Syntheses of Dimetallamacrocycles by Intramolecular Oxidative Couplings of Dinuclear Bis(1,3-butadiynyl) Complexes: A New Approach to Steric Shielding in (sp-Carbon chain)dirhenium Complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(PR_3)(C{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}C)(R_3P)(ON)Re(\eta^5\text{-}C_5Me_5)]$

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Reactions of the chiral racemic carbonyl complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(NCCH_3)(CO)]^+\cdot BF_4^-$ and diphosphanes $Ph_2P(CH_2)_nPPh_2$ [2.4:1.0 mol ratio; n = 10 (**a**), 14 (**b**)] give the (bridging phosphane)dirhenium complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(CO)\{\mu\text{-}[PPh_2(CH_2)_nPh_2P]\text{-}P,P\}(OC)(ON)Re(\eta^5\text{-}C_5Me_5)]^{2+}\cdot 2BF_4^-$ (73–80%), which are reduced ($LiAlH_4$) to the dimethyl complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(CH_3)\{\mu\text{-}[PPh_2(CH_2)_nPh_2P]\text{-}P,P\}(ON)(H_3C)Re(\eta^5\text{-}C_5Me_5)]$ (92–96%). Reactions with $HBF_4\cdot OEt_2/C_6H_5Cl$, $HC{\equiv}CC{\equiv}CSiMe_3$, and tBuOK give, via π-$HC{\equiv}C$ adducts (89–94%), the bis(trimethylsilylbutadiynyl) complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(C{\equiv}CC{\equiv}CSiMe_3)\{\mu\text{-}[PPh_2(CH_2)_nPh_2P]\text{-}P,P\}(Me_3SiC{\equiv}CC{\equiv}C)(ON)Re(\eta^5\text{-}C_5Me_5)]$ (**9a**,**b**; 95–66%). Desilylation (wet nBu$_4$NF) yields labile bis(butadiynyl) complexes, which are coupled [$Cu(OAc)_2$/pyridine] to the μ-octatetraynediyl complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)\{\mu\text{-}[PPh_2(CH_2)_nPh_2P]\text{-}P,P\}\{\mu\text{-}(C^1{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}C^8)\text{-}C^1,C^8\}(ON)Re(\eta^5\text{-}C_5Me_5)]$ (**3a**,**b**; 10–23% from **9a**,**b**). These represent some of the few cases of intramolecular oxidative homocouplings of terminal alkynes in metal coordination spheres. The electrochemical properties of **3a**,**b**, which undergo two one-electron oxidations, are compared to nonmacrocyclic analogs that lack the diphosphane bridge.

Introduction

Macrocyclization methodologies have played an important role in the development of synthetic organic chemistry.[1] A variety of general strategies are now established, with applications ranging from complex natural products to theoretically interesting unnatural substances such as annulenes. Many relevant physical organic studies have been conducted to define optimum substrate characteristics and conditions.[2] In contrast, macrocyclizations have attracted less focused or systematic attention to date in synthetic inorganic or organometallic chemistry.

Nonetheless, there has been a diverse range of activity. We have used olefin and alkyne metathesis reactions to effect macrocyclizations of a variety of transition-metal complexes, giving products in which metal atoms are part of the new ring (metall***a***macrocycle) or attached to the new ring (metall***o***macrocycle).[3−6] Sauvage has, in the pursuit of catenanes, molecular knots, and related novel species, investigated a number of macrocyclizations of coordination compounds.[7−9] Any complex in which *trans* positions are spanned by a chelate ligand is by definition macrocyclic, and Bessel and Takeuchi have recently reviewed this scattered literature.[10] There are also growing numbers of metallacrown species,[11] nearly all of which are macrocyclic. However, there are very few comparative evaluations of synthetic strategies.

The intramolecular oxidative coupling of organic compounds that contain two terminal alkynes has played a critical role in the development of macrocycle chemistry, particularly with annulenes and dehydroannulenes.[12,13] Many intermolecular oxidative couplings of transition-metal-containing terminal alkynes are also known. However, to the best of our knowledge there are few if any cases where an isolated inorganic or organometallic compound containing two terminal alkynes has undergone an intramolecular oxidative macrocyclization.[14] Oxidative cyclodimerizations and cyclooligomerizations can be effected with some such species, and representative examples are depicted in Scheme 1.[8,15] These entail the macrocyclization of an intermediate with two terminal alkynes.

We wondered whether such intramolecular oxidative couplings might prove applicable to a synthetic problem in our group. As detailed in the previous paper in this series,[5] we have sought (μ-octatetraynediyl)dirhenium or $ReC{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}CRe$ systems with sterically shielded sp-carbon chains. One motivation is the possibility of enhanced stabilities for the corresponding radical cations $[ReC{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}CRe]^{+\cdot}X^-$ and dications [Re=C=

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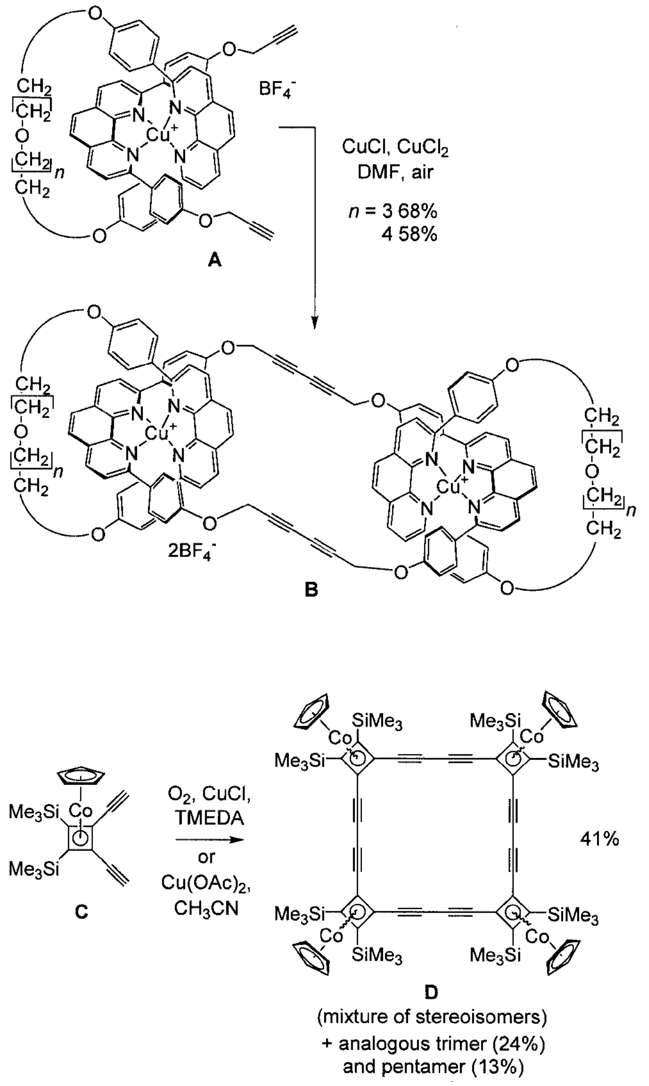
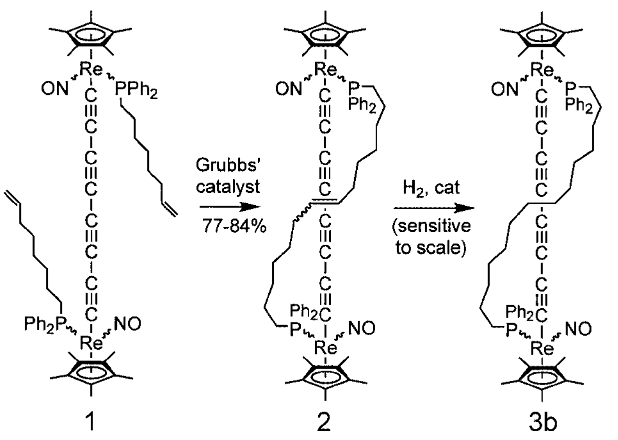


Scheme 1. Representative macrocycle syntheses involving oxidative dimerization or oligomerization of inorganic and organometallic compounds that contain two terminal alkynes[15]

C=C=C=C=C=C=C=Re]$^{2+}$·2X^{-}. Much evidence suggests that decomposition involves bimolecular chain/chain or chain/solvent reactions. As shown in Scheme 2, the complex **1**, which features an alkene-containing phosphane on each rhenium atom, undergoes olefin metathesis to give the macrocycle **2** in good yield. However, subsequent hydrogenations of the residual C=C bond, while sometimes giving the target molecule **3b**, were difficult to reproduce or scale up.[5]

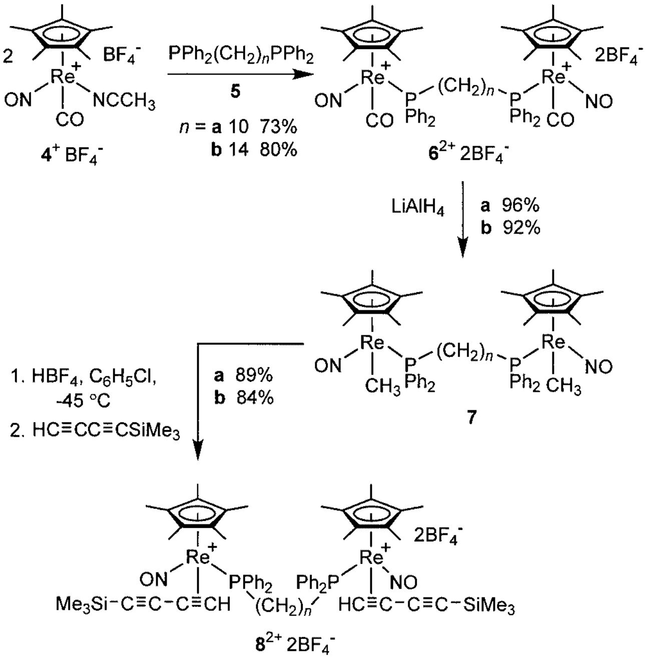
We therefore considered alternative routes to **3b** by retrosynthetic analysis. One obvious possibility would be to generate the macrocycle by the intramolecular oxidative coupling of two butadiynylrhenium or ReC≡CC≡CH moieties.[13,16] This would in turn require linking two chiral rhenium fragments by an α,ω-diphosphane $Ph_2P(CH_2)_nPPh_2$. No hydrogenation step would be required, and intermolecular oxidative homocouplings of ReC≡CC≡CH complexes commonly proceed in high yield.[5,17] Accordingly, we set out to investigate this alternative route to **3b** and related compounds, and describe its successful implementation below.



Scheme 2. Syntheses of macrocyclic dirhenium complexes by ring closing olefin metathesis

Results

The readily available chiral racemic cationic (acetonitrile)(carbonyl) complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(CO)(NCCH_3)]^+\cdot BF_4^-$ ($\mathbf{4}^+BF_4^-$) reacts with a variety of phosphanes in refluxing 2-butanone to give the corresponding (carbonyl)(phosphane) complexes.[18] As shown in Scheme 3, similar reactions were conducted with the diphosphanes $Ph_2P(CH_2)_nPPh_2$ [**5**; n = 10 (**a**),[4,19] 14 (**b**)[4,19b]], but at 2.4:1.0 stoichiometries. Workups gave the target dicationic (bridging phosphane)dirhenium complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(CO)\{\mu\text{-}[PPh_2(CH_2)_nPh_2P]\text{-}P,P\}(OC)(ON)Re(\eta^5\text{-}C_5Me_5)]^{2+}\cdot 2BF_4^-$ ($\mathbf{6a,b}^{2+}2BF_4^-$) as yellow-



Scheme 3. Syntheses of nonmacrocyclic dirhenium complexes

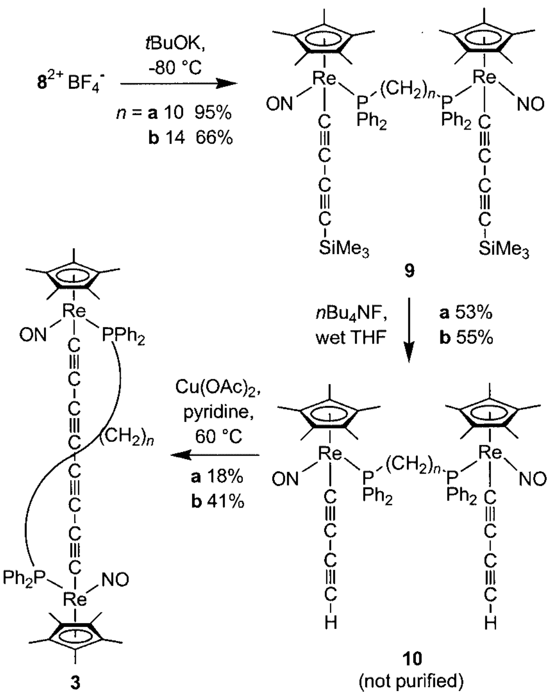
orange solids in 73−80% yields based on the limiting reactants **5a**,**b**. A third series of compounds derived from a diphosphane with a much longer methylene chain (**5c**; *n* = 32) were not as tractable and are detailed elsewhere.[20]

Complexes **6a**,**b**$^{2+}$2BF_4^- and all new species below were characterized by IR, NMR (^{1}H, ^{13}C, ^{31}P), mass spectrometry, and microanalysis, as summarized in the Exp. Sect. Most features were very similar to those of triarylphosphane homologs reported previously.[17] However, the PPh_2 phenyl groups are diastereotopic, and the aryl ^{13}C NMR signals are therefore more complex. Although **6a**,**b**$^{2+}$2BF_4^- must be mixtures of *rac* and *meso* diastereomers, only one set of ^{31}P and pentamethylcyclopentadienyl ^{1}H and ^{13}C NMR signals was observed. All of the nonmacrocyclic compounds below behaved similarly. The mass spectra of **6a**,**b**$^{2+}$2BF_4^-, and all other dications below, showed doubly charged ions corresponding to the (bridging phosphane)-dirhenium assemblies.

Complexes **6a**,**b**$^{2+}$2BF_4^- were elaborated to butadiynyl complexes as described for many related species. As shown in Scheme 3, reductions with $LiAlH_4$ gave the dimethyldirhenium complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(CH_3)\{\mu\text{-}[PPh_2(CH_2)_nPh_2P]\text{-}P,P\}(H_3C)(ON)Re(\eta^5\text{-}C_5Me_5)]$ (**7a**,**b**) as red powders in 92−96% yields. Reactions with HBF_4 in C_6H_5Cl generated substitution-labile chlorobenzene complexes,[21] which were treated with the diyne $HC{\equiv}CC{\equiv}CSiMe_3$.[22,23] Workups gave the π-bis(diyne) complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(HC{\equiv}CC{\equiv}CCSiMe_3)\{\mu\text{-}[PPh_2(CH_2)_nPh_2P]\text{-}P,P\}(Me_3SiC{\equiv}CC{\equiv}CH)(ON)Re(\eta^5\text{-}C_5Me_5)]^{2+}\cdot 2BF_4^-$ (**8a**,**b**$^{2+}$2BF_4^-), with each rhenium atom bound to an $HC{\equiv}C$ moiety, as black powders in 89−84% yields. Such compounds can exist as mixtures of $Re{-}(C{\equiv}C)$ rotamers, and NMR spectroscopic data indicated 67−76:33−24 ratios [(PPh_3)monorhenium analog: 67−79:33−21].[22,24]

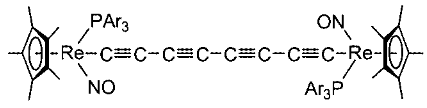
As shown in Scheme 4, complexes **8a**,**b**$^{2+}$2BF_4^- were deprotonated with *t*BuOK to give the σ-bis(trimethylsilylbutadiynyl) complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(C{\equiv}CC{\equiv}CSiMe_3)\{\mu\text{-}[PPh_2(CH_2)_nPh_2P]\text{-}P,P\}(Me_3SiC{\equiv}CC{\equiv}C)(ON)Re(\eta^5\text{-}C_5Me_5)]$ (**9a**,**b**) as red powders in 95−66% yields. In previous studies, such compounds have been desilylated to the parent butadiynyl complexes using wet *n*Bu_4NF.[5,17] However, the resulting $ReC{\equiv}CC{\equiv}CH$ species are always much more labile. Indeed, all efforts to purify the bis(butadiynyl) complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(C{\equiv}CC{\equiv}CH)\{\mu\text{-}[PPh_2(CH_2)_nPh_2P]\text{-}P,P\}(HC{\equiv}CC{\equiv}C)(ON)Re(\eta^5\text{-}C_5Me_5)]$ (**10a**,**b**) gave only impure, partially decomposed samples. Nonetheless, many NMR and IR signals could be assigned (Exp. Sect.).

In order to minimize this problem, combined deprotection/oxidation sequences were investigated. Eglinton conditions − stoichiometric $Cu(OAc)_2$ in pyridine − have proven to be most reliable for oxidative homocouplings of butadiynylmonorhenium complexes.[5,17] Thus, solutions of **9a**,**b** were first treated with wet *n*Bu_4NF, and then filtered through alumina. Solvent removal gave crude **10a**,**b** (53−55%), which were taken up in pyridine and treated with $Cu(OAc)_2$. Substrate concentrations were ca. 0.0088 M. Workups gave the target, macrocyclic (μ-octatetraynediyl)-dirhenium complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)\{\mu\text{-}[PPh_2(CH_2)_nPh_2P]\text{-}P,P\}\{\mu\text{-}(C^1{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}C^8)\text{-}C^1,C^8\}(ON)Re(\eta^5\text{-}C_5Me_5)]$ (**3a**,**b**) in 18−41% yields from crude **10a**,**b** or 10−23% yields from **9a**,**b**.



Scheme 4. Syntheses of macrocyclic dirhenium complexes by intramolecular oxidative coupling

Complexes **3a**,**b** were homogeneous by HPLC and TLC, and the latter gave a good microanalysis. Mass spectra showed intense molecular ion peaks (100%). In the case of **3a**, a small peak corresponding to a dimeric tetrarhenium by-product was also detected (8%). Dimeric and oligomeric by-products often form in couplings of organic compounds containing two terminal alkynes, and several cyclooligomers are obtained from **C** in Scheme 1. Thus, we believe that additional polyrhenium species likely form, but are perhaps not solubilized by the extractive workup employed. IR spectra of **3a**,**b** showed $\nu_{C\equiv C}$ and ν_{NO} bands (2104−2108 m, 1953 m, 1640−1637 s cm^{-1}) very close to those of the nonmacrocyclic triarylphosphane analogs **11** and **12**.[17]



Ar = Ph: **11**
p-tol: **12**

The ^{1}H NMR spectrum of **3a** exhibited a doubled pentamethylcyclopentadienyl signal, and the ^{31}P NMR spectrum a doubled PAr_2 signal. Area ratios were ca. 50:50, and the latter is illustrated in Figure 1. Complex **3b** also showed two doubled signals, but the chemical shift differences were much smaller. For both compounds, these were assigned to the *rac* and *meso* diastereomers. Since none of the other dirhenium complexes show separate signals for the two diastereomers, steric communication between the chiral endgroups appears to be enhanced in the macrocycles **3a**,**b**. As would be intuitively expected, the shorter methylene tether in **3a** leads to more differentiated signals. The ^{13}C NMR chemical shifts of the sp-carbon atoms were within 1−2 ppm of those of **11** and **12**.[17] The ^{1}H and ^{31}P chemical shifts of **3a**,**b** were quite similar to those of the precursors **9a**,**b** and **10a**,**b**. The most pronounced differences were in the PCH_2 signals of **3a** ($\Delta\delta = 0.20-0.10$).

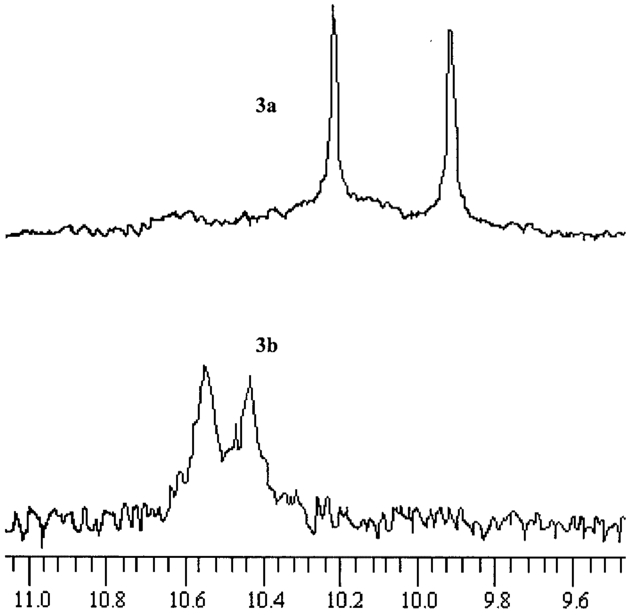


Figure 1. ^{31}P NMR spectra of macrocyclic dirhenium complexes

Finally, cyclic voltammograms of **3a**,**b** were recorded in CH_2Cl_2 under the standard conditions employed in earlier studies.[17] Two sequential oxidations were observed, and data are summarized in Table 1. Since comparisons to non-macrocyclic complexes were sought, **1** and **2** (Scheme 2) were also examined. Some previously reported data are included for reference, and analyzed in the discussion section. Preparative reactions of **3a**,**b** with the one-electron oxidant $(\eta^5\text{-}C_5H_5)_2Fe^{+\cdot}SbF_6^-$ in CH_2Cl_2 did not afford any tractable products.

Table 1. Summary of cyclic voltammetry data

Complex[a]	$E_{p,a}(1)$ $E_{p,a}(2)$ [V]	$E_{p,c}(1)$ $E_{p,c}(2)$ [V]	$E°(1)$ $E°(2)$ [V]	$\Delta E(1)$ $\Delta E(2)$ [mV]	$i_c/i_a(1)$ $i_c/i_a(2)$	K_c[b]
3a	0.23	0.16	0.20	70	0.2	$1.2\cdot10^4$
	0.50	0.38	0.44	120	0.5	
3b	0.24	0.16	0.20	80	0.8	$8.8\cdot10^4$
	0.53	0.45	0.49	80	1	
11	0.27	0.20	0.24	70	< 1	$5.9\cdot10^4$
	0.56	0.49	0.52	70	< 1	
12	0.20	0.12	0.16	80	1	$8.8\cdot10^4$
	0.49	0.41	0.45	80	1	
1	0.24	0.16	0.20	80	0.4	$5.9\cdot10^4$
	0.51	0.44	0.48	70	0.7	
2	0.24	0.16	0.20	80	0.7	$8.8\cdot10^4$
	0.52	0.45	0.49	70	0.9	

[a] CH_2Cl_2, 100 mV/s, $E°$ vs. SCE [E(ferrocene) = 0.46 V]. [b] Comproportionation constant; $\ln(K_c) = nF[E°(2) - E°(1)]/RT = 39.25[E°(2) - E°(1)]$ at 22.5 °C.

Discussion

The reactions in Scheme 4 establish that organometallic compounds containing two terminal alkynes or diynes can undergo intramolecular oxidative macrocyclization. The overall yields of **3a**,**b** from the protected diyne **9a**,**b** are only 10−23%, but rise to 18−44% when based upon the crude bis(butadiyne) complexes **10a**,**b**. The substrate concentrations are somewhat greater than those employed for the olefin metathesis of **1** in Scheme 2 (0.0088 vs. 0.0012−0.0007 M). Thus, there is some possibility that the yields in Scheme 4 could be improved at higher dilution. Nonetheless, we would still expect them to remain lower than that of the metathesis product **2** (77−84%). This is consistent with Sauvage's experience with systems such as **A** (Scheme 1). Although the oxidative coupling is successful,[7,8] olefin metatheses of related species proved superior.[9a,9b]

However, with respect to the target molecule **3b**, an additional hydrogenation step is needed after olefin metathesis (Scheme 2). This has proved very problematic, and without the new methodology in Scheme 4, it would not be possible to reliably access this molecule. Although this constitutes a strategic weakness of olefin metathesis, many alkene-containing metalla- and metallomacrocycles are readily hydrogenated.[3,4,9] Perhaps the triple bonds in **3b** are the origin of the problem. Nonetheless, it has proved possible to hydrogenate alkene moieties in macrocycles containing $PtC{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}CPt$ linkages.[4]

In **3a**, the linear ten-atom $ReC{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}CRe$ linkage must be spanned by a 12-atom $P(CH_2)_{10}P$ linkage. Thus, **3a** should be considerably more strained than **3b**. Accordingly, the yield is lower, and a dimeric product can be detected by mass spectrometry. Nonetheless, the same phosphane is also capable of bridging a $PtC{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}CPt$ linkage.[4] In both cases, the methylene or sp^3-carbon chain must remain very close to the sp-carbon chain. However, there appears to be little effect on NMR or IR properties. In **3b**, there is the possibility of helical coiling of the sp^3-chain about the sp-chain, as recently demonstrated with similar diplatinum complexes.[4] Unfortunately, consistent with past experience with this series of compounds, all efforts to obtain single crystals have been unsuccessful. The presence of both diastereomers is believed to be a contributing factor.

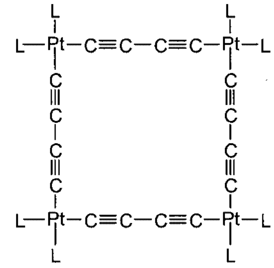
These structural issues lead naturally to the effect of molecular architecture upon redox properties. The cyclic voltammogram of **3b** (Table 1) is qualitatively similar to those other $ReC{\equiv}CC{\equiv}CC{\equiv}CC{\equiv}CRe$ species reported earlier. A cation radical and dication are readily generated. The oxidation potentials are intermediate between those of the PPh_3- and $P(p\text{-tol})_3$-substituted analogs **11** and **12**, befitting a alkyldiphenylphosphane adduct [$E^\circ(1)$ = 0.20 vs. 0.24 vs. 0.16 V; $E^\circ(2)$ = 0.47 vs. 0.52 vs. 0.45 V]. The ΔE and i_c/i_a values indicate a high degree of reversibility. However, **12** gives a i_c/i_a ratio of 1 for both oxidations, whereas one value for **3b** is slightly less. Thus, there is no electrochemical indication of enhanced cation radical and dication stabilities, in agreement with our chemical data.

Complex **3a** exhibits similar oxidation potentials. However, the ΔE and i_c/i_a values indicate processes that are not electrochemically reversible, and only partially chemically reversible. This suggests that the more strained nature of this macrocycle somehow promotes decomposition of the cation radical and dication. The phosphane ligand in nonmacrocyclic **1** (Scheme 2) should electronically resemble a alkyldiphenylphosphane, and similar oxidation potentials are again observed. However, the alkene linkages can potentially react with the cation radical and/or dication. Accordingly, the reversibilities are between those of **3a** and **3b**. The metathesis product **2**, which is a mixture of C=C isomers, appears to give slightly more reversible oxidations.

There is only one example to date of an MC≡CC≡CC≡CC≡CM system that can be oxidized to spectroscopically detectable species, Lapinte's very electron-rich diiron complex [$(\eta^5\text{-}C_5Me_5)Fe(dppe)(C{\equiv}C)_4(dppe)Fe(\eta^5\text{-}C_5Me_5)$].[25] Remarkably, the corresponding radical cation can be isolated in analytically pure form.[26] However, when the sp-carbon chains of dirhenium complexes **11** or **12** are shielded by an additional sp^3- or sp^3/sp^2-carbon chain, as in **2** and **3b**, no evidence for enhanced kinetic stabilities of oxidation products is found. In contrast, PtC≡CC≡CC≡CC≡CPt assemblies that are doubly bridged by the diphosphane **5b** exhibit significantly more reversible oxidations.[4] We therefore conclude that the sp-carbon chain of our first-generation system **3b** is sterically not shielded enough. Approaches to sterically more congested analogs are under investigation.[27]

Finally, **3a**,**b** are not the only metallamacrocycles that contain an $M(C{\equiv}CC{\equiv}C)_nM$ linkage. Extremely interesting tetraplatinamacrocycles of the formula **13** have been previously reported by Tessier, Youngs, and Bruce.[28] All sixteen carbon atoms in these twenty-membered rings are sp-hybridized. However, the syntheses do not involve the oxidative homocoupling of alkynes. Rather, bis(butadiynyl)platinum complexes of the formula [$cis\text{-}(L)_2Pt(C{\equiv}CC{\equiv}CH)_2$] are condensed with platinum chloride or triflate complexes $cis\text{-}(L)_2Pt(X)_2$. Yields of **13** are routinely high (70−98%).

In conclusion, we have compared the applicability of two macrocyclization strategies for the synthesis of novel types of (μ-octatetraynediyl)dirhenium complexes. The new intramolecular oxidative coupling of bis(butadiynyl) complexes is successful, and increased application of such reactions in the synthesis of inorganic and organometallic macrocycles can be anticipated. However, olefin metathesis appears to constitute a generally superior macrocyclization method, and is problematic only in the few instances where subsequent alkene hydrogenation is unsuccessful. Future reports will describe the utility of alkyne metathesis for accessing similar types of targets.[6]



13

L = 1/2 diphosphane
or monophosphane

Experimental Section

General: General procedures, solvent and reagent purifications, and instrumentation were identical with those listed in recent full papers,[3c,17,18b] and are further detailed elsewhere.[20]

[$(\eta^5\text{-}C_5Me_5)Re(NO)(CO)\{\mu\text{-}[PPh_2(CH_2)_nPh_2P]\text{-}P,P\}(OC)(ON)Re(\eta^5\text{-}C_5Me_5)]^{2+}\cdot 2BF_4^-$ ($6^{2+}2BF_4^-$). a (n = 10): A Schlenk flask was charged with [$(\eta^5\text{-}C_5Me_5)Re(NO)(CO)(NCCH_3)]^+\cdot BF_4^-$ ($4^+BF_4^-$;[18a] 2.430 g, 4.793 mmol), 1,2-dichloroethane (10 mL), and $Ph_2P(CH_2)_{10}PPh_2$ (**5a**;[4,19] 1.020 g, 2.000 mmol), and fitted with a reflux condenser. The solution was refluxed for 14 h. The solvent was removed by oil-pump vacuum. The residue was dissolved in a small amount of acetone and poured into rapidly stirred Et_2O. The precipitate was isolated by filtration and dried by oil-pump vacuum to give $\mathbf{6a}^{2+}2BF_4^-$ as a yellow orange solid (2.013 g, 1.457 mmol, 73%). M.p. 88 °C. ^1H NMR (400 MHz, $CDCl_3$, 32 °C, TMS): δ = 7.58−7.40 (m, 20 H, $4C_6H_5$), 2.63 (m, 4 H, 2 PCH_2), 1.95 (s, 30 H, 2 $C_5(CH_3)_5$], 1.33−1.10 (m, 16 H, 8 CH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 32 °C, TMS): δ = 201.8 (d, $^2J_{C,P}$ = 9 Hz, CO), 132.4−129.5 (Ph signals), 105.9 [$C_5(CH_3)_5$], 32.1 (d, $^1J_{C,P}$ = 32 Hz, PCH_2),[29] 30.1 (d, $J_{C,P}$ = 12 Hz, CH_2), 29.9 (s, CH_2), 28.7 (s, CH_2), 23.9 (s, CH_2), 9.8 [s, $C_5(CH_3)_5$] ppm. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$, 32 °C, H_3PO_4): δ = 9.1 (s) ppm. IR (solid film): $\tilde{\nu}$ = 1984 (s, CO), 1722 (s, NO) cm^{-1}. MS (FAB, 3-NBA/CH_2Cl_2):[30] m/z (%) = 1355 (72) [$M + BF_4^-]^+$, 890 (100) [$M - \{(\eta^5\text{-}C_5Me_5)Re(NO)(CO)\}]^+$, 634 (50) $[M]^{++}$. $C_{56}H_{70}B_2F_8N_2O_4P_2Re_2$ (1443.15): calcd. C 46.61, H 4.89, N 1.94; found C 46.74, H 4.99, N 1.90.

b (n = 14): Complex 4^+ BF_4^- (0.803 g, 1.584 mmol), 1,2-dichloroethane (10 mL), and $Ph_2P(CH_2)_{14}PPh_2$ (**5b**;[4,19b] 0.376 g, 0.664 mmol) were combined in a procedure analogous to that for $\mathbf{6b}^{2+}$ $2BF_4^-$. An identical reaction and workup gave $\mathbf{6b}^{2+}$ $2BF_4^-$ as a yellow solid (0.792 g, 0.528 mmol, 80%). M.p. 84 °C. ^1H NMR (400 MHz, $CDCl_3$, 32 °C, TMS): δ = 7.60−7.26 (m, 20 H, 4 C_6H_5), 2.63 (m, 4 H, 2 PCH_2), 1.96 [s, 30 H, 2 $C_5(CH_3)_5$], 1.36−1.16 (m, 24 H, 12 CH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 32 °C, TMS): δ = 202.0 (d, $^2J_{C,P}$ = 8 Hz, CO), 132.4−129.6 (Ph signals), 106.0 [s, $C_5(CH_3)_5$], 32.2 (d, $^1J_{C,P}$ = 32 Hz, PCH_2),[29] 30.6 (d, $J_{C,P}$ = 15 Hz, CH_2), 30.2 (s, CH_2), 29.7 (s, CH_2), 29.6 (s, CH_2), 28.4 (s, CH_2), 24.0 (s, CH_2), 9.8 [s, $C_5(CH_3)_5$] ppm. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$, 32 °C, H_3PO_4): δ = 9.3 (s) ppm. IR (solid film): $\tilde{\nu}$ = 1984 (s, CO), 1722 (s, NO) cm^{-1}. MS (FAB, 3-NBA/CH_2Cl_2):[30] m/z (%) = 1411 (10) [$M + BF_4^-]^+$, 962 (50) [$(\eta^5\text{-}C_5Me_5)Re(NO)(CO)(PPh_2(CH_2)_{14}POPh_2)]^+$, 662 (40) $[M]^{++}$, 421

(100) $[(\eta^5\text{-}C_5Me_5)Re(NO)(CO)]^+$. $C_{60}H_{78}B_2F_8N_2O_4P_2Re_2$ (1499.25): calcd. C 48.07, H 5.24, N 1.87; found C 48.67, H 5.36, N 1.75.

$[(\eta^5\text{-}C_5Me_5)Re(NO)(CH_3)\{\mu\text{-}[PPh_2(CH_2)_nPh_2P]\text{-}P,P\}(H_3C)(ON)\text{-}Re(\eta^5\text{-}C_5Me_5)]$ (7). a (*n* = 10): A Schlenk flask was charged with $LiAlH_4$ (0.087 g, 2.272 mmol), $\mathbf{6a}^{2+}\ 2BF_4^-$ (0.549 g, 0.380 mmol), and THF (20 mL). The suspension was stirred for 14 h. Small amounts of water were added until gas evolution ceased. The mixture was filtered through a 2-cm alumina pad. The solvent was removed from the filtrate by rotary evaporation and oil-pump vacuum to give **7a** as a red solid (0.453 g, 0.365 mmol, 96%). M.p. 54 °C. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.88−7.05 (m, 20 H, 4 C_6H_5), 2.83, 2.45 (2 m, 4 H, 2 PCH_2), 1.63 [s, 30 H, 2 $C_5(CH_3)_5$], 1.43−1.15 (m, 16 H, 8 CH_2), 0.80 (apparent m, 6 H, 2 $ReCH_3$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 25 °C): δ = 136.6/136.3 (2 d, $^1J_{C,P}$ = 48/47 Hz, *i*-Ph), 134.1/132.8 (2 d, $^2J_{C,P}$ = 9/9 Hz, *o*-Ph), 131.2/131.0 (2 s, *p*-Ph), 129.8/128.6 (2 d, $^3J_{C,P}$ = 11/11 Hz, *m*-Ph), 97.4 [s, $C_5(CH_3)_5$], 33.5 (d, $^1J_{C,P}$ = 33 Hz, PCH_2),[29] 31.4 (d, $J_{C,P}$ = 15 Hz, CH_2), 29.4 (s, CH_2), 25.8 (s, CH_2), 23.9 (s, CH_2), 9.7 [s, $C_5(CH_3)_5$], −25.2 (d, $^2J_{C,P}$ = 7 Hz, $ReCH_3$) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6, 25 °C, H_3PO_4): δ = 11.5 (s). IR (solid film): ṽ = 1633 (s, NO) cm^{-1}. MS (FAB, 3-NBA/CH_2Cl_2):[30] *m*/*z* (%) = 1242 (80) $[M]^+$, 877 (100) $[M - \{(\eta^5\text{-}C_5Me_5)Re(NO)(CH_3)\}]^+$. $C_{56}H_{76}N_2O_2P_2Re_2$ (1243.58): calcd. C 54.09, H 6.16, N 2.25; found C 53.57, H 6.12, N 2.10.

b (*n* = 14): Complex $\mathbf{6b}^{2+}2BF_4^-$ (1.122 g, 0.748 mmol), $LiAlH_4$ (0.171 g, 4.502 mmol), and THF (20 mL) were combined in a procedure analogous to that for **7a**. An identical reaction and workup gave **7b** as a red solid (0.893 g, 0.687 mmol, 92%). M.p. 57 °C. ^1H NMR (400 MHz, C_6D_6, 32 °C): δ = 7.63−7.24 (m, 20 H, 4 C_6H_5), 3.08, 2.45 (2 m, 4 H, 2 PCH_2), 1.68 [s, 30 H, 2 $C_5(CH_3)_5$], 1.23−1.16 (m, 24 H, 12 CH_2), 0.82 (apparent m, 6 H, 2 $ReCH_3$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 32 °C): δ = 136.4/136.2 (2 d, $^1J_{C,P}$ = 42/42 Hz, *i*-Ph), 135.5/133.4 (2 d, $^2J_{C,P}$ = 9/9 Hz, *o*-Ph), 131.2/130.2 (2 s, *p*-Ph), 129.0/128.6 (2 d, $^3J_{C,P}$ = 11/11 Hz, *m*-Ph), 100.2 [s, $C_5(CH_3)_5$], 33.6 (d, $^1J_{C,P}$ = 33 Hz, PCH_2),[29] 31.5 (d, $J_{C,P}$ = 17 Hz, CH_2), 30.43 (s, CH_2), 30.39 (s, CH_2), 30.2 (s, CH_2), 29.9 (s, CH_2), 25.7 (s, CH_2), 9.8 [s, $C_5(CH_3)_5$], −25.3 (d, $^2J_{C,P}$ = 7 Hz, $ReCH_3$) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6, 32 °C, H_3PO_4): δ = 11.6 (s) ppm. IR (solid film): ṽ = 1633 (s, NO) cm^{-1}. MS (FAB, 3-NBA/CH_2Cl_2):[30] *m*/*z* (%) = 1298 (30) $[M]^+$, 933 (100) $[M - \{(\eta^5\text{-}C_5Me_5)Re(NO)(CH_3)\}]^+$. $C_{60}H_{84}N_2O_2P_2Re_2$ (1299.69): calcd. C 55.45, H 6.51, N 2.16; found C 55.14, H 6.59, N 2.22.

$[(\eta^5\text{-}C_5Me_5)Re(NO)(HC{\equiv}CC{\equiv}CCSiMe_3)\{\mu\text{-}[PPh_2(CH_2)_n\text{-}Ph_2P]\text{-}P,P\}(Me_3SiC{\equiv}CC{\equiv}CH)(ON)Re(\eta^5\text{-}C_5Me_5)]^{2+}\cdot 2BF_4^-$ (8^{2+} $2BF_4^-$). a (*n* = 10): A Schlenk flask was charged with **7a** (0.225 g, 0.181 mmol) and C_6H_5Cl (5 mL), and cooled to −45 °C (acetonitrile/CO_2). Then $HBF_4{\cdot}OEt_2$ (54% in Et_2O; 0.050 mL, 0.366 mmol) was added with stirring. After 10 min, $HC{\equiv}CC{\equiv}CSiMe_3$ (0.176 g, 1.443 mmol; mass of loaded/discharged syringe)[22,23] was added, and the cold bath was removed. After 2 h, the solvent was removed by rotary evaporation. The residue was extracted with CH_2Cl_2. The extract was poured into vigorously stirred pentane. The precipitate was collected by filtration and dried by oil-pump vacuum to give $\mathbf{8a}^{2+}2BF_4^-$ as a black powder (0.263 g, 0.161 mmol, 89%, 69−75:31−25 mixture of Re−(C≡C) rotamers[22,24]). M.p. 90 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.56−7.24 (m, 20 H, 4 C_6H_5), 8.17/7.02 (2 br. s, 2 H, 2 $HC{\equiv}$),[32] 2.61 (m, 4 H, 2 PCH_2), 1.79/1.69 [2 s, 71:29, 30 H, 2 $C_5(CH_3)_5$],[32] 1.27−1.12 (m, 16 H, 8 CH_2), 0.30/−0.14 [2 s, 69:31, 18 H, 2 $Si(CH_3)_3$] ppm.[32] $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C):[31] δ ($C{\equiv}CH$ not observed) = 133.0−127.4 (Ph signals), 114.2 (s, $C{\equiv}CSi$), 109.8/109.5 [s, $C_5(CH_3)_5$],[32] 95.0 (s, $C{\equiv}CSi$), 92.5 (br. s, $C{\equiv}CH$), 32.0−28.1 (CH_2 signals), 24.1 (br. s, CH_2), 9.1 [s, $C_5(CH_3)_5$], −0.5/−0.8 [2 s, 69:31, $Si(CH_3)_3$] ppm.[32] $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$, 25 °C, H_3PO_4): δ = 7.1/13.2 (2 s, 75:25) ppm.[32] IR (solid film): ṽ = 2138 (m, C≡C), 1683 (s, NO) cm^{-1} ppm. MS (FAB, 3-NBA/CH_2Cl_2):[30] *m*/*z* (%) = 1544 (30) $[M + BF_4^-]^+$, 1458 (70) $[M]^+$, 984 (100) $[M - \{(\eta^5\text{-}C_5Me_5)Re(NO)(HC{\equiv}CC{\equiv}CSiMe_3)\}]^+$, 729 (10) $[M]^{++}$. $C_{68}H_{90}B_2F_8N_2O_2P_2Re_2Si_2$ (1631.61): calcd. C 50.06, H 5.56, N 1.72; found C 49.80, H 5.47, N 1.52.

b (*n* = 14): Complex **7b** (0.824 g, 0.634 mmol), C_6H_5Cl (5 mL), $HBF_4{\cdot}OEt_2$ (54% in Et_2O; 0.172 mL, 1.262 mmol), and $HC{\equiv}CC{\equiv}CSiMe_3$ (0.615 g, 5.041 mmol) were combined in a procedure analogous to that for $\mathbf{8a}^{2+}2BF_4^-$. An identical reaction and workup gave $\mathbf{8b}^{2+}2BF_4^-$ as a black powder (0.901 g, 0.534 mmol, 84%, 67−76:33−24 mixture of Re−(C≡C) rotamers[22,24]). M.p. 92 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.56−7.24 (m, 20 H, 4 C_6H_5), 8.20/7.01 (2 br. s, 2 H, 2 $HC{\equiv}$),[32] 2.61 (m, 4 H, 2 PCH_2), 1.81/1.71 [2 s, 70:30, 30 H, 2 $C_5(CH_3)_5$],[32] 1.27−1.12 (m, 24 H, 12 CH_2), 0.30/−0.14 [2 s, 71:29, 18 H, 2 $Si(CH_3)_3$] ppm.[32] $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C):[31] δ ($C{\equiv}CH$ not observed) = 133.9−128.4 (Ph signals), 114.3 (s, $C{\equiv}CSi$), 109.9/109.6 [2 s, $C_5(CH_3)_5$],[32] 94.9 (s, $C{\equiv}CSi$), 32.9−28.2 (CH_2 signals), 24.2 (br. s, CH_2), 9.2 [s, $C_5(CH_3)_5$], −0.5/−0.8 [2 s, 67:33, $Si(CH_3)_3$] ppm.[32] $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$, 32 °C, H_3PO_4): δ = 7.2/13.4 (2 s, 76:24) ppm.[32] IR (solid film): ṽ = 2140 (m, C≡C), 1683 (s, NO) cm^{-1}. MS (FAB, 3-NBA/CH_2Cl_2):[30] *m*/*z* (%) = 1602 (2) $[M + BF_4^-]^+$, 1041 (100) $[M - \{(\eta^5\text{-}C_5Me_5)Re(NO)(HC{\equiv}CC{\equiv}CSiMe_3)\}]^+$, 757 (10) $[M]^{++}$. $C_{72}H_{98}B_2F_8N_2O_2P_2Re_2Si_2$ (1687.71): calcd. C 51.24, H 5.85, N 1.66; found C 50.81, H 6.17, N 1.47.

$[(\eta^5\text{-}C_5Me_5)Re(NO)(C{\equiv}CC{\equiv}CSiMe_3)\{\mu\text{-}[PPh_2(CH_2)_nPh_2P]\text{-}P,P\}(Me_3SiC{\equiv}CC{\equiv}C)(ON)Re(\eta^5\text{-}C_5Me_5)]$ (9). a (*n* = 10): A Schlenk flask was charged with $\mathbf{8a}^{2+}2BF_4^-$ (0.170 g, 0.104 mmol) and *t*BuOK (0.030 g, 0.273 mmol) and cooled to −75 °C (CO_2/acetone). Then pre-cooled THF (5 mL) was added. After 10 min, the cold bath was removed. The solution was stirred at room temperature for an additional 2 h, and then passed through an alumina pad (3 cm). The solvent was removed by oil-pump vacuum to give **9a** as a red solid (0.144 g, 0.099 mmol, 95%). M.p. 110−115 °C. ^1H NMR (400 MHz, C_6D_6, 32 °C): δ = 7.79−7.61 (m, 8 H of 4 C_6H_5), 7.18−6.93 (m, 12 H of 4 C_6H_5), 3.25, 2.49 (2 m, 4 H, 2 PCH_2), 1.53 [s, 30 H, 2 $C_5(CH_3)_5$], 1.42−1.04 (m, 16 H, 8 CH_2), 0.25 [s, 18 H, 2 $Si(CH_3)_3$] ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 32 °C): δ = 135.2/133.7 (2 d, $^1J_{C,P}$ = 46/49 Hz, *i*-Ph), 134.8/132.7 (2 d, $^2J_{C,P}$ = 11/11 Hz, *o*-Ph), 131.2/130.7 (2 s, *p*-Ph), 128.7/127.8 (2 d, $^3J_{C,P}$ = 11/11 Hz, *m*-Ph), 111.5 (s, $ReC{\equiv}C$),[31] 107.1 (d, $^2J_{C,P}$ = 15 Hz, $ReC{\equiv}$),[31] 100.3 [s, $C_5(CH_3)_5$], 93.6 (s, $C{\equiv}CSi$),[31] 80.6 (s, ${\equiv}CSi$),[31] 34.1 (d, $^1J_{C,P}$ = 36 Hz, PCH_2),[29] 31.2 (d, $J_{C,P}$ = 15 Hz, CH_2), 29.6 (s, CH_2), 25.7 (s, CH_2), 24.0 (s, CH_2), 9.8 [s, $C_5(CH_3)_5$], 0.9 [s, $Si(CH_3)_3$] ppm. $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6, 32 °C, H_3PO_4): δ = 10.4 (s) ppm. IR (solid film): ṽ = 2118 (w, C≡C), 2096 (m, C≡C), 1640 (s, NO) cm^{-1}. MS (FAB, 3-NBA/CH_2Cl_2):[30] *m*/*z* (%) = 1456 (100) $[M]^+$, 983 (40) $[M - \{(\eta^5\text{-}C_5Me_5)Re(NO)(C{\equiv}CC{\equiv}CSiMe_3)\}]^+$. $C_{68}H_{88}N_2O_2P_2Re_2Si_2$ (1455.98): calcd. C 56.10, H 6.09, N 1.92; found C 55.99, H 6.11, N 2.01.

b (*n* = 14): Complex $\mathbf{8b}^{2+}2BF_4^-$ (0.200 g, 0.118 mmol), *t*BuOK (0.027 g, 0.245 mmol), and THF (5 mL) were combined in a procedure analogous to that for **9a**. An identical reaction and workup gave **9b** as a red solid (0.118 g, 0.078 mmol, 66%). M.p. 111−120 °C. ^1H NMR (400 MHz, C_6D_6, 32 °C): δ = 7.64−7.60 (m, 8 H of

4 C_6H_5), 7.15−6.93 (m, 12 H of 4 C_6H_5), 3.33, 2.53 (m, 4 H, 2 PCH_2), 1.52 [s, 30 H, 2 $C_5(CH_3)_5$], 1.42−1.04 (m, 24 H, 12 CH_2), 0.25 [s, 18 H, 2 $Si(CH_3)_3$] ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 32 °C): δ = 135.1/133.5 (2 d, $^1J_{C,P}$ = 47/49 Hz, *i*-Ph), 134.9/132.8 (2 d, $^2J_{C,P}$ = 10/11 Hz, *o*-Ph), 131.1/130.7 (2 s, *p*-Ph), 128.7/127.9 (2 d, $^3J_{C,P}$ = 10/10 Hz, *m*-Ph), 111.3 (s, ReC≡*C*),[31] 106.9 (d, $^2J_{C,P}$ = 14 Hz, Re*C*≡),[31] 100.1 [s, $C_5(CH_3)_5$], 93.5 (s, *C*≡CSi),[31] 80.9 (s, ≡*C*Si),[31] 33.9 (d, $^1J_{C,P}$ = 32 Hz, PCH_2),[29] 31.2 (d, $J_{C,P}$ = 8 Hz, CH_2), 29.8 (s, double intensity, CH_2), 29.6 (s, CH_2), 25.7 (s, CH_2), 24.0 (s, CH_2), 9.8 [s, $C_5(CH_3)_5$], 1.0 [s, $Si(CH_3)_3$] ppm. $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6, 32 °C, H_3PO_4): δ = 10.2 (s) ppm. IR (solid film): ṽ = 2173 (w, C≡C), 2096 (m, C≡C), 1640 (s, NO) cm^{-1}. MS (FAB, 3-NBA/CH_2Cl_2):[30] *m/z* (%) = 1513 (100) $[M]^+$, 1039 (50) [M − {(η^5-C_5Me_5)Re(NO)(C≡CC≡CSiMe$_3$)}]$^+$. $C_{72}H_{96}N_2O_2P_2Re_2Si_2$ (1512.10): calcd. C 57.19, H 6.40, N 1.85; found C 56.70, H 6.20, N 1.60.

[(η^5-C_5Me_5)Re(NO){μ-[$PPh_2(CH_2)_nPh_2P$]-*P,P*}[μ-(C^1≡CC≡CC≡CC≡C^8)-C^1,C^8)](ON)Re(η^5-C_5Me_5)] (3). a (*n* = 10): A Schlenk flask was charged with **9a** (0.120 g, 0.082 mmol) and THF (10 mL), and wet *n*Bu_4NF (1 M in THF; 0.032 mL, 0.032 mmol) was added with stirring. After 2 h, the solution was filtered through an alumina pad (1 cm) into a weighed Schlenk flask. The solvent was removed from the filtrate by oil-pump vacuum. To the red solid (**10a**; 0.060 g, 0.044 mmol, 53%) was added $Cu(OAc)_2$ (0.016 g, 0.090 mmol) and pyridine (5 mL). The suspension was stirred at 60 °C. After 24 h, the solvent was removed by oil-pump vacuum (the reaction can be monitored by TLC). The residue was extracted with CH_2Cl_2. The extract was filtered through a silica gel pad (2 cm). The solvent was removed by oil-pump vacuum to give **3a** as a red solid (0.010 g, 0.008 mmol, 10% from **9a** or 18% from **10a**).[33] **10a**: ^1H NMR (400 MHz, C_6D_6, 32 °C): δ = 7.72−7.05 (m, 20 H, 4 C_6H_5), 3.35, 2.47 (2 m, 4 H, 2 PCH_2), 2.14 (s, 2 H, ≡C*H*), 1.54 [s, 30 H, 2 $C_5(CH_3)_5$], 1.40−1.00 (m, 16 H, 8 CH_2) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6, 32 °C, H_3PO_4): δ = 10.6 (s) ppm. IR (solid film): ṽ (≡CH not observed) = 2112 (w, C≡C), 1978 (m, C≡C), 1643 (s, NO) cm^{-1}. **3a**: ^1H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.71−6.79 (m, 20 H, 4 C_6H_5), 3.19, 2.67 (2 m, 4 H, 2 PCH_2), 1.52, 1.51 [2 s, 30 H, 2 $C_5(CH_3)_5$], 1.47−1.20 (m, 16 H, 8 CH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 25 °C): δ = 136.3−127.9 (Ph signals), 113.3 (s, ReC≡*C*),[31] 110.6 (br. s, Re*C*≡C),[31] 100.5 [s, $C_5(CH_3)_5$], 66.2 (s, ReC≡C*C*≡C),[31] 63.5 (s, ReC≡CC≡*C*),[31] 33.2−28.2 (CH_2 signals), 24.3 (br. s, CH_2), 9.8 [s, $C_5(CH_3)_5$] ppm. $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6, 25 °C, H_3PO_4): δ = 10.2, 9.9 (2 s, 51:49) ppm. IR (solid film): ṽ = 2104 (m, C≡C), 1953 (m, C≡C), 1637 (s, NO) cm^{-1}. MS (FAB, 3-NBA/CH_2Cl_2):[30] *m/z* (%) = 1310 (100) $[M]^+$, 2619 (8) $[2 M]^+$; no peak *m/z* (%) = 200 (> 5).

b (*n* = 14): Complex **9b** (0.136 g, 0.090 mmol), THF (10 mL), wet *n*Bu_4NF (1 M in THF; 0.036 mL, 0.036 mmol), $Cu(OAc)_2$ (0.016 g, 0.090 mmol) and pyridine (5 mL) were combined in procedures analogous to those for **3a** (**10b**; 0.060 g, 0.044 mmol, 55%). Similar reactions (14 h, 65 °C) and workups gave **3b** as a red solid (0.024 g, 0.018 mmol; 23% from **9b** or 41% from **10b**). **10b**: ^1H NMR (400 MHz, C_6D_6, 32 °C): δ = 7.68−6.99 (m, 20 H, 4 C_6H_5), 3.31, 2.45 (2 m, 4 H, 2 PCH_2), 2.09 (s, 2 H, ≡C*H*), 1.52 [s, 30 H, 2 $C_5(CH_3)_5$], 1.49−1.07 (m, 16 H, 12 CH_2) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6, 32 °C, H_3PO_4): δ = 10.4 (s) ppm. IR (solid film): ṽ = 3290 (w, ≡C*H*), 2112 (w, C≡C), 1978 (m, C≡C), 1643 (s, NO) cm^{-1}. **3b**: ^1H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.63−6.95 (m, 20 H, 4 C_6H_5), 3.25, 2.58 (2 m, 4 H, 2 PCH_2), 1.60, 1.59 [2 s, 30 H, 2 $C_5(CH_3)_5$], 1.45−1.19 (m, 24 H, 12 CH_2) ppm. ^1H NMR (400 MHz, $CDCl_3$, 32 °C): δ = 7.63−7.59 (m, 4 H of 4 C_6H_5), 7.48−7.43 (m, 8 H of 4 C_6H_5), 7.35−7.28 (m, 8 H of 4 C_6H_5), 3.29, 2.48 (2 m, 4 H, 2 PCH_2), 1.68 [br. s, 30 H, 2 $C_5(CH_3)_5$], 1.36−1.23 (m, 24 H, 12 CH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 25 °C): δ (Re*C*≡ not observed) = 135.3−129.2 (Ph signals), 113.8 (s, ReC≡*C*),[31] 100.9 [s, $C_5(CH_3)_5$], 66.8 (s, ReC≡C*C*),[31] 64.3 (s, ReC≡CC≡*C*),[31] 33.6−28.1 (CH_2 signals), 24.2 (br. s, CH_2), 11.3 [s, $C_5(CH_3)_5$] ppm. $^{31}P\{^1H\}$ NMR (161 MHz, C_6D_6, 25 °C, H_3PO_4): δ = 10.6, 10.4 (2 s, 47:53) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$, 32 °C, H_3PO_4): δ = 10.6, 10.3 (2 s, 48:52) ppm. IR (solid film): ṽ = 2108 (m, C≡C), 1953 (m, C≡C), 1640 (s, NO) cm^{-1}. MS (FAB, 3-NBA/CH_2Cl_2):[30] *m/z* (%) = 1366 (100) $[M]^+$; no peak *m/z* (%) = 200 (> 5). $C_{66}H_{78}N_2O_2P_2Re_2$ (1365.71): calcd. C 58.05, H 5.76, N 2.05; found C 57.95, H 5.70, N 1.80.

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[30] The $[M]^+$ ions represent the most intense peak in the isotope envelope.

[31] The assignments follow from coupling constant and chemical shift patterns established earlier.[22]

[32] These signals are for the major and minor rotamers, respectively.

[33] A correct microanalysis was not obtained for this compound.

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