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Synthesis of a TREN in Which the Aryl Substituents are Part of a 45 Atom Macrocycle

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Supporting Information

ABSTRACT: A substituted TREN has been prepared in which the aryl groups in $(ArylNHCH_2CH_2)_3N$ are substituted at the 3- and 5-positions with a total of six $OCH_2(CH_2)_nCH{=}CH_2$ groups ($n = 1, 2, 3$). Molybdenum nitride complexes, $[(ArylNCH_2CH_2)_3N]Mo(N)$, have been isolated as adducts that contain $B(C_6F_5)_3$ bound to the nitride. Two of these $[(ArylNCH_2CH_2)_3N]Mo(NB(C_6F_5)_3)$ complexes ($n = 1$ and 3) were crystallographically characterized. After removal of the borane from $[(ArylNCH_2CH_2)_3N]Mo(NB(C_6F_5)_3)$ with PMe_3, ring-closing olefin metathesis (RCM) was employed to join the aryl rings with $OCH_2(CH_2)_nCH{=}CH(CH_2)_nCH_2O$ links ($n = 1$−3) between them. RCM worked best with a $W(O)(CHCMe_3)(Me_2Pyr)(OHMT)(PMe_2Ph)$ catalyst (OHMT = hexamethylterphenoxide, Me_2Pyr = 2,5-dimethylpyrrolide) and $n = 3$. The macrocyclic ligand was removed from the metal through hydrolysis and isolated in 70−75% yields relative to the borane adducts. Crystallographic characterization showed that the macrocyclic TREN ligand in which $n = 3$ contains three *cis* double bonds. Hydrogenation produced a TREN in which the three links are saturated, i.e., $O(CH_2)_{10}O$.

The first example of the catalytic reduction of N_2 to NH_3 under mild conditions (22 °C) employing protons and electrons was reported in 2003.[1] The catalyst is a molybdenum complex that contains a TREN-based ligand, $[(HIPTNCH_2CH_2)_3N]^{3-}$ ($HIPTN_3N^{3-}$), where HIPT (hexaisopropylterphenyl) is 3,5-$(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2C_6H_3$ (Figure 1).

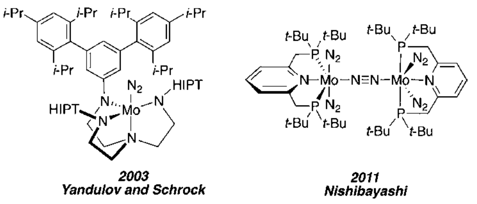

Figure 1. Mo-based dinitrogen reduction catalysts.

The reaction employs $Cr(\eta^5\text{-}C_5Me_5)_2$ as the reducing agent and [2,6-lutidinium]$[BAr_F]$ ($BAr_F^- = \{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}^-$) as the proton source in heptane as a solvent. The $HIPTN_3N^{3-}$ ligand makes all intermediate species in the reduction cycle soluble in heptane, creates and protects the binding pocket for N_2 and subsequent partially reduced intermediates in the catalytic cycle, and prevents the formation of μ-N_2 complexes. A total of approximately four turnovers (to give a maximum of 8 equiv of ammonia) was found along with ∼1 equiv of hydrogen per N_2 reduced. Eight of the proposed catalytic intermediates in the Mo-catalyzed TREN-based system were characterized by X-ray crystallography. The proposed reaction mechanism also has been scrutinized through extensive calculations.[2] All steric and electronic modifications of the successful "HIPT catalysts" resulted in poorer activity, and in some cases no catalytic reduction at all.[3] Ligands that were not based on TREN frameworks were also unsuccessful.[4] It was clear that much free ligand, $(HIPTNHCH_2CH_2)_3N$, was present at the end of a catalytic reaction. Protonation of an amido ligand, or strong H-bonding of $[LutH]^+$ to it, was proposed to be the beginning of a process that stripped the ligand off the metal under catalytic conditions and led to irreversible loss of catalytic activity.

In 2011 a Mo PNP pincer complex (Figure 1) was disclosed as a catalyst precursor for catalytic reduction of dinitrogen under conditions similar to those employed for the $[HIPTN_3N]Mo$ system, namely $Co(\eta^5\text{-}C_5H_5)_2$ as the reducing agent and [LutH][OTf] as the acid source.[5] Approximately 50% more ammonia (per Mo) was formed in the Mo(PNP) system than in the $Mo(HIPTN_3N)$ system. No catalytically competent intermediates could be identified. Scission of the N_2 bond to form terminal nitrido complexes, as observed with Mo(POCOP) complexes[6] and heterobimetallic Mo/Nb complexes,[7] cannot be excluded. Loss of the PNP ligand from the metal was also proposed to be a limitation in the (PNP)Mo system.

A third dinitrogen reduction has been published recently that involves an iron-containing catalyst, $H(ether)_2[BAr_F]$ as the acid, and potassium graphite as the reducing agent.[8] Approximately 8 equiv of ammonia are formed.

A TREN-based ligand that is not readily lost from the metal, even in the presence of acid and reducing agent, *could* be highly beneficial to the catalytic reduction of nitrogen, if that ligand also has the favorable properties displayed by the $HIPTN_3N^{3-}$ ligand. Therefore, for years we have entertained the idea of synthesizing a TREN-based ligand in which the three phenyl rings on the three amido nitrogens are connected to one another. Ultimately, we chose ring-closing metathesis (RCM) as the method of covalently linking the NAr groups together (Figure 2). An RCM-based method was also attractive because it has been employed in recent years to prepare Pt and Pd complexes in which the metal is encapsulated in a macrocyclic ligand framework.[9]

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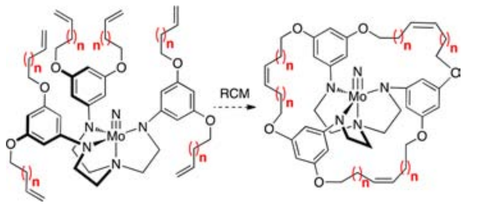
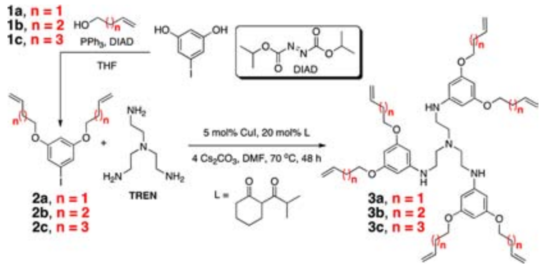


Figure 2. Targeted macrocyclic TRENs (*n* = 1, 2, 3).

We report here the successful implementation of an RCM approach that affords a macrocyclic TREN-based ligand of the type shown Figure 2 in which *n* = 3.

We decided to connect the phenyl rings through the 3- and 5-positions with alkenyloxy groups that contain a terminal double bond. The synthesis of **3a−c** (Scheme 1) began with 5-iodobenzene-1,3-diol, which was synthesized in two steps from commercially available starting material (see Supporting Information (SI) for details.) Sonication of 5-iodobenzene-1,3-diol, PPh_3, and **1a−c** in THF gave homogeneous solutions, which upon treatment with DIAD (diisopropylazodicarboxylate) afforded aryl iodides **2a−c.**[10,11] C−N bond formation between **2a−c** and TREN was achieved using a modification of a Cu(I)-catalyzed approach reported by Buchwald.[12] The desired compounds **3a−c** were isolated as orange oils in good yields following filtration through a silica plug.[13] Analysis by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy showed that each contained an impurity (<5%) that could not be identified.

Scheme 1. Synthesis of TRENs 3a−c

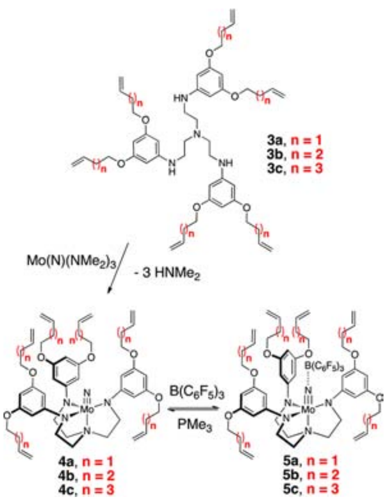


Treatment of **3a−c** with 1.25 equiv of $(NMe_2)_3Mo{\equiv}N$[14] in benzene at 40 °C afforded purple solutions that we propose contain largely **4a−c** (Scheme 2), according to NMR studies. Removal of the solvent and $NHMe_2$ *in vacuo*, followed by addition of 1.5 equiv of $B(C_6F_5)_3$ in toluene, resulted in the formation of orange borane adducts **5a−c** (Scheme 2). Recrystallization of the crude reaction mixture from toluene layered with pentane at −40 °C afforded **5a−c** as orange crystalline solids in 60−75% yields. The origin of the intense purple color in the mixtures that contain **4a−c** is not known.

X-ray crystallography confirmed that the $B(C_6F_5)_3$ group is bound to the nitride ligand in **5a** and **5c** (Figures 3 and S1 in the SI). The expected trigonal bipyramidal geometry is observed with N−B bond lengths of 1.583(5) and 1.580(5) Å, respectively. These N−B bond lengths are in the range found in other $B(C_6F_5)_3$ adducts of nitride complexes.[15,16]

The borane could be removed by refluxing **5a−c** in neat PMe_3 at 80 °C. Use of NEt_3, pyridine, and other phosphines (e.g., PMe_2Ph, PEt_3, or $P(TMS)_3$) in place of PMe_3 proved ineffective, typically leading to no reaction or to ligand dissociation from the metal. Purple solutions are again formed upon refluxing **5a−c** in neat PMe_3. All efforts to purify **4a−c** through recrystallization failed. Therefore, RCM was carried out on samples of crude **4a−c**. We are hesitant at this stage to conclude that monomeric Mo(VI) nitrides, **4a−c**, are intense purple; the current theory is that **4a−c** are thermally unstable above ∼40 °C and that a small amount of an intensely colored decomposition product is formed as an impurity when solutions of **4a−c** are heated for an extended period.

Scheme 2. Metallation of 3a−c To Yield 4a−c and Borane Adducts 5a−c



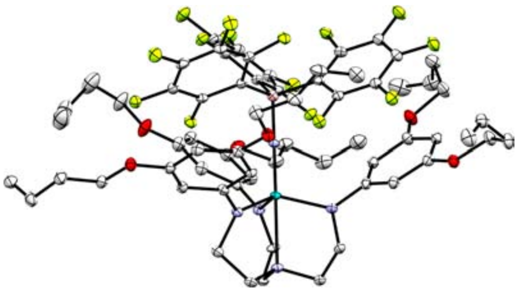
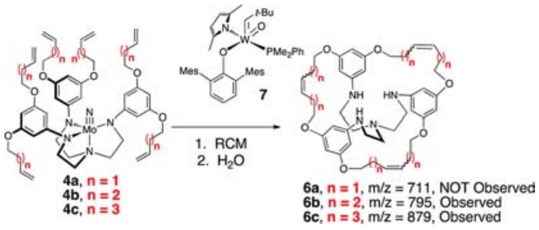


Figure 3. Thermal ellipsoid drawing of **5a**. H-atoms and solvent molecules are omitted for clarity.

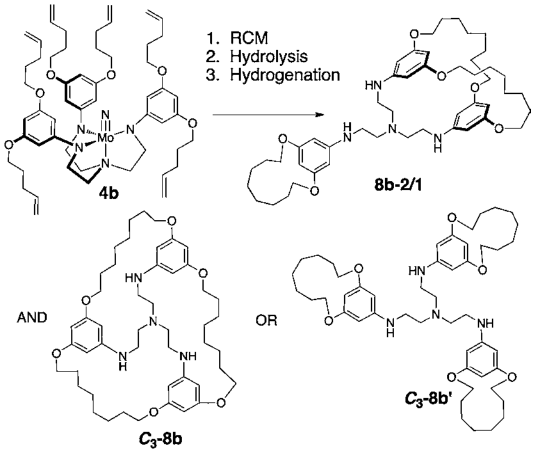
Fourteen Mo-, W-, and Ru-based catalysts were screened for RCM of **4a−c** that had been generated *in situ* (see SI for a complete list). After RCM the product mixture was hydrolyzed and the crude organic products were analyzed by ^{1}H NMR spectroscopy and mass spectrometry (see SI for details). Tungsten-based MAP (MonoAryloxide Pyrrolide) catalysts[17] most effectively promoted the three intramolecular metathesis reactions to generate TREN-based ligands **6b** and **6c**. In particular, the recently reported *Z*-selective catalyst, W(O)-$(CHCMe_3)(Me_2Pyr)(OHMT)(PMe_2Ph)$ (**7**; OHMT = hexamethylterphenoxide, Me_2Pyr = 2,5-dimethylpyrrolide; Scheme 3),[18] is the best catalyst tested to date. Mo- and Ru-based catalysts[19] typically led to dissociation (with subsequent protonation of the ligand) to give the metal-free **3**; no significant amount of **6** was observed. Macrocycle **6a** (*n* = 1) did not appear to form with any catalyst, including **7**, which led us to conclude that the $OCH_2CH_2CH{=}CH_2$ chain was "too short." We propose that the $OCH_2CH_2CH{=}CHCH_2CH_2O$ link could not be formed via metathesis for kinetic reasons associated with the steric requirements of the metathesis method itself, not necessarily because hypothetical **6a** is inherently too strained.

Scheme 3. Triple intramolecular RCM To Yield 6a−c



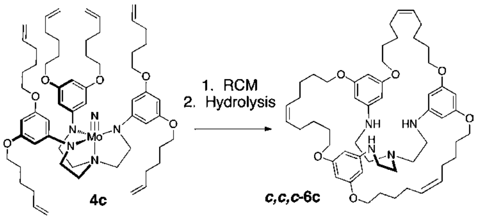
Scaling up the triple intramolecular RCM reactions in **4b** and **4c** revealed that the RCM of **4b** (derived from a $\mathrm{OCH_2CH_2CH_2CH{=}CH_2}$ link where n = 2) yielded two different products. After hydrogenation of the ligand, the minor product, **8b-2/1**, was separated from the mixture of **8b-2/1** and **C_3-8b** or **C_3-8b′** (Scheme 4) through fractional recrystallization and was fully characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. C_2-Symmetric **8b-2/1** is the result of two "interarm" metathesis reactions and one "intraarm" metathesis reaction. It is not known whether two "interarm" metathesis reactions precede the one "intraarm" metathesis reaction, or *vice versa*. In any case, **8b-2/1** is obviously not a potential ligand of the desired type. The C_3-symmetric product (either **C_3-8b** or **C_3-8b′**) could not be purified by crystallization or separated from the small amount of **8b-2/1** remaining in the mixture. However, the C_3-symmetric ligand could be characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy (see SI). Unfortunately, X-ray quality crystals of neither **C_3-8b** nor **8b-2/1** have been obtained.

Scheme 4. TRENs Derived from 4b



The most successful RCM reactions employed **4c** in which the alkenyloxy is $\mathrm{OCH_2CH_2CH_2CH_2CH{=}CH_2}$ (n = 3). The optimized RCM was carried out at 0.001 M concentration of **4c** in benzene. Four batches of catalyst **7**, a total of 44 mol % per Mo, or 7.3% per double bond, were added in 3 h intervals (20, 10, 10, 4 mol %). After RCM the hydrolysis product (**6c**, Scheme 5) was obtained in 76%, 71%, and 67% (some lost) overall yield in three runs. The ligand (before hydrogenation) was found (according to proton NMR spectra) to contain only *cis* double bonds (>95% estimated). This "*cis,cis,cis*-$\mathrm{OC_{10}O}$" ligand (*c,c,c*-**6c**; Scheme 5) could be recrystallized from a benzene solution layered with pentane at rt and has been fully characterized by NMR spectroscopy, elemental analysis, and an X-ray structural study (see Figure 4). Obtaining *c,c,c*-**6c** in 70−75% yield from **5c**, without isolation of **4c**, suggests that the yield of **4c** is high, that the ring-closing reaction takes place with a high degree of selectivity for the Z C=C bond (estimated as >98%), and that post-metathesis isomerization of Z to E in *c,c,c*-**6c** is slow. It should be noted that the metathesis homocoupling of simple terminal olefins at a loading of 0.2 mol % **7** was reported to be >99% Z-selective.[18a] Nevertheless, we are still surprised that the overall isolated yield of *c,c,c*-**6c** prepared from **5c** is 70−75%.

Scheme 5. Synthesis of *c,c,c*-6c



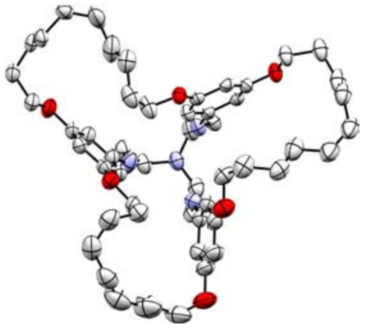


Figure 4. A top view of the structure of *c,c,c*-**6c**. Solvent molecules, minor components of disordered atoms, and all H-atoms are omitted for clarity.

Top and side views of the structure of *c,c,c*-**6c** are shown in Figures 4 and 5. The *cis* double bond is that between C5 and C6 in any given linkage. The number of atoms in the largest ring in the multicyclic molecule, i.e., the macrocycle that includes the three $\mathrm{O(CH_2)_{10}O}$ links and three aryl carbons in each aryl ring, is 45. Although each aryl ring is twisted about the N−C$_{ipso}$ bond in the solid state, on the NMR time scale in solution *c,c,c*-**6c** has C_{3v} symmetry. Therefore, we expect the ligand to be flexible enough to allow a metal to be inserted. The "depth" and "breadth" of *c,c,c*-**6c** (Figure 5) are impressive.

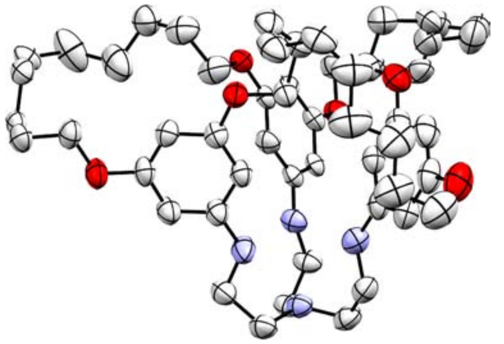


Figure 5. A side view of the structure of *c,c,c*-**6c** (red = O; blue = N). Solvent molecules, minor components of disordered atoms, and all H-atoms are omitted for clarity.

Hydrogenation of the *c,c,c*-**6c** with PtO$_2$ under 40 psi of hydrogen produced the saturated ligand, **8c**. So far we have not been able to crystallize **8c**, although NMR data and mass spec data are all consistent with formation of **8c** from structurally characterized *c,c,c*-**6c**. Apparently three *cis* C=C bonds between C5 and C6 in each link in *c,c,c*-**6c** provide enough rigidity to allow it to be crystallized readily.

The reaction between *c,c,c*-**6c** and $(NMe_2)_3Mo{\equiv}N$ (1.75 equiv) in C_6D_6 at 50 °C for 23 h led to the consumption of *c,c,c*-**6c** and formation of 3 equiv of dimethylamine and a new C_3-symmetric Mo complex, according to NMR studies. The same is true of the reaction between **8c** and $(NMe_2)_3Mo{\equiv}N$ for 20 h. Both reactions are qualitatively slower than analogous reactions between **3c** and $(NMe_2)_3Mo{\equiv}N$ (Scheme 2), as one might expect. Unfortunately, no product has yet been isolated in crystalline form.

We conclude that olefin metathesis can be employed to prepare a TREN-derived macrocycle through intramolecular RCM of **4c** with W=O-based catalyst **7**, a highly *Z*-selective catalyst for metathesis homocoupling of terminal olefins. The optimum linkage contains 12 atoms between aryl rings and gives rise to a 45 atom macrocyclic ring that contains all *cis* C=C bonds, *c,c,c*-**6c**. Hydrogenation of *c,c,c*-**6c** produces the saturated version, **8c**. It is clear that Mo can be reinserted into *c,c,c*-**6c** and **8c**, although no nitrido complex has been isolated yet. Future studies will be aimed at evaluating the chemistry of Mo complexes that contain this and related macrocyclic TREN-based ligands.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic details for all X-ray structural studies. Experimental details for the synthesis of all organic and inorganic compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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