-(2-aminoethyl)-3,4-dimethyl-cyclopenta-1,3-diene (**9**) has been prepared from 3,4-dimethylcyclopent-2-enone (**7**) via Knoevenagel condensation, followed by reduction of the $\alpha,\beta,\gamma,\delta$-unsaturated nitrile **8** with $LiAlH_4/AlCl_3$. Cyclization of **9** produced the first example of crown ether-substituted cyclopentadienes, *N*-[2-(3,4-dimethylcyclopenta-1,3-dienyl)ethyl]aza-12-C-4 (**10**) (12-C-4-HCp″), and as the result of a 2 + 2 addition, *N*,*N*′-bis[2-(3,4-dimethylcyclopenta-1,3-dienyl)ethyl]-1,13-diaza-24-crown-8 (**11**) (24-C-8-HCp''_2). Reaction of **10** with NaH, $(CO)_3W(CH_3CN)_3$, and CH_3I affords the η^5-bound complex (12-C-4-Cp″)$W(CO)_3CH_3$ (**12**), which in turn can complex Na^+ to give **13** (=$(\mathbf{12})_2{\cdot}Na^+BPh_4^-$).

Introduction

The chemistry of cyclopentadiene (HC_5H_5) and it's numerous substituted relatives[1] (e.g. HC_5Me_5 and indene) is inherently linked to the development of organometallic chemistry.[2] Crown ethers on the other hand are modern representatives of classical coordination chemistry.[3] Our interest in forging a link between these two major areas of chemistry is motivated by several attractive features, which might be offered by these ligands: (i) Attaching electrochemically active metallocenes results in redox-switchable crown ethers.[4] (ii) Ligands of this type will be able to occupy all coordination sites of a metal, thereby effectively encapsulating even large cations. (iii) The combination of a hard and soft metal center might result in cooperative behavior of the two metal centers.[5] (iv) Cations bound to the crown ether unit will polarize carbonyl ligands generating new reactivity patterns.[6]

We have linked these two branches of chemistry by designing crown ethers which carry a substituted cyclopentadiene (indene) in a pendant side arm.[7]

Results and Discussion

Two different synthetic strategies leading to N-substituted aza crowns were developed by Calverly and Dale[8] (A), Gokel et al.[9] (B) for aza-12-C-4, and by Gokel et al.[10] for diaza-18-C-6. The key material for both routes A and

A: $RNH_2 + I(CH_2CH_2O)_nCH_2CH_2I \rightarrow RNcrown$

B: $R'Br + HNcrown \rightarrow R'Ncrown$

B is the known monoindenyl compound **1**, which is available by the reaction of indene with 1,3-dibromopropane under phase-transfer conditions.[11] We found it possible to synthesize compounds **4** and **5** via alkylation (B) of aza-12-C-4 and aza-15-C-5 with compound **1**, albeit in moderate yield. However the synthesis of indenyl crown ethers **4** and **6** is more efficiently effected along route A (Scheme I). The transformation into the amine **3** is accomplished via the phthalimide **2** and its cleavage with hydrazine hydrate. The indenylamine **3** serves as the starting material for both the 12-membered aza crown **4** (yield 61%) and the 18-membered diaza crown **6** (yield 18%). As route B requires the synthesis of two different unsubstituted aza crowns, which both require a protection–deprotection sequence to obtain the free NH group, route A clearly is superior. Only when the unsubstituted aza crowns are directly accessible, as is the case for aza-15-C-5 and aza-18-C-6,[12] is the alkylation sequence more economic.

The investigations into the organometallic chemistry of **4**, **5**, and **6** were not met by success. It is possible to

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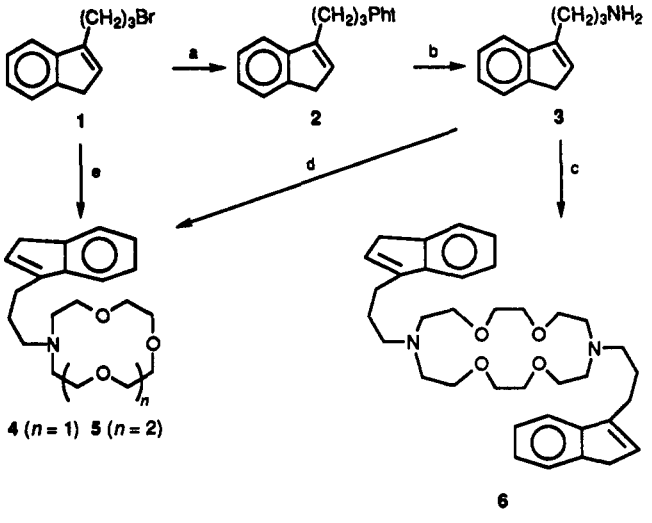
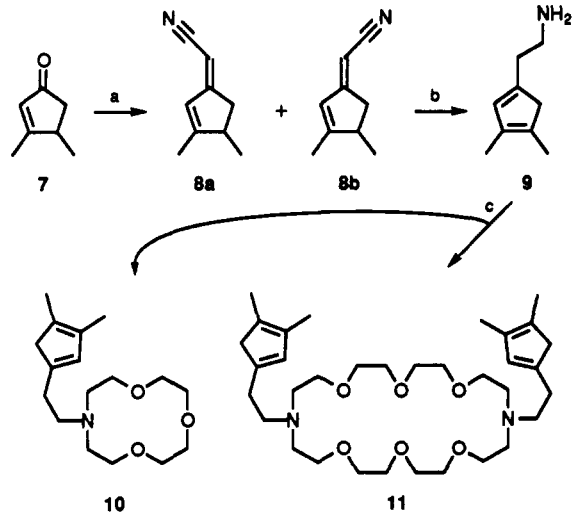
Scheme I[a]



[a] (a) Potassium phthalimide; (b) $N_2H_4 \cdot H_2O$; (c) $ICH_2CH_2(OC_2H_4)_2I$; (d) $ICH_2CH_2(OC_2H_4)_3I$; (e) aza-12-C-4 or aza-15-C-5.

Scheme II[a]



[a] (a) $CH_2(COOH)(CN)$; (b) $LiAlH_4/AlCl_3$; (c) 1,11-diiodo-3,6,9-trioxaundecane.

deprotonate **4** or **5** with BuLi, as evidenced by a D_2O quench of the lithium salt and isolation of the monodeuterated product. However reactions of the lithium salts with transition metal halides ($FeCl_2$, $CpTiCl_3$, $TiCl_3$, $ZrCl_4$, $CpZrCl_3$, $BrMn(CO)_5$) did not produce any stable compounds. We attribute this failure to the relatively low stability of η^5-indenyl complexes as compared to related cyclopentadienyl compounds. Therefore we attempted to prepare ligands with a cyclopentadienyl moiety instead of an indenyl group.

A synthetic strategy leading to cyclopentadienyl crown ethers is limited by the CH acidity of cyclopentadienes on one side and their ability to Diels–Alder dimerize on the other side. To inhibit Diels–Alder reactions, sterically demanding substituents at the ring are required. Unfortunately anions of such cyclopentadienes are not well suited for C–C bond formation, as they are strong bases but poor nucleophiles.[13]

Cyclopentenones on the other hand are highly useful synthons for cyclopentadienes with umpoled reactivity.[14] The optimum balance between high reactivity of the carbonyl group and the stabilizing effect of bulky substituents is available in 3,4-dimethylcyclopent-2-enone (**7**).

Knoevenagel condensation of **7** and cyanoacetic acid, followed by thermal decarboxylation, gave an isomer mixture of the nitriles **8a**/**8b** in a 40% yield (Scheme II). The $\alpha,\beta,\gamma,\delta$-unsaturated nitriles **8a**/**8b** were reduced with $AlCl_3/LiAlH_4$, leaving the double bonds intact, to produce 1-(2-aminoethyl)-3,4-dimethylcyclopenta-1,3-diene (**9**) in 55% yield. The cyclopentadienylethylamine **9** represents an interesting building block for the construction of novel functionalized cyclopentadienes, bridged metallocenes, or other crown ethers.[15]

The 1 + 1 addition of **9** and 1,11-diiodo-3,6,9-trioxaundecane in acetonitrile in the presence of Na_2CO_3 affords *N*-[2-(3,4-dimethylcyclopenta-1,3-dienyl)ethyl]aza-12-C-4 (**10**) (12-C-4-HCp″) in 55% yield. The 24-membered crown ether **11** was isolated in approximately 10% yield as a result of a 2 + 2 addition. In spite of the long reaction time chromatographic separation also gave small amounts (ca. 5%) of the corresponding open-chain products, which still contain NH and CH_2I groups. Surprisingly neither Calverly and Dale[8] nor Gokel et al.,[9] who reacted amines in an analogous manner, reported on the formation of 2 + 2 addition products.

Deprotonation of Cp″12-C-4 (**10**) with bases like NaH, BuLi, or MeMgBr gave the corresponding colorless metal cyclopentadienides, which invariably precipitated as insoluble solids in THF. Reactions with D_2O regenerated **10**, now monodeuterated. The reactivity of the sodium, lithium, or magnesium salts of **10** with transition metal halides parallels the chemistry of the crown ether-substituted indenes. Reactions with $CpTiCl_3$, $TiCl_3$, $CpZrCl_3$, $ZrCl_4$, $CoCl_2$, or $BrMn(CO)_5$ did not produce any η^5-bound complex. The reaction of $Li^+(10)^-$ with $FeCl_2$ did not result in the expected ferrocene in our hands. Instead formation of a green paramagnetic solid of unknown composition was observed. The failure of all these experiments may be explained by a reduced driving force for salt formation in the presence of solubilizing crown ethers.

To avoid the problems associated with salt formation we tested other leaving groups at the metal. Metal amides like $Ti(NMe_2)_4$ are known to react with cyclopentadiene to give $C_5H_5Ti(NMe_2)_3$.[16] However in the case of **10**, CH acidity is too low to allow reaction with $Ti(NMe_2)_4$ or $Zr(NMe_2)_4$ even under prolonged toluene reflux.

Finally we were successful in the reaction of the sodium salt of **10** with $(CO)_3W(CH_3CN)_3$. The tungstate, generated in situ, is converted into yellow **12** upon treatment with CH_3I (75% yield) (Scheme III). It is interesting to note that the stabilities of $(C_5H_5)W(CO)_3CH_3$ and **12** are rather different. Whereas $(C_5H_5)W(CO)_3CH_3$ is quite stable thermally and chemically, the crown ether-substituted relative **12** is rather unstable. Warming a toluene solution to 70 °C decomposed **12** within minutes. This is all the more surprising since $CpW(CO)_3CH_3$ complexes are not known to be substitutionally labile. The analogous

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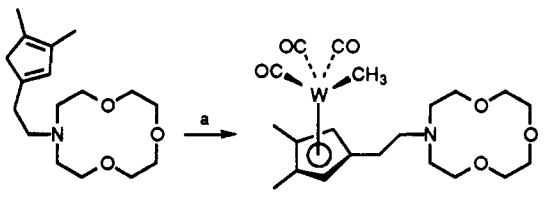
Scheme III[a]



10 12

[a] (a) NaH, $(CO)_3W(CH_3CN)_3$, CH_3I.

reaction of the disodium salt of **11** with 2 equiv of $(CO)_3W(CH_3CN)_3$ and CH_3I affords a yellow solid, which is thermally even more sensitive. This compound, most likely the corresponding ditungsten compound, decomposed completely within a few minutes at room temperature.

Following the synthesis of the half-sandwich **12**, it was interesting to see if the crown ether subunit was still available for complexation of metal cations. A ^{13}C NMR titration experiment of **12** with $LiAsF_6$ in CD_3OD showed formation of an unstable 1:1 crown ether lithium complex in solution. Addition of a methanol solution of **12** to a solution of $NaBPh_4$ in the same solvent precipitated the pale-yellow 2:1 complex **13** (= $(8)_2{\cdot}Na^+BPh_4^-$).

Conclusion

We have been successful in synthesizing the first examples of crown ether-substituted cyclopentadienes. The formation of η^5-bound transition metal complexes, however, is not straightforward. Synthetic routes relying on salt abstraction were not successful. Substitution reactions of labile ligands in the coordination sphere of transition metals are possible, even though the crown ether subunit apparently destabilizes the complexes. The comparison of the stabilities of **12** and $(C_5H_5)W(CO)_3CH_3$ reveals a strong influence of the crown ether subunit on the behavior of the organometallic group. Furthermore it was shown that different metals can be attached simultaneously to the heterotopic faces of these ligands, either η^5-bound to the cyclopentadienyl or as σ-donor crown ether complexes.

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen. Acetonitrile was distilled from CaH_2, and THF from Na/K. NMR spectra: Bruker AC 200 F for ^1H NMR (200 MHz) and ^{13}C NMR (50 MHz) and Varian Unity 300 for ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz). Spectra were recorded at 300 K in $CDCl_3$ and referenced to residual $CHCl_3$ (7.26 ppm) unless otherwise noted. Elemental analyses were performed at the Mikroanalytisches Laboratorium der Chemischen Laboratorien Universität Freiburg. Chromatography was carried out with silica MN60. IR spectra: Bruker IFS 25. Mass spectra: Finnigan MAT 312. Starting materials were commercially available or were prepared according to literature procedures: 1-bromo-3-inden-3-ylpropane,[11] 1,8-diiodo-3,6-dioxaoctane,[17] 1,11-diiodo-3,6,9-trioxaundecane,[8] aza-12-crown-4,[8,9] aza-15-crown-5,[12] $W(CO)_3(CH_3CN)_3$.[18] The preparation by Conia and Leriverend[19] for 3,4-dimethylcyclopent-2-enone was modified and upscaled 20-fold.

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***N*-(3-Inden-3-ylpropyl)phthalimide (2).** To a stirred solution of potassium phthalimide (25.8 g, 139 mmol) in DMF (120 mL) was added dropwise 1-bromo-3-inden-3-ylpropane (29.5 g, 124 mmol). The reaction mixture was heated to 80 °C for 2 h and stirring was continued at room temperature for 24 h. The precipitate was filtered and washed with ethanol to yield 26.6 g (70%) of a yellow solid: ^1H NMR δ 2.12 (pent, J = 7.2 Hz, $CH_2CH_2CH_2$, 2H), 2.63 (dt, J = 8.0 Hz, 1.7 Hz, CH_2CH_2-ind, 2H), 3.30 (d, J = 2.0 Hz, ind CH_2, 2H), 3.82 (t, J = 7.0 Hz, NCH_2, 2H), 6.29 (pent, J = 1.7 Hz, ind CH, 1H), 7.15–7.41 (m, ind, 4H), 7.67–7.71 (m, phenyl, 2H), 7.81–7.85 (m, phenyl, 2H); ^{13}C NMR δ 24.96 (CH_2), 26.62 (CH_2), 37.65 (CH_2), 37.86 (CH_2), 118.78 (ind H), 123.05 (ind H), 123.62, 124.49, 125.93, 128.11, 132.05 (phthal), 133.77 (phthal), 142.98 (ind), 144.31 (ind), 145.05 (ind), 168.32 (CO). Anal. Calcd for $C_{20}H_{17}NO_2$ (303.36): C, 79.19; H, 5.65. Found: C, 79.50; H, 5.53.

1-Amino-3-inden-3-ylpropane (3). The phthalimide **2** (20.0 g, 66 mmol) was dissolved in ethanol (350 mL) and heated to reflux. $N_2H_4{\cdot}H_2O$ (4.3 g, 86 mmol) was added dropwise, whereupon a solid precipitated. After refluxing overnight, the reaction mixture was cooled to 0 °C, acidified to pH 1 with concd HCl, and refluxed for an additional 30 min. The solid was filtered, washed with water, and dried. The yellow precipitate was dissolved in water and a small amount of insoluble material was filtered. The aqueous solution was basified with $NaHCO_3$ and extracted with Et_2O (50 mL × 4). The ethereal layer was dried over $MgSO_4$ and filtered and the orange liquid distilled (160 °C, 0.1 Torr) to give 8.75 g (76%) of a colorless liquid: ^1H NMR δ 1.10 (s, NH_2, 2H), 1.81 (pent, J = 6.5 Hz, $CH_2CH_2CH_2$, 2H), 2.58 (dt, J = 6.0 Hz, 1.5 Hz, CH_2CH_2-ind, 2H), 2.77 (t, J = 7.0 Hz, NCH_2, 2H), 3.30 (d, J = 1.9 Hz, ind CH_2, 2H), 6.19 (s, ind CH, 1H), 7.18–7.42 (m, ArH, 4H); ^{13}C NMR δ 24.74 (CH_2), 31.65 (CH_2), 37.37 (CH_2), 41.77 (CH_2), 118.60 (ind H), 123.41 (ind H), 124.20 (ind H), 125.66 (ind H), 127.46 (ind H), 143.77 (ind), 144.17 (ind), 145.07 (ind). Anal. Calcd for $C_{12}H_{15}NO_2$ (205.26): C, 70.22; H, 7.37. Found: C, 70.02; H, 7.21.

***N*-(3-Inden-3-ylpropyl)aza-12-crown-4 (4) (via 3).** A mixture of Na_2CO_3 (11.8 g, 112 mmol), 1-amino-3-indenylpropane (**3**) (4.0 g, 23 mmol), 1,11-diiodo-3,6,9-trioxaundecane (9.0 g, 21.8 mmol), and 250 mL of CH_3CN was heated under reflux for 16 h. The cooled suspension was filtered and the solvent evaporated. Water (25 mL) was added to the residue and the product extracted repeatedly with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and filtered, and the CH_2Cl_2 was evaporated. The remaining oil was chromatographed (ethyl acetate/hexane/Et_2NH = 10:10:1) to yield 4.6 g (63%) of a pale-yellow oil.

***N*-(3-Inden-3-ylpropyl)aza-12-crown-4 (4) (via 1 and aza-12-crown-4).** A mixture of aza-12-crown-4 (1.0 g, 5.7 mmol) and Na_2CO_3 (0.6 g, 7.0 mmol) in 30 mL of CH_3CN was heated to reflux. 1-Bromo-3-(1-inden-3-yl)propane (1.4 g, 6.0 mmol) was added dropwise and heating was continued for 24 h. The cooled solution was filtered, the volatiles were evaporated in vacuo, and the residue was chromatographed (hexane/ethyl acetate = 10:1): yield 0.9 g (47%); ^1H NMR 1.86 (pent, J = 7.3 Hz, $CH_2CH_2CH_2$, 2H), 2.53–2.64 (m, ind-CH_2CH_2 and NCH_2, 4H), 2.72 (t, J = 4.8 Hz, NCH_2, 4H), 3.32 (d, J = 1.7 Hz, ind CH_2, 2H), 3.55–3.72 (m, OCH_2, 12H), 6.21 (s, ind CH, 1H), 7.15–7.47 (m, ind H, 4H); ^{13}C NMR 25.45 (CH_2), 25.64 (CH_2), 37.62 (CH_2), 55.13 (NCH_2), 56.91 (NCH_2), 70.39 (OCH_2), 71.31 (OCH_2), 118.90 (ind H), 123.62 (ind H), 124.39 (ind H), 125.89 (ind H), 127.65 (ind H), 144.27 (ind), 144.40 (ind), 145.41 (ind). Anal. Calcd for $C_{20}H_{29}NO_3$ (331.46): C, 72.47; H, 8.82. Found: C, 72.10; H, 8.88.

***N*-(3-inden-3-ylpropyl)aza-15-crown-5 (5) (via 1 and aza-15-C-5):** procedure analogous to that used for compound **4**; chromatography (hexane/ethyl acetate/Et_2NH = 10:10:2), yield 54%; ^1H NMR δ 1.86 (pent, J = 7.3 Hz, $CH_2CH_2CH_2$, 2H), 2.51–2.67 (m, ind-CH_2CH_2 and NCH_2, 4H), 2.79 (t, J = 4.8 Hz, NCH_2, 4H), 3.32 (d, J = 1.7 Hz, ind CH_2, 2H), 3.63–3.70 (m, OCH_2, 14H), 6.21 (s, ind CH, 1H), 7.15–7.46 (m, ind H, 4H); ^{13}C NMR δ 25.40 (CH_2), 25.75 (CH_2), 37.62 (CH_2), 54.64 (NCH_2), 56.76 (NCH_2), 70.10 (OCH_2), 70.14 (OCH_2), 71.01 (OCH_2), 118.90 (ind H), 123.64 (ind H), 124.40 (ind H), 125.89 (ind H), 127.68 (ind H), 144.24 (ind), 144.43 (ind), 145.41 (ind). Anal. Calcd for $C_{22}H_{33}NO_4$ (375.51): C, 70.37; H, 8.86. Found: C, 70.64; H, 9.02.

***N,N'*-Bis(3-inden-3-ylpropyl)-1,10-diaza-18-crown-6 (6).** To a stirred mixture of 1,8-diiodo-3,6-dioxaoctane (3.1 g, 8.4 mmol)

and Na_2CO_3 (2.68 g, 25.2 mmol) in refluxing CH_3CN (100 mL) was added dropwise a solution of 1-amino-3-inden-3-ylpropane (3) (1.46 g, 8.4 mmol) in 10 mL of CH_3CN. After 36 h under reflux, the mixture was cooled and filtered. The volatiles were evaporated and the residue was chromatographed (ethyl acetate/hexane/Et_2NH = 10:20:3) to yield 0.86 g (17%) of a pale-yellow oil: ^1H NMR δ 1.87 (pent, J = 7.3 Hz, $CH_2CH_2CH_2$, 4H), 2.59 (dt, J = 6.4 Hz, 1.6 Hz, 4H), 2.70 (t, J = 7.6 Hz, NCH_2, 4H), 2.85 (t, J = 4.5 Hz, NCH_2, 8H), 3.33 (d, J = 1.9 Hz, 4H), 3.74–3.79 (m, OCH_2, 16H), 6.22 (s, ind CH, 2H), 7.19–7.47 (m, ind, 8H); ^{13}C NMR δ 25.47 (CH_2), 26.25 (CH_2), 37.67 (CH_2), 55.54 (NCH_2), 57.70 (NCH_2), 72.27 (OCH_2), 72.64 (OCH_2), 118.91 (ind H), 123.72 (ind H), 124.49 (ind H), 125.97 (ind H), 127.81 (ind H), 144.18 (ind), 144.49 (ind), 145.50 (ind). Anal. Calcd for $C_{36}H_{50}N_2O_4$ (574.81): C, 75.22; H, 8.77. Found: C, 75.42; H, 8.86.

3,4-Dimethylcyclopenten-2-one (7). To vigorously stirred 85% H_3PO_4 (200 g) was added P_4O_{10} (300 g), whereupon the mixture became very hot (it is important to obtain a homogeneous mixture). The polyphosphoric acid was cooled to 55 °C and crotonic acid isopropyl ester (76.8 g, 0.6 mol) added dropwise. During addition of the ester the temperature must be kept below 70 °C. The orange-colored mixture was heated to 100 °C for 90 min. The hot reaction mixture was poured into water and stirred until the polyphosphoric acid had dissolved. The aqueous phase was saturated with NH_4Cl, the product extracted several times with ether, and the organic layer separated and washed with 10% aqueous Na_2CO_3. The ethereal solution was separated, dried over $MgSO_4$, and filtered and the ether evaporated. The product was distilled from the residue under reduced pressure (bp 85–90 °C/15 Torr): yield 36–42.5 g (55–65%); ^1H NMR δ 1:12 (d, 7.2 Hz, CH_3), 1.91 (dd, 18, 2 Hz, CH*H*), 2.00 (s, CH_3), 2.55 (dd, 18, 6.5 Hz, C*H*H), 2.74 (m, C*H*CH_3), 5.78 (s, CH).

3,4-Dimethylcyclopentadienylideneacetonitrile (8). A 250-mL flask containing a stirred mixture of 3,4-dimethylcyclopentenone (7) (32.7 g, 300 mmol) and cyanoacetic acid (38.3 g, 300 mmol) was immersed in a water bath. Piperidine (38.3 g, 300 mmol) was added slowly (care has to be taken to keep the temperature below 50 °C). After addition of base the reaction mixture was heated to 100 °C for 2 h. After cooling to room temperature, Et_2O (300 mL) was added and the organic phase extracted three times each with 10% HCl and aqueous $NaHCO_3$. The ethereal solution was dried over $MgSO_4$ and filtered, the solvent was evaporated, and the product was distilled in vacuo (60 °C/0.1 Torr) to produce a colorless liquid as a mixture of two isomers. Yield: 15.0 g (40%). NMR data are given in pairs for the cis/trans isomers, with the more abundant isomer A (ratio A/B = 60/40) listed first: ^1H NMR (300 MHz) δ 1.108, 1.090 (d, 6.8 Hz, CH_3), 1.901, 1.925 (m, CH_3), 2.38, 2.23 (d, 18.4 Hz, 17.5 Hz, C*H*H), 2.83 (t, br, 6 Hz, C*H*CH_3), 3.04, 2.89 (ddd, J = 18.2, 6.8, 1.7 Hz; isomer B partially obscured by broad C*H*CH_3), 4.92, 4.79 (br, CH), 5.97, 6.29 (br, CH); ^{13}C NMR (75 MHz) δ 15.768, 15.732 (CH_3), 18.897, 18.836 (CH_3), 39.17, 39.69 (CH_2), 42.70, 42.51 ($CHCH_3$), 82.93, 81.99 (*C*HCN), 118.84, 118.27 (CN), 127.73, 126.94 (ring sp^2-CH), 166.75, 166.33 (C), 170.09, 170.54 (C); IR (cm^{-1}) ν 1613 (C=C), 2204 (C≡N). Anal. Calcd for $C_9H_{11}N$ (133.19): C, 81.16; H, 8.32. Found: C, 81.30; H, 8.21.

1-(2-Aminoethyl)-3,4-dimethylcyclopentadiene (9). To a solution of $AlCl_3$ (13.3 g, 100 mmol) in Et_2O (200 mL) was first added $LiAlH_4$ (5.1 g, 134 mmol) and then dropwise a solution of the nitrile 8 (13.3 g, 100 mmol) in Et_2O (50 mL). After stirring for 4 h the reaction mixture was hydrolyzed carefully. The suspension was filtered and the precipitate washed several times with Et_2O. The organic layer was separated and the aqueous phase extracted with Et_2O. The combined organic phases were dried over $MgSO_4$, filtered, and extracted with 10% HCl. The acid aqueous phase was basified with NaOH and reextracted with Et_2O. The organic layer was dried over $MgSO_4$ and filtered and the ether evaporated. The remaining oil was distilled under vacuo to produce a colorless liquid: yield 7.5 g (55%); ^1H NMR δ 1.16 (s, NH_2), 1.78 (s, CH_3), 1.86 (s, CH_3), 2.43 (t, 6.7 Hz, CH_2), 2.77 (s, ring-CH_2), 2.81 (t, 6.7 Hz, CH_2N), 5.95 (s, CH); ^{13}C NMR δ 12.41 (CH_3), 13.00 (CH_3), 34.89 (CH_2), 41.94 (CH_2), 47.17 (CH_2), 132.04 (CH), 133.42 (C), 134.20 (C), 142.53 (C). Anal. Calcd for $C_9H_{15}N$ (137.23): C, 78.77; H, 11.01. Found: C, 78.81; H, 10.92.

***N*-[2-(3,4-Dimethylcyclopenta-1,3-dienyl)ethyl]aza-12-crown-4 (10) and *N,N'*-Bis[2-(3,4-dimethylcyclopenta-1,3-dienyl)ethyl]-1,13-diaza-24-crown-8 (11).** A stirred mixture of $Cp''C_2H_4NH_2$ (9) (6.9 g, 50 mmol), 1,11-diiodo-3,6,9-trioxaundecane (20.7 g, 50 mmol), Na_2CO_3 (15.9 g, 150 mmol), and 500 mL of CH_3CN was heated to reflux for 36 h. The reaction mixture was filtered and evaporated to dryness, water (50 mL) was added, and the product was extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$ and filtered and the solvent removed in vacuo. The remaining oil was purified by chromatography (cyclohexane/Et_2NH = 10:1) and has to be stored at −30 °C.

12-C-4-(HCp'') (10): yield 8.1 g (55%); MS-CI (170 eV) m/z (rel inten) 296 (M^+, 100), 188 ($M^+ - Cp''CH_2$, 95); ^1H NMR δ 1.78 (s, CH_3), 1.85 (s, CH_3), 2.43–2.53 (m, $Cp''CH_2$), 2.60–2.74 (m, 6 H), 2.78 (s, ring-CH_2), 3.65 (CH_2O, 12 H), 5.90 (s, CH); ^{13}C NMR δ 12.44 (CH_3), 12.98 (CH_3), 28.18 ($Cp''CH_2$), 47.46 (ring-CH_2), 54.90 (NCH_2), 57.16 (NCH_2), 70.33 (OCH_2), 71.15 (OCH_2), 131.05, 133.08, 134.14, 143.27. Anal. Calcd for $C_{17}H_{29}NO_3$ (295.43): C, 69.12; H, 9.89; N, 4.74. Found: C, 68.95; H, 9.81; N, 4.67.

24-C-8-(HCp'')$_2$ (11): yield 1.4 g (10%); MS-CI (170 eV) m/z (rel inten) 591 (M^+, 46), 471 ($M^+ - Cp''CH_2$, 94), 363 ($M^+ - Cp''CH_2 - Cp''CH_2$, 84), 351 ($M^+ - Cp''CH_2 - Cp''C_2H_4$, 100); ^1H NMR δ 1.79 (s, CH_3), 1.86 (s, CH_3), 2.40–2.50 (m, $Cp''CH_2$), 2.65–2.81 (m, 4 × NCH_2), 3.55–3.67 (m, 12 × CH_2O), 5.91 (s, CH); ^{13}C NMR δ 12.51 (CH_3), 13.08 (CH_3), 28.25 ($Cp''CH_2$), 47.53 (ring-CH_2), 53.95 (NCH_2), 55.98 (NCH_2), 69.95 (CH_2O), 70.56 (CH_2O), 70.80 (CH_2O), 70.56 (CH_2O), 70.80 (CH_2O), 131.12, 134.25, 143.31. Anal. Calcd for $C_{34}H_{58}N_2O_6$ (590.85): C, 69.12; H, 9.89. Found: C, 68.95; H, 9.97.

[[2-(3,4-Dimethylcyclopentadienyl)ethyl]aza-12-crown-4] (tricarbonyl)methyl tungsten (12). To a solution of 12-C-4-(HCp'')(10) (148 mg, 0.5 mmol) in THF (25 mL) was added NaH (24 mg, 1 mmol) followed after 30 min by $(CO)_3W(CH_3CN)_3$ (196 mg, 0.5 mmol). The reaction mixture was stirred at 50 °C for 60 min. The brown solution of the tungstate was quenched with MeI (143 mg, 1 mmol). After 60 min the volatiles were removed in vacuo. The remaining solid was extracted three times with toluene (50 mL). The toluene was evaporated and the remaining yellow oil stirred with pentane. The pentane was decanted and the yellow sticky solid dried in vacuo: yield 216 mg (75%); ^1H NMR δ 0.26 (s, WCH_3), 1.95 (s, $Cp''CH_3$), 2.44 (m, $Cp''CH_2$), 2.71 (m, 3 × NCH_2), 3.59–3.68 (m, 6 × CH_2O), 5.14 (s, Cp''H); ^{13}C NMR δ −27.31 (WCH_3), 11.68 ($Cp''CH_3$), 26.38 ($Cp''CH_2$), 54.88 (NCH_2), 58.69 (NCH_2), 70.08 (CH_2O), 70.41 (CH_2O), 71.13 (CH_2O), 90.82 (Cp''H), 105.64, 106.36, 218.51 (CO), 231.55 (CO); IR ν (CO) 1915, 2006 cm^{-1}; ^1H NMR (CD_3OD) δ 0.20, 1.93, 2.41, 2.61, 2.67, 3.55–3.65, 5.34; ^{13}C NMR (CD_3OD) δ −27.28, 11.80, 26.80, 55.35, 59.12, 69.88, 70.79, 71.21, 92.42, 108.20, 220.09, 233.22. Anal. Calcd for $C_{21}H_{31}NO_6W$ (577.34): C, 43.69; H, 5.41. Found: C, 43.80; H, 5.57.

(Na^+(12)$_2$-BPh_4^-) (13). A methanol solution of (12) (100 mg, 0.17 mmol) and $NaBPh_4$ (30 mg, 0.085 mmol) was stirred for 30 min and evaporated to dryness and the residue recrystallized from MeOH/H_2O. (13) (cation resonances only): ^1H NMR (DMSO-d_6) δ 0.35 (s, WCH_3), 2.07 (s, $Cp''CH_3$), 2.65 (br, CH_2), 2.74 (br, CH_2), 3.68 (br, FcH), 5.75 (s, Cp''H); ^{13}C NMR (DMSO-d_6) δ −27.62 (WCH_3), 11.07 ($Cp''CH_3$), 26.0 (CH_2), 54.31, 57.54, 69.08, 69.43, 70.16, 91.39, 106.3, 106.61, 219.74 (CO), 232.56 (CO). Anal. Calcd for $C_{45}H_{51}BNNaO_6W$ (919.6) C, 58.77; H, 5.59. Found: C, 59.04; H, 5.63.

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