Olefin Metatheses in Metal Coordination Spheres: A New Approach to Steric Shielding in Dirhenium sp Carbon Chain Complexes of the Formula (η^5-C_5Me_5)-Re(NO)(PR_3)(C≡CC≡CC≡CC≡C)(R_3P)(ON)Re(η^5-C_5Me_5)

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Reaction of chiral racemic [(η^5-C_5Me_5)Re(NO)($NCCH_3$)(CO)]$^+BF_4^-$ and the olefin-containing phosphine $Ph_2P(CH_2)_6CH{=}CH_2$ (2-butanone, reflux) gives [(η^5-C_5Me_5)Re(NO)($PPh_2(CH_2)_6$-$CH{=}CH_2$)(CO)]$^+BF_4^-$ (95%), which is reduced ($LiAlH_4$) to the phosphine methyl complex (η^5-C_5Me_5)Re(NO)($PPh_2(CH_2)_6CH{=}CH_2$)(CH_3) (92%). Reactions with HBF_4·OEt_2/chlorobenzene, HC≡CC≡C$SiMe_3$, and *t*-BuOK give (η^5-C_5Me_5)Re(NO)($PPh_2(CH_2)_6CH{=}CH_2$)(C≡CC≡C$SiMe_3$) (two steps, 96%/81%). Desilylation (wet *n*-$Bu_4N^+F^-$) yields a butadiynyl complex (88%), which is coupled ($Cu(OAc)_2$/pyridine) to the μ-octatetraynediyl complex (η^5-C_5Me_5)-Re(NO)($PPh_2(CH_2)_6CH{=}CH_2$)(C≡CC≡CC≡CC≡C)($H_2C{=}CH(CH_2)_6PPh_2$)(ON)Re(η^5-C_5Me_5) (**16**, 63%), believed to be a mixture of diastereomers. The reaction of **16** and Grubbs' catalyst, Ru(=CHPh)(PCy_3)$_2$(Cl_2), gives (η^5-C_5Me_5)Re(NO)($PPh_2(CH_2)_6CH{=}CH$)(C≡CC≡CC≡CC≡C)-(($CH_2)_6PPh_2$)(ON)Re(η^5-C_5Me_5) (**17**, 77−84%) as a mixture of isomers. However, the hydrogenation of **17** to the target molecule (η^5-C_5Me_5)Re(NO)($PPh_2(CH_2)_7$)(C≡CC≡CC≡CC≡C)(($CH_2)_7PPh_2$)(ON)Re(η^5-C_5Me_5) (**18**), while sometimes successful, could not be scaled or effected in a reproducible manner.

Introduction

Over the last four years, the olefin metathesis reaction[1] has been applied with increasing frequency in organometallic syntheses.[2−8] These efforts have been both exploratory and focused upon specific types of targets. The first directed synthesis of a molecular species can be attributed to Sauvage, who reported the sequence in Scheme 1, and several related efforts.[4,5] He found that the copper complex **1** reacted with Grubbs' catalyst, Ru(=CHPh)(PCy_3)$_2$(Cl_2), to yield ethylene and the catenane **2**. The C=C linkage, which was obtained as a mixture of *E*/*Z* isomers, was then hydrogenated to give the saturated system **3**.

We have subsequently used olefin metathesis to access several other types of novel molecular architectures.[6,8] Of particular relevance to the present study is the sequence shown in Scheme 2.[8] In complex **4**, each terminus of a PtC≡CC≡CC≡CC≡CPt moiety features two olefin-containing $Ph_2P(CH_2)_6CH{=}CH_2$ ligands. Metathesis can in theory deliver two types of products. One arises from cyclization between phosphines on opposite platinum atoms (**5**). The other arises from cyclization between phosphines on the same platinum atom (**6**). In

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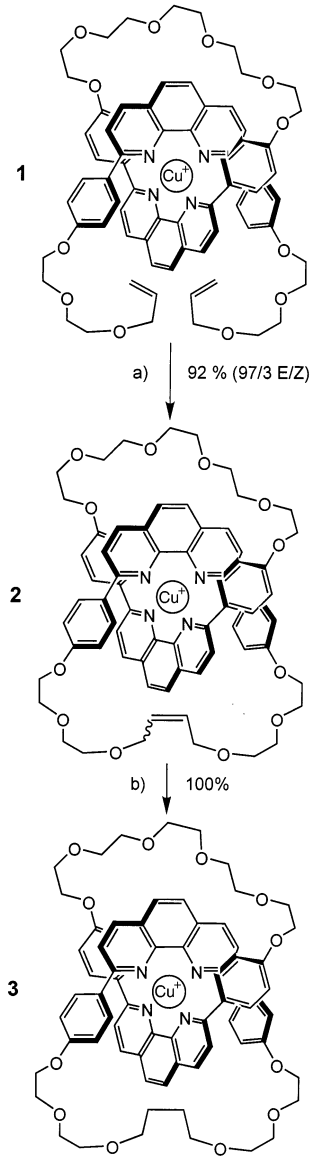
Scheme 1. Synthesis of a Metal-Containing Catenane via Olefin Metathesis[a]



[a] (a) cat. Ru(=CHPh)$(PCy_3)_2(Cl)_2$; (b) H_2, cat. [Ir(PCy_3)(COD)(py)]$^+PF_6^-$.

practice, the former dominates. Hydrogenation reduces the C=C linkages, but not the C≡C linkages, giving **7** and **8**.

Complex **7** and similar species prepared via olefin metathesis or alternative procedures adopt unprecedented double-helical structures in the solid state.[8] The sp^3 carbon chains coil about the sp carbon chain at van der Waals distance, giving at least a half-twist. Similar conformations are believed to dominate in solution. These afford the potentially reactive PtC≡CC≡CC≡CC≡CPt moiety a considerable degree of steric protection. This may be a critical factor in the hydrogenation chemoselectivity in Scheme 2, as alkynes are normally more reactive than alkenes.

One of our original motivations for developing the chemistry in Scheme 2 was to facilitate access to additional redox states of $M(C{\equiv}C)_mM$ compounds, particularly at longer carbon chain lengths. Some key issues are illustrated with the dirhenium complexes **9**^{n+}nX$^-$ in Scheme 3.[9,10] With $m = 2$ (C_4), three oxidation states were easily isolated: a neutral ReC≡CC≡CRe species (**9a**), a radical cation [ReC≡CC≡CRe]$^{\bullet+}$ species (**9a**$^{\bullet+}$ X$^-$), and a dication $^+$Re=C=C=C=C=Re$^+$ species (**9a**$^{2+}2$X$^-$).[9] However, with $m = 4$ (C_8), it was not possible to spectroscopically detect a radical cation or dication (**9b**$^{\bullet+}$X$^-$, **9b**$^{2+}2$X$^-$), even at low temperature.[10] The longer C_8 chains in **9b**^{n+}nX$^-$ are much more exposed, and various evidence suggests that the radical cations undergo rapid chain−chain coupling and/or atom abstraction reactions involving the solvent.

Analogues of **9b** with more electron-rich triarylphosphines or tricyclohexylphosphine gave similar results.[10b] We therefore turned our attention to bulkier phosphines and/or systems that would in some way sterically protect the ReC≡CC≡CC≡CC≡CRe moiety. In this paper, we describe our attempts to extend the sequence applied in Scheme 2 with platinum diphosphine end groups to rhenium monophosphine end groups. This would give dirhenium complexes with more shielded sp carbon chains and in principle capable of adopting single-helical conformations.

Results

The readily available chiral racemic acetonitrile carbonyl complex [(η^5-C_5Me_5)Re(NO)(NCCH$_3$)(CO)]$^+BF_4^-$ (**10**$^+BF_4^-$) reacts with a variety of phosphines in refluxing 2-butanone to give the corresponding phosphine carbonyl complexes.[11] As shown in Scheme 4, a similar reaction with the phosphine utilized in Scheme 2, $Ph_2P(CH_2)_6CH{=}CH_2$,[6c] gave the target complex [(η^5-C_5Me_5)Re(NO)($PPh_2(CH_2)_6CH{=}CH_2$)(CO)]$^+BF_4^-$ (**13**$^+BF_4^-$) in 95% yield after workup.

Complex **11**$^+BF_4^-$ was elaborated to a butadiynyl complex as described for many related species. First, reduction with $LiAlH_4$ gave the methyl complex (η^5-C_5Me_5)Re(NO)($PPh_2(CH_2)_6CH{=}CH_2$)(CH$_3$) (**12**, 92%). Reactions with HBF_4 in C_6H_5Cl generated a substitution-labile chlorobenzene complex,[12] which was treated with an excess of the diyne HC≡CC≡CSiMe$_3$.[13,14] Workup gave the π complex [(η^5-C_5Me_5)Re(NO)($PPh_2(CH_2)_6CH{=}CH_2$)(HC≡CC≡CSiMe$_3$)]$^+BF_4^-$ (**13**$^+BF_4^-$), with rhenium bound to the terminal alkyne moiety, in 96% yield. No intramolecular coordination of the CH=CH$_2$ moiety of the phosphine ligand was observed. The reaction of the chlorobenzene complex derived from (η^5-C_5H_5)Re(NO)(PPh$_3$)(CH$_3$) and vinylacetylene also gives predominantly an alkyne complex.[15]

The preceding compounds and all new species below were characterized by IR, NMR (^{1}H, ^{13}C, ^{31}P), mass

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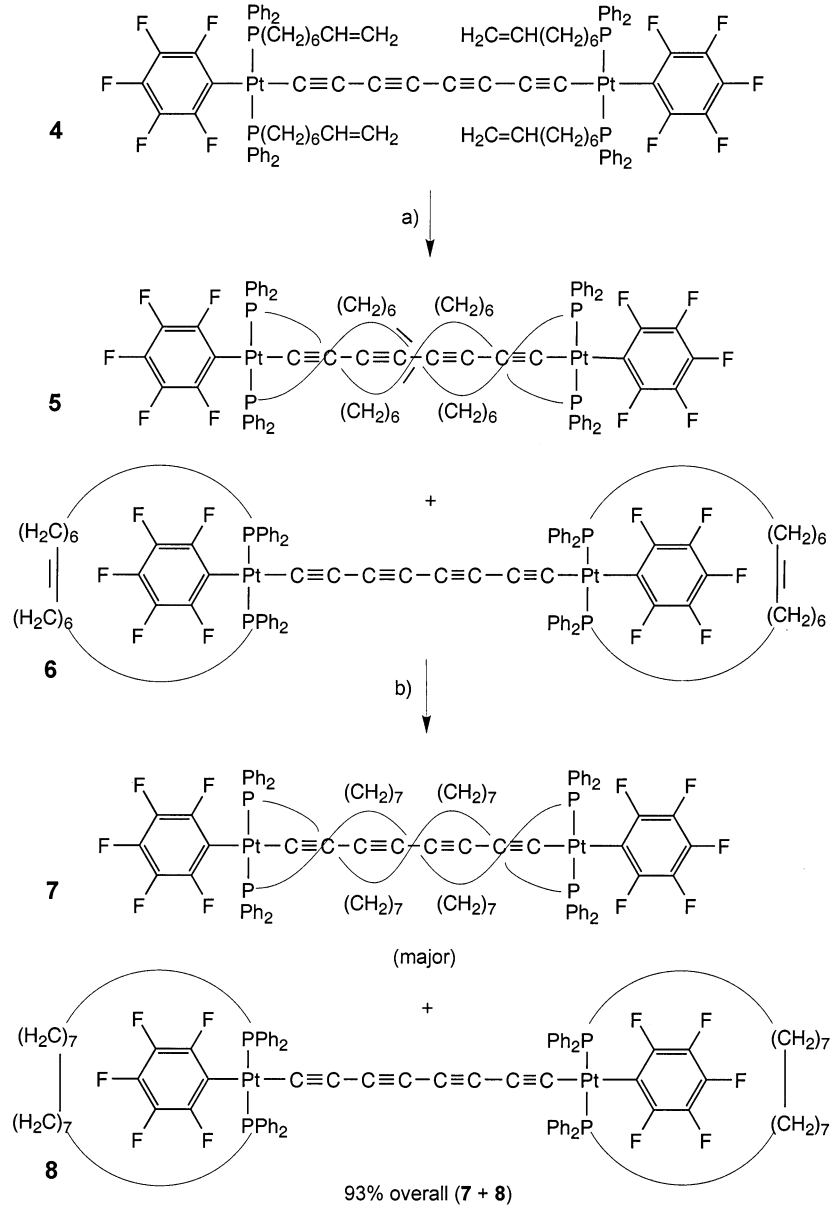
Scheme 2. Synthesis of PtC_8Pt Complexes with Sterically Protected sp Carbon Chains via Olefin Metathesis[a]



[a] (a) cat. Ru(=CHPh)$(PCy_3)_2(Cl)_2$; (b) H_2 (1 bar), cat. 10% Pd/C.

spectrometry, and microanalysis. Most features were very similar to those of related compounds reported earlier.[10] However, the PPh_2 phenyl groups are diastereotopic. Therefore, the aryl ^{13}C NMR signals were more complex than with the corresponding triarylphosphine complexes. NMR spectra also showed **13**$^+BF_4^-$ to be a 77−81:23−19 mixture of Re−(C≡C) rotamers, analogous to the PPh_3 analogue (79−67:21−33).[13,16]

As shown in Scheme 5, reaction of **13**$^+BF_4^-$ and *t*-BuOK gave the σ trimethylsilylbutadiynyl complex (η^5-C_5Me_5)Re(NO)($PPh_2(CH_2)_6CH{=}CH_2$)(C≡CC≡CSiMe_3) (**14**) in 81% yield after workup. Desilylation with wet *n*-$Bu_4N^+F^-$ afforded the corresponding butadiynyl complex (η^5-C_5Me_5)Re(NO)($PPh_2(CH_2)_6CH{=}CH_2$)(C≡CC≡CH) (**15**) in 88% yield. In accord with past experience,[10] **15** was much more labile than the precursor **14**, and it also appeared more labile than the PPh_3 analogue. A correct microanalysis could not be obtained.

The oxidative homocoupling of **15** was effected under Eglinton conditions ($Cu(OAc)_2$, pyridine) that have previously proved very successful for this series of compounds. Column chromatography gave the target μ-octatetraynediyl complex (η^5-C_5Me_5)Re(NO)(PPh_2-$(CH_2)_6CH{=}CH_2$)(C≡CC≡CC≡CC≡C)($H_2C{=}CH(CH_2)_6$-PPh_2)(ON)Re(η^5-C_5Me_5) (**16**) as a red powder in 63% yield. Alternatively, the desilylation and coupling could be carried out in a single flask from **14**, giving **16** in 53% overall yield.

Complex **16** contains two rhenium stereocenters, but NMR spectra showed only a single set of signals. Analogues with para-substituted triarylphosphines show two signals for some resonances, indicative of Re/Re configurational diastereomers (p-Me, 50:50; p-*t*-Bu, 75:25; p-Ph, 71:29).[10b] However, the diastereomers of the corresponding triphenylphosphine complex have never

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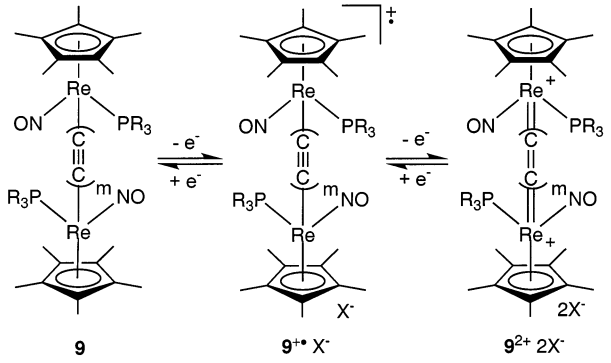
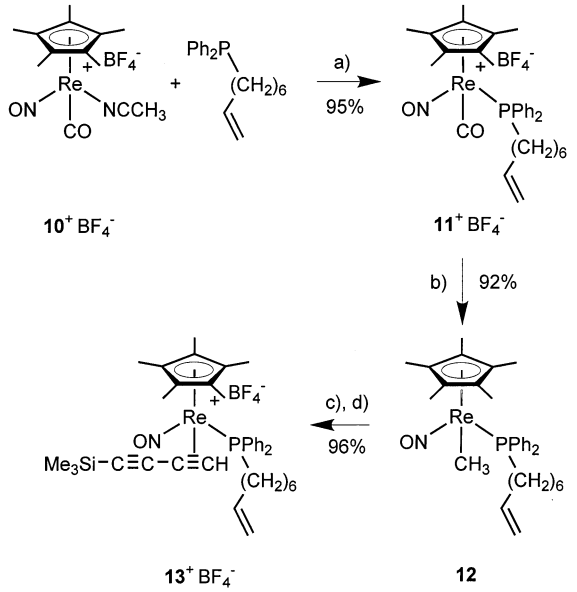
Scheme 3. Redox Chemistry of ReC_xRe Complexes



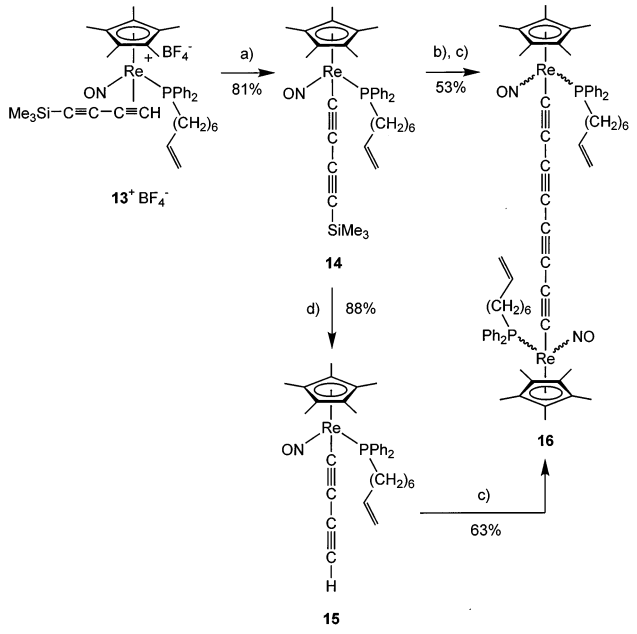
a, m = 2: **9**, $\mathbf{9}^{+\bullet}$ X^-, $\mathbf{9}^{2+}$ $2X^-$ isolable
b, m = 4: **9** isolable, $\mathbf{9}^{+\bullet}$ X^-, $\mathbf{9}^{2+}$ $2X^-$ observed via cyclic voltammetry

Scheme 4. Syntheses of Precursor Rhenium Complexes[a]



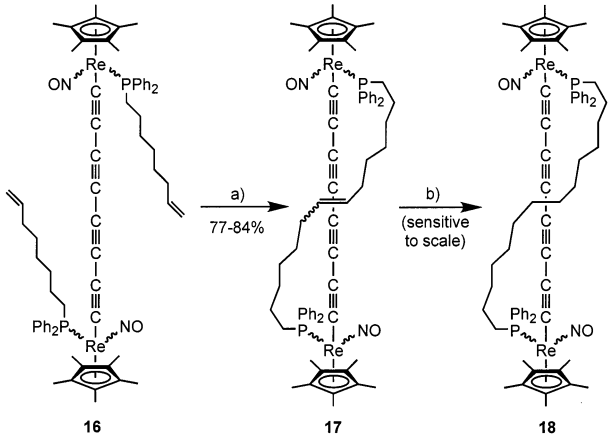
[a] (a) reflux; (b) $LiAlH_4$; (c) HBF_4, C_6H_5Cl, −45 °C; (d) $HC{\equiv}CC{\equiv}CSiMe_3$.

Scheme 5. Syntheses of ReC_4X and ReC_8Re Complexes[a]



[a] (a) *t*-BuOK, −80 °C; (b) K_2CO_3; (c) $Cu(OAc)_2$, 60 °C; (d) $n\text{-}Bu_4N^+F^-$.

Scheme 6. Ring-Closing Olefin Metathesis Involving a ReC_8Re Complex[a]



[a] (a) cat. $Ru(=CHPh)(PCy_3)_2(Cl)_2$; (b) H_2, cat. $Rh(PPh_3)_3Cl$; see text.

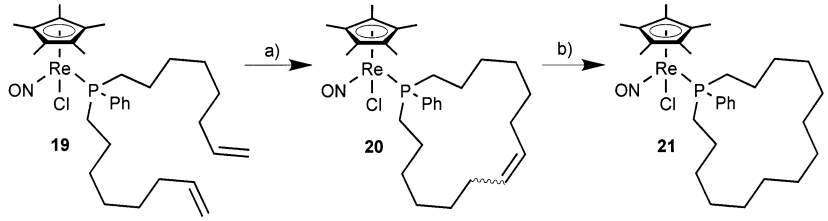
been resolved by NMR, although when the stereocenters are brought closer together in the C_4 homologue, the diastereomers are easily distinguished.[10a] We therefore presume that both diastereomers of **16** are similarly present. Importantly, most physical properties in this series of compounds (e.g., IR and UV−visible spectra, redox potentials) do not appear to depend on the relative end group configurations.

This set the stage for the title sequence. As shown in Scheme 6, **16** (0.0012−0.0007 M in CH_2Cl_2) and Grubbs' catalyst, $Ru(=CHPh)(PCy_3)_2(Cl)_2$ (6−7 mol %), were reacted under conditions similar to those used in Scheme 2. Workup gave the target 26-membered macrocycle (η^5-C_5Me_5)Re(NO)($PPh_2(CH_2)_6CH{=}CH(C{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}C)(CH_2)_6PPh_2$)(ON)Re($\eta^5$-$C_5Me_5$) (**17**), in 77−84% yield. The structure of **17** followed from various data. First, the ^1H and ^{13}C NMR spectra showed the characteristic $CH{=}CH_2$ signals of **16** to be absent. A ^1H NMR spectrum was expanded, and the region where the $CH{=}CH_2$ signals would have appeared carefully analyzed. No trace could be detected, and the maximum amount that could be masked by the baseline noise was shown to be less than 1%.

The mass spectrum of **17** showed an intense molecular ion (*m*/*z* 1364, 100%). There were no significant monorhenium ions and no trace of residual **16** at 28 mass units higher. A small peak at *m*/*z* 2728 (>3%) was evident, corresponding to a dimer derived from intermolecular metathesis. However, HPLC analyses showed only a single band. Many NMR signals of **17** were broader or less well resolved than those of **16**, particularly the unsymmetrically shaped ^{31}P resonance with a $w_{1/2}$ of ca. 84−90 Hz. This is consistent with a mixture of Re/Re configurational and C=C geometric isomers[6,17]

(17) For representative data on *Z*/*E* isomer ratios in organic macrocycles formed by ring-closing olefin metathesis, see: (a) Fürstner, A.; Langemann, K. *J. Org. Chem.* **1996**, *61*, 3942. (b) Fürstner, A.; Langemann, K. *Synthesis* **1997**, 792.

Scheme 7. Model Studies[a]



[a] (a) cat. Ru(=CHPh)(PCy_3)$_2$(Cl)$_2$; (b) H_2 (4 bar), cat. Rh(PPh_3)$_3$(Cl) or 10% Pd/C.

and might also reflect an increased level of steric communication between the chiral rhenium termini. To simplify analysis, we sought to hydrogenate the C=C linkage to give the target molecule (η^5-C_5Me_5)Re(NO)-(PPh_2(CH_2)$_7$(C≡CC≡CC≡CC≡C)(CH_2)$_7$PPh_2)(ON)Re(η^5-C_5Me_5) (**18**).

Both we[6,8] and Sauvage[5] have been able to hydrogenate a variety of metal-containing olefin metathesis products (Schemes 1, 2). On the other hand, the sp carbon chains in **17** and **18** are not as shielded as in **5** and **7** in Scheme 2. Thus, some model studies were undertaken. As shown in Scheme 7, the previously reported ring-closing metathesis of the related rhenium chloride complex, (η^5-C_5Me_5)Re(NO)(PPh((CH_2)$_6$CH=CH_2)$_2$)(Cl) (**19**), was repeated, giving the unsaturated macrocycle (η^5-C_5Me_5)Re(NO)(P(Ph)(CH_2)$_6$CH=CH-(CH_2)$_6$)(Cl) (**20**).[6c] This compound reacts with hydrogen in the presence of Rh(PPh_3)$_3$(Cl) (4 bar, 7 mol %) to give the saturated macrocycle (η^5-C_5Me_5)Re(NO)(P(Ph)-(CH_2)$_{14}$)(Cl) (**21**). We attempted analogous reactions with two new catalysts, Pd/C (10%) and Crabtree's [Ir(PCy_3)(COD)(py)]$^+PF_6^-$ (see Scheme 1). The former afforded comparable results, but the latter gave decomposition.

Accordingly, the hydrogenation of **17** was attempted on small scales with Rh(PPh_3)$_3$(Cl) and Pd/C under a variety of conditions as tabulated in the Experimental Section. Reactions were monitored by HPLC, and the retention time of **18** has been established by virtue of an independent synthesis that will be reported separately.[18,19] The reaction of **17** and hydrogen (2 bar) in toluene/ethanol in the presence of Rh(PPh_3)$_3$(Cl) gave >90% conversion to **18** after 24 min, as assayed by HPLC peak areas. However, after 40 min, considerable product decomposition was evident, indicating a very narrow time window for workup. The solvent, pressure, and temperature were varied, but the results were usually poorer. No **18** was detected on preparative scales or in reactions involving Pd/C. Thus, olefin metathesis efficiently assembles the carbon skeleton of the target molecules in Scheme 6, but the removal of the C=C linkage is problematic.

The cyclic voltammogram of **17** was qualitatively similar to those of other compounds of the type **9b** (Scheme 3). Two one-electron oxidations were observed under our standard conditions in CH_2Cl_2.[10] The potentials were slightly thermodynamically more favorable than those of the PPh_3 analogue and slightly less favorable than those of the P(p-tol)$_3$ analogue ($E°$(1), 0.20 vs 0.24 vs 0.16 V; E°(2), 0.47 vs 0.52 vs 0.45 V). Both steps were only partially reversible (i_c/i_a 0.4 and 0.7; ΔE 80 and 70 mV), consistent with the generation of highly reactive radical cation and dication species (Scheme 3). Preparative reactions of **17** and the one-electron oxidant (η^5-C_5H_5)$_2$Fe$^{\bullet+}$$SbF_6^-$ in CH_2Cl_2 did not afford any tractable products.

Discussion

Scheme 6 shows that the rhenium end groups of a sp carbon chain complex can be further tethered via their phosphine ligands using ring-closing olefin metathesis. This constitutes yet another very useful application of olefin metathesis in metal coordination spheres. In preliminary work, an analogous reaction using a phosphine ligand with nine methylene groups, $Ph_2P(CH_2)_9$-$CH=CH_2$, has been executed with comparable results.[20] The chemoselectivities of these transformations are noteworthy, as facile stoichiometric C≡C additions to (Cl)$_2$$L_2$Ru=CHPh linkages have been observed.[21] This furthermore represents the key step in catalytic ene/yne metathesis.[22] Nonetheless, the sp carbon chains in Schemes 2 and 6 remain intact.

Unfortunately, our inability to develop a scalable protocol for the hydrogenation of the C=C bond in **17** restricts the potential range of applications, particularly in view of the stereochemical inhomogeneity. Also, with regard to radical cations of the type **9b**$^{\bullet+}$$X^-$ (Scheme 3), the C=C and allylic carbon−hydrogen bonds in **17** constitute potential reactive sites that could facilitate intramolecular decomposition. Accordingly, the cyclic voltammetry data suggest lowered stability with respect to triarylphosphine analogues. There is only one example to date of a MC≡CC≡CC≡CC≡CM system that can be oxidized to spectroscopically detectable species: Lapinte's very electron-rich diiron complex (η^5-C_5Me_5)-Fe(dppe)(C≡C)$_4$(dppe)Fe(η^5-C_5Me_5).[23] Remarkably, the corresponding radical cation can be isolated in analytically pure form.

The 26-membered macrocyclic rings in **17** and **18** can adopt the two limiting conformations shown in Scheme 8. In **I**, the flexible 14-carbon sp^3/sp^2 (**17**) or sp^3 (**18**) chain twists around the sp carbon chain in a single-helical motif. In **II**, the flexible chain forms a small cavity or folded assembly, similar to those of aliphatic macrocycles.[24] The former creates a three-dimensional protective sheath for the sp carbon chain, while the

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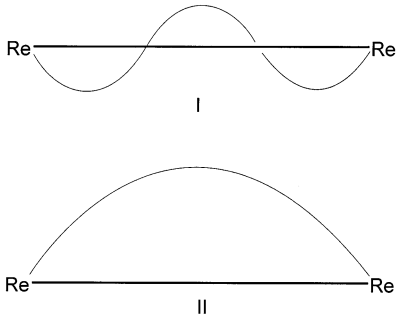
Scheme 8. Limiting Macrocycle Conformations for 17 and 18



latter shields one side. No data that bear on this issue are presently available. One complication is that all ReC_8Re complexes are difficult to crystallize, a factor we attribute to the presence of diastereomers. However, the platinum complex **7** in Scheme 2 provides precedent for conformation **I**.

In conclusion, the preceding data establish that ring-closing olefin metathesis reactions can be effected in the presence of a variety of potentially sensitive MC≡CC≡CC≡CC≡CM linkages. This further expands the scope of this macrocyclization process for directed organometallic synthesis. The inability to develop a scalable hydrogenation of **17** illustrates a potential strategic limitation. However, such reactions are normally successful. With **18**, the problem is somewhat ameliorated by a successful but low-yield independent synthesis via an intramolecular oxidative coupling.[18,19] Also, the recent catalysis of C≡C metathesis reactions in metal coordination spheres allows carbon skeletons to be fixed without generating mixtures of geometric isomers.[25] Additional applications of olefin metathesis to complex organometallic target molecules will be reported soon.

Experimental Section

General procedures, solvent and reagent purifications, and instrumentation were identical with those listed in four recent full papers[6c,10,11b] and are further detailed elsewhere.[19] Grubbs' catalyst, $Ru(=CHPh)(PCy_3)_2(Cl)_2$ (Strem), was used as received. NMR spectra were referenced to TMS or the residual solvent signal (^1H, ^{13}C) or external H_3PO_4 (^{31}P). HPLC was conducted on a Thermoquest instrument package (pump/autosampler/detector P4000/AS3000/UV6000LP).

$[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_2(CH_2)_6CH{=}CH_2)(CO)]^+BF_4^-$ ($11^+BF_4^-$). A Schlenk flask was charged with solutions of $[(\eta^5\text{-}C_5Me_5)Re(NO)(NCCH_3)(CO)]^+BF_4^-$ ($\mathbf{10}^+BF_4^-$; 4.543 g, 8.960 mmol)[11] in 2-butanone (50 mL) and $PPh_2(CH_2)_6CH{=}CH_2$ (3.185 g, 10.75 mmol)[6c] in 2-butanone (5 mL). The solution was refluxed (14 h) and cooled to room temperature. The solvent was removed by oil-pump vacuum. The oily residue was triturated with ether to give a yellow powder, which was collected by filtration and dissolved in acetone. The solution was layered with ether. After 48 h, yellow-tan prisms of $\mathbf{11}^+BF_4^-$ were collected by filtration and dried by oil-pump vacuum (6.494 g, 8.515 mmol, 95%).

Mp: 149 °C. ^1H NMR (400 MHz, [D]$CHCl_3$, 25 °C): δ 7.60−7.26 (m, 10 H; $2C_6H_5$), 5.71 (m, 1 H; C*H*=), 4.94−4.86 (m, 2 H; =CH_2), 2.63 (m, 2 H; PCH_2), 1.96 (s, 15 H; $C_5(CH_3)_5$), 1.38−1.10 (m, 10 H; 5CH_2).[26] $^{13}C\{^1H\}$ NMR (100 MHz, [D]$CHCl_3$, 25 °C): δ 202.0 (d, ^2J(C,P) = 8 Hz, *C*O), 138.8 (s, CH_2CH=), 132.6/132.5 (2 s, *p*-Ph/Ph′), 132.6/132.2 (2 d, ^2J(C,P) = 10/10 Hz, *o*-Ph/Ph′), 130.0/128.7 (2 d, ^1J(C,P) = 55/55 Hz, *i*-Ph/Ph′), 130.0/129.8 (2 d, ^3J(C,P) = 10/11 Hz, *m*-Ph/Ph′), 114.5 (s, =CH_2), 106.2 (s, $C_5(CH_3)_5$), 33.6 (s, CH_2CH=), 32.8 (d, ^1J(C,P) = 36 Hz, PCH_2),[27] 30.2 (d, J(C,P) = 15 Hz, CH_2), 28.6 (s, CH_2), 28.5 (s, CH_2), 24.1 (s, CH_2), 9.6 (s, $C_5(CH_3)_5$). $^{31}P\{^1H\}$ NMR (161 MHz, [D]$CHCl_3$, 25 °C): δ 9.4 (s). IR (solid film): $\tilde{\nu}$ 1990 (s, CO), 1732 (s, NO) cm^{-1}. MS (FAB, 3-NBA/CH_2Cl_2):[28] *m*/*z* (%) 676 (100) [M^+]. Anal. Calcd for $C_{31}H_{40}BF_4NO_2PRe$ (762.65): C 48.82, H 5.29, N 1.84. Found: C 49.05, H 5.34, N 1.75.

$(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_2(CH_2)_6CH{=}CH_2)(CH_3)$ (12). A Schlenk flask was charged with $\mathbf{11}^+BF_4^-$ (1.501 g, 1.968 mmol), THF (50 mL), and $LiAlH_4$ (0.224 g, 5.904 mmol; added in three portions). The mixture was stirred (2 h) and monitored by TLC (more $LiAlH_4$ can be added if needed). Then water was added until gas evolution ceased. Solvent was removed by oil-pump vacuum. The residue was extracted with THF (2 mL). The extract was filtered through a pad of alumina, and solvent was removed by oil-pump vacuum to give **12** as a red gum (1.196 g, 1.804 mmol, 92%).

^1H NMR (400 MHz, [D]$CHCl_3$, 25 °C): δ 7.59−7.30 (m, 10 H; $2C_6H_5$), 5.76 (m, 1 H; C*H*=), 4.98−4.89 (m, 2 H; =CH_2), 2.63, 2.34 (2 m, 2 H; PCH_2), 1.97 (m, 2 H; CH_2CH=), 1.61 (s, 15 H; $C_5(CH_3)_5$), 1.39−1.19 (m, 8 H; 4CH_2), 0.87 (d, ^3J(H,P) = 6 Hz, 3 H; ReCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, [D]$CHCl_3$, 25 °C): δ 139.1 (s, CH_2CH=), 135.8/135.2 (2 d, ^1J(C,P) = 40/39 Hz, *i*-Ph/Ph′), 133.7/132.3 (2 d, ^2J(C,P) = 10/10 Hz, *o*-Ph/Ph′), 129.7/129.2 (2 s, *p*-Ph/Ph′), 128.1/127.9 (2 d, ^3J(C,P) = 9/9 Hz, *m*-Ph/Ph′), 114.1 (s, =CH_2), 97.6 (s, $C_5(CH_3)_5$), 33.7 (s, CH_2-CH=), 32.7 (d, ^1J(C,P) = 33 Hz, PCH_2),[27] 30.9 (d, J(C,P) = 15 Hz, CH_2), 28.7 (s, CH_2), 28.6 (s, CH_2), 23.4 (s, CH_2), 9.6 (s, C_5-$(CH_3)_5$), −24.3 (d, ^2J(C,P) = 6 Hz, CH_3). $^{31}P\{^1H\}$ NMR (161 MHz, [D]$CHCl_3$, 25 °C): δ 11.0 (s). IR (solid film): $\tilde{\nu}$ 1604 (s, NO) cm^{-1}. MS (FAB, 3-NBA/CH_2Cl_2):[28] *m*/*z* (%) 663 (100) [M^+]. Anal. Calcd for $C_{31}H_{43}NOPRe$ (662.86): C 56.17, H 6.54, N 2.11. Found: C 56.20, H 6.51, N 1.99.

$[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_2(CH_2)_6CH{=}CH_2)(HC{\equiv}C\text{-}C{\equiv}CSiMe_3)]^+BF_4^-$ ($13^+BF_4^-$). A Schlenk flask was charged with **12** (1.722 g, 2.673 mmol) and C_6H_5Cl (10 mL) and cooled to −45 °C (acetone/CO_2 slurry). Then $HBF_4{\cdot}OEt_2$ (54% in ether, 0.350 mL, 2.74 mmol) was added with stirring. After 10 min, HC≡CC≡C$SiMe_3$ (1.6 mL, 1.31 g (mass of loaded/discharged syringe), 10.7 mmol)[13,14] was added, and the cold bath removed. After 2 h, the solvent was removed by oil-pump vacuum and the residue extracted with CH_2Cl_2. The resulting suspension was filtered through a short Celite pad. The filtrate was concentrated by rotary evaporation to ca. 2 mL. This solution was added dropwise into rapidly stirred hexane. The tan powder was collected by filtration and dried by oil-pump vacuum to give $\mathbf{13}^+BF_4^-$ (2.188 g, 2.553 mmol, 96%; 77−81:23−19 mixture of Re−(C≡C) rotamers[13,16]).

Mp: 59 °C (dec). ^1H NMR (400 MHz, [D]$CHCl_3$, 25 °C): δ 8.1 (br s, 1 H; *H*C≡), 7.59−7.30 (m, 10 H; $2C_6H_5$), 5.70 (m, 1 H; CH_2CH=), 4.98−4.89 (m, 2 H; =CH_2), 2.63 (m, 2 H; PCH_2), 1.94 (m, 2 H; CH_2CH=), 1.83/1.75[29] (2 s, 15 H; $C_5(CH_3)_5$), 1.39−1.19 (m, 8 H; 4CH_2), 0.33/−0.12[29] (2 s, 81:19, 9 H; $Si(CH_3)_3$).

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(26) The ^1H NMR spectra of the other complexes show a CH_2CH= signal at δ = 1.94−1.98. This may coincide with the cyclopentadienyl signal of $\mathbf{11}^+BF_4^-$, but an assignment cannot unambiguously be made based upon the integration.

(27) A ^1H,^{13}C COSY experiment established that the PCH_2 protons of $\mathbf{11}^+BF_4^-$ and **12** reside on the carbon with the largest J(C,P) value. These correlations were used to assign the PCH_2 ^{13}C signals in all compounds.

(28) The M^+ ions represent the most intense peak in the isotope envelope. There were no other significant nonmatrix-derived peaks (≥15% of the M^+ ion) above *m*/*z* 200.

(29) These signals are for the major and minor rotamers, respectively.

$^{13}C\{^1H\}$ NMR (100 MHz, [D]$CHCl_3$, 25 °C): δ 138.9 (s, *C*H═), 132.9−126.4 (unresolved Ph signals), 114.5 (s, ═*C*H_2), 114.1 (s, *C*≡CSi), 107.8 (br, s, *C*$_5(CH_3)_5$), 95.1 (s, C≡*C*Si), 33.4 (s, *C*H_2CH═), 32.4 (d, ^1J(C,P) = 34 Hz, P*C*H_2),[27] 30.2 (d, J(C,P) = 14 Hz, *C*H_2), 28.5 (s, *C*H_2), 28.3 (s, *C*H_2), 24.1 (s, *C*H_2), 9.6 (s, C$_5(CH_3)_5$), −0.5/−0.8[29] (2 s, Si(*C*$H_3)_3$). $^{31}P\{^1H\}$ NMR (161 MHz, [D]$CHCl_3$, 25 °C): δ 7.3/13.4[29] (2 s, 77:23). IR (solid film): $\tilde{\nu}$ 2139 (m, C≡C), 1697 (s, NO) cm^{-1}. MS (FAB, 3-NBA/CH_2Cl_2):[28] *m*/*z* (%) 770 (100) [M^+]. Anal. Calcd for $C_{37}H_{50}BF_4NOPReSi$ (856.86): C 51.86, H 5.88, N 1.64. Found: C 52.02, H 6.08, N 1.64.

(η^5-C$_5$Me$_5$)Re(NO)(PPh$_2$(CH$_2$)$_6$CH═CH$_2$)(C≡C-C≡CSiMe$_3$) (14). A Schlenk flask was charged with **13**$^+$BF$_4^-$ (0.112 g, 0.131 mmol) and *t*-BuOK (0.015 g, 0.136 mmol) and cooled to −75 °C (acetone/CO_2 slurry). Precooled THF (5 mL) was added via cannula. After 10 min, the cold bath was removed. After 2 h, the solution was concentrated to ca. 2 mL and passed through an alumina pad (3 cm). The solvent was evaporated from the filtrate by oil-pump vacuum to give **14** as a dark red solid (0.082 g, 0.106 mmol, 81%).

Mp: 103−106 °C. ^1H NMR (400 MHz, [D]$CHCl_3$, 25 °C): δ 7.69−7.35 (m, 10 H; 2C$_6H_5$), 5.76 (m, 1 H; C*H*═), 4.98−4.88 (m, 2 H; ═CH_2), 3.15, 2.52 (2 m, 2 H; PCH_2), 1.98 (m, 2 H; CH_2CH═), 1.72 (s, 15 H; C$_5$(CH_3)$_5$), 1.39−1.19 (m, 8 H; 4CH_2), 0.20 (s, 9 H; Si(CH_3)$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, [D]$CHCl_3$, 25 °C): δ 139.2 (s, CH$_2$*C*H═), 134.5/132.0 (2 d, ^1J(C,P) = 48/48 Hz, *i*-Ph/Ph′), 134.5/132.1 (2 d, ^2J(C,P) = 10/10 Hz, *o*-Ph/Ph′), 130.5/129.6 (2 s, *p*-Ph/Ph′), 128.4/128.0 (2 d, ^3J(C,P) = 10/9 Hz, *m*-Ph/Ph′), 114.0 (s, ═*C*H$_2$), 110.1 (s, ReC≡*C*),[30] 107.3 (d, ^2J(C,P) = 15 Hz, Re*C*≡C),[30] 100.3 (s, *C*$_5$(CH$_3$)$_5$), 92.0 (s, *C*≡CSi),[30] 80.5 (s, C≡*C*Si),[30] 33.63 (s, *C*H$_2$CH═), 33.57 (d, ^1J(C,P) = 36 Hz, P*C*H$_2$),[27] 30.6 (d, J(C,P) = 16 Hz, *C*H$_2$), 28.7 (s, *C*H$_2$), 28.4 (s, *C*H$_2$), 23.4 (s, *C*H$_2$), 9.8 (s, C$_5$(*C*H$_3$)$_5$), 0.7 (s, Si(*C*H$_3$)$_3$). $^{31}P\{^1H\}$ NMR (161 MHz, [D]$CHCl_3$, 25 °C): δ 10.1 (s). IR (solid film): $\tilde{\nu}$ 2114 (m, C≡C), 2093 (m, C≡C), 1645 (s, NO) cm^{-1}. MS (FAB, 2-NPOE/benzene):[28] *m*/*z* (%) 769 (100) [M^+]. Anal. Calcd for $C_{37}H_{49}NOPReSi$ (769.06): C 57.79, H 6.42, N 1.82. Found: C 56.95, H 6.15, N 1.81.

(η^5-C$_5$Me$_5$)Re(NO)(PPh$_2$(CH$_2$)$_6$CH═CH$_2$)(C≡CC≡CH) (15). A Schlenk flask was charged with **14** (1.373 g, 1.785 mmol) and THF (20 mL). Then *n*-Bu$_4$N$^+$F$^-$ (1.0 M in wet THF, 0.357 mL, 0.357 mmol) was added dropwise with stirring. The reaction was monitored by alumina TLC (the spot for **15** shows rapid decomposition). After 2 h, the solution was passed through a short pad of alumina. The solvent was removed by oil-pump vacuum to give **15** as a red oil (1.098 g, 1.576 mmol, 88%).

^1H NMR (400 MHz, [D]$CHCl_3$, 32 °C): δ 7.70−7.06 (m, 10 H; 2C$_6H_5$), 5.76 (m, 1 H; C*H*═), 4.98−4.89 (m, 2 H; ═CH_2), 3.42, 2.49 (2 m, 2 H; PCH_2), 2.16 (s, 1 H; ≡C*H*), 1.98 (m, 2 H; CH_2CH═), 1.58 (s, 15 H; C$_5$(CH_3)$_5$), 1.39−1.19 (m, 8 H; 4CH_2). $^{31}P\{^1H\}$ NMR (161 MHz, [D]$CHCl_3$, 32 °C): δ 10.5 (s). IR (solid film): $\tilde{\nu}$ 3302 (w, ≡CH), 2114 (m, C≡C), 1973 (m, C≡C), 1645 (s, NO) cm^{-1}. MS (FAB, 2-NPOE/benzene):[28] *m*/*z* (%) 697 (100) [M^+]. A correct microanalysis could not be obtained.

(η^5-C$_5$Me$_5$)Re(NO)(PPh$_2$(CH$_2$)$_6$CH═CH$_2$)(C≡CC≡CC≡CC≡C)(H$_2$C═CH(CH$_2$)$_6$PPh$_2$)(ON)Re(η^5-C$_5$Me$_5$) (16). A. A Schlenk flask was charged with **15** (0.062 g, 0.089 mmol), Cu(OAc)$_2$ (0.016 g, 0.089 mmol), and pyridine (5 mL) and heated to 60 °C. After 2 h, the solvent was removed by oil-pump vacuum. The residue was extracted with CH_2Cl_2. Column chromatography (silica gel, CH_2Cl_2) gave a fast-moving band, which was concentrated to ca. 10 mL. Hexane was added, and the sample was further concentrated by rotary evaporation. The precipitate was collected by filtration and dried by oil-pump vacuum to give **16** as a red powder (0.039 g, 0.028 mmol, 63%). **B**. A Schlenk flask was charged with **14** (0.204 g, 0.265 mmol), K_2CO_3 (0.117 g, 0.780 mmol), Cu(OAc)$_2$ (0.282 g, 1.560 mmol), MeOH (5 mL), and pyridine (5 mL). The green suspension was stirred at 60 °C for 2 h and worked up as in method A to give **16** (0.098 g, 0.141 mmol, 53%).

Mp: 102−106 °C. ^1H NMR (400 MHz, [D]$CHCl_3$, 32 °C): δ 7.67−7.36 (m, 20 H; 4C$_6H_5$), 5.77 (m, 2 H; 2C*H*═), 4.98−4.89 (m, 4 H; 2═CH_2), 3.13, 2.49 (m, 4 H; 2PCH_2), 1.98 (m, 4 H; 2CH_2CH═), 1.72 (s, 30 H; 2C$_5$(CH_3)$_5$), 1.39−1.16 (m, 16 H; 8CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, [D]$CHCl_3$, 20 °C (Re*C*≡ not observed)): δ 139.0 (s, CH$_2$*C*H═), 134.2/131.9 (2 br s, *i*-Ph/Ph′),[31] 134.7/132.4 (2 d, ^2J(C,P) = 9/9 Hz, *o*-Ph/Ph′), 130.8/130.0 (2 s, *p*-Ph/Ph′), 128.7/128.3 (2 d, ^3J(C,P) = 10/9 Hz, *m*-Ph/Ph′), 114.0 (s, ═*C*H$_2$), 113.7 (s, ReC≡*C*),[30] 100.7 (s, *C*$_5$(CH$_3$)$_5$), 69.9 (s, ReC≡C*C*),[30] 67.0 (s, ReC≡CC≡*C*),[30] 33.9, 33.7, 33.5, 33.2 (4 s or br s, P*C*H$_2$, *C*H$_2$CH═), 30.6 (br s, 2*C*H$_2$), 29.0 (s, *C*H$_2$), 28.5 (s, *C*H$_2$), 24.4 (s, *C*H$_2$), 11.3 (s, C$_5$(*C*H$_3$)$_5$). $^{31}P\{^1H\}$ NMR (161 MHz, [D]$CHCl_3$, 32 °C): δ 9.9 (s). IR (solid film): $\tilde{\nu}$ 2108 (m, C≡C), 1956 (w, C≡C), 1642 (s, NO) cm^{-1}. MS (FAB, 2-NPOE/benzene):[28] *m*/*z* (%) 1392 (100) [M^+]. Anal. Calcd for $C_{68}H_{80}N_2O_2P_2Re_2$ (1391.75): C 58.69, H 5.79, N 2.01. Found: C 58.01, H 5.32, N 1.78.

(η^5-C$_5$Me$_5$)Re(NO)(PPh$_2$(CH$_2$)$_6$CH═CH)(C≡CC≡CC≡CC≡C)((CH$_2$)$_6$PPh$_2$)(ON)Re(η^5-C$_5$Me$_5$) (17). A. A Schlenk flask was charged with **16** (0.114 g, 0.082 mmol) and CH_2Cl_2 (70 mL). Another Schlenk flask was charged with Ru(═CHPh)(PCy$_3$)$_2$(Cl)$_2$ (0.005 g, 0.006 mmol, 7 mol %) and CH_2Cl_2 (10 mL). This purple solution was added by cannula to the red solution of **16**. The mixture was refluxed (3 h). The brown solution was concentrated to ca. 3 mL and passed through a silica gel pad (with CH_2Cl_2 rinses). The filtrate was concentrated to ca. 10 mL. Hexane was added, and the sample was further concentrated by rotary evaporation. The red powder was collected by filtration and dried under oil-pump vacuum to give **17** (0.094 g, 0.069 mmol, 84%). **B**. A Schlenk flask was charged with **16** (0.098 g, 0.071 mmol), CH_2Cl_2 (100 mL), and Ru(═CHPh)(PCy$_3$)$_2$(Cl)$_2$ (0.002 g, 0.002 mmol, 3 mol %). The mixture was refluxed. After 1 h, more Ru(═CHPh)(PCy$_3$)$_2$(Cl)$_2$ (0.002 g, 0.002 mmol, 3 mol %) was added. After an additional 2 h, the brown solution was concentrated to ca. 5 mL and passed through a silica gel pad (with CH_2Cl_2 rinses). The filtrate was concentrated to ca. 10 mL. Hexane was added, and the sample was further concentrated by rotary evaporation. The red powder was collected by filtration and dried under oil-pump vacuum to give **17** (0.074 g, 0.055 mmol, 77%).

Mp: 145−146 °C. ^1H NMR (400 MHz, [D]$CHCl_3$, 32 °C): δ 7.63−7.36 (m, 20 H; 4C$_6H_5$), 5.42, 5.10 (m, 2 H; 2C*H*═), 3.13, 2.49 (2 m, 4 H; 2PCH_2), 2.05 (m, 4 H; 2CH_2CH═), 1.72 (br s, 30 H; 2C$_5$(CH_3)$_5$), 1.39−1.16 (m, 16 H; 8CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, [D]$CHCl_3$, 20 °C): δ 134.4/132.2 (2 br s, $w_{1/2}$ = 7/6 Hz, *i*-Ph/Ph′), 134.8/132.4 (2 br s, $w_{1/2}$ = 6/5 Hz, *o*-Ph/Ph′), 130.6/129.7 (2 br s, $w_{1/2}$ = 2/6 Hz, *p*-Ph/Ph′), 130.1 (s, *C*H═*C*H), 128.5/128.1 (2 br s, $w_{1/2}$ = 5/4 Hz, *m*-Ph/Ph′), 111.8 (s, ReC≡*C*), 109.3 (br s, Re*C*≡C), 99.2 (s, *C*$_5$(CH$_3$)$_5$), 66.0 (s, ReC≡C*C*≡C), 64.2 (s, ReC≡CC≡*C*), 33.1 (*C*H$_2$),[32] 30.9 (*C*H$_2$CH═),[32] 29.8 (*C*H$_2$),[32] 28.8 (*C*H$_2$),[32] 28.0 (*C*H$_2$),[32] 22.6 (*C*H$_2$),[32] 11.3 (s, C$_5$(*C*H$_3$)$_5$). $^{13}C\{^1H\}$ NMR (100 MHz, [D]$CHCl_3$, 20 °C): δ 134.5/132.3 (2 br s, $w_{1/2}$ = 8/8 Hz, *i*-Ph/Ph′), 134.8/131.9 (2 br s, $w_{1/2}$ = 17/15 Hz, *o*-Ph/Ph′), 130.7/129.8 (2 br s, $w_{1/2}$ = 9/12 Hz, *p*-Ph/Ph′), 130.2 (s, *C*H═*C*H), 128.5/128.1 (2 br s, $w_{1/2}$ = 8/8 Hz, *m*-Ph/Ph′), 113.9 (s, ReC≡*C*), 111.2 (br s, Re*C*≡C), 99.2 (s, *C*$_5$-(CH$_3$)$_5$), 66.4 (s, ReC≡C*C*≡C), 63.8 (s, ReC≡CC≡*C*), 33.2 (*C*H$_2$),[32] 30.5 (*C*H$_2$CH═),[32] 29.8 (*C*H$_2$),[32] 28.6 (*C*H$_2$),[32] 27.8 (*C*H$_2$),[32] 23.2 (*C*H$_2$),[32] 10.9 (s, C$_5$(*C*H$_3$)$_5$). $^{31}P\{^1H\}$ NMR (161 MHz, [D]$CHCl_3$, 32 °C): δ 10.4 (br s, $w_{1/2}$ = 90 Hz). IR (solid film): $\tilde{\nu}$ 2108 (m, C≡C), 1955 (w, C≡C), 1645 (s, NO) cm^{-1}. MS (FAB, 3-NBA/CH_2Cl_2):[28] *m*/*z* (%) 1364 (100) [M^+], 2728 (3)

(30) These assignments follow from coupling constant and chemical shift patterns rigorously established earlier.[13]

(31) One line of the expected doublet is obscured.

(32) Consistent with the mixture of isomers (see text), the CH_2 ^{13}C NMR signals did not exhibit good signal/noise, and some were doubled and/or broad.

[dimer$^+$]. Anal. Calcd for $C_{66}H_{76}N_2O_2P_2Re_2$ (1363.69): C 58.13, H 5.62, N 2.05. Found: C 58.52, H 5.72, N 1.85.

Hydrogenation of 17. A. A Fischer−Porter bottle was charged with **17** (ca. 0.005 g, 0.004 mmol), toluene/ethanol (50 mL, 1:1 v/v), and $Rh(PPh_3)_3(Cl)$ (ca. 0.001 g, 0.001 mmol) and placed under H_2 (2 bar). After 24 min, an aliquot (1 mL) was filtered through alumina and taken to dryness, and *n*-hexane/2-propanol (0.5 mL, 98:2 v/v) was added. HPLC analysis (isocratic, Nucleosil 100-5 column) showed a ca. 91:09 ratio of $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_2(CH_2)_7)(C{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}C)\text{-}((CH_2)_7PPh_2)(ON)Re(\eta^5\text{-}C_5Me_5)$ (**18**)[18,19] and **17** (relative absorbance, 254 nm). After 40 min, the peak for **18** had diminished, and decomposition products with shorter retention times were present. **B**. Many similar reactions were conducted using (a) 0.0059 g (0.003 mmol) of **17**, 0.004 g of Pd/C (10%; 0.0004 mmol), 1 bar H_2, 3 mL of toluene; (b) as in a but 4 bar H_2; (c) 0.0048 g (0.003 mmol) of **17**, 0.005 g of Pd/C (10%; 0.0004 mmol), 1 bar H_2, 4 mL of 50:50 v/v $ClCH_2CH_2Cl$/EtOH; (d) 0.0053 g (0.003 mmol) of **17**, 0.003 g (0.003 mmol) of $Rh(PPh_3)_3(Cl)$, 4 mL of 50:50 v/v toluene/EtOH, 4 bar H_2; (e) 0.0056 g (0.003 mmol) of **17**, 0.004 g (0.004 mmol) of $Rh(PPh_3)_3(Cl)$, 3 mL of toluene, 1 bar H_2; (f) as in e but at 40 °C. In each of these experiments, HPLC analyses showed either unreacted **17** or decomposition products.

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