Olefin Metatheses in Metal Coordination Spheres: Versatile New Strategies for the Construction of Novel Monohapto or Polyhapto Cyclic, Macrocyclic, Polymacrocyclic, and Bridging Ligands

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Abstract: The broad applicability of the title reaction is established through studies of neutral and charged, coordinatively saturated and unsaturated, octahedral and square planar rhenium, platinum, rhodium, and tungsten complexes with cyclopentadienyl, phosphine, and thioether ligands which contain terminal olefins. Grubbs' catalyst, $[Ru(=CHPh)(PCy_3)_2(Cl)_2]$, is used at 2–9 mol% levels (0.0095–0.00042 M, CH_2Cl_2). Key data are as follows: $[(\eta^5\text{-}C_5H_4(CH_2)_6CH{=}CH_2)Re(NO)(PPh_3)(CH_3)]$, intermolecular metathesis (95%); $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(E\text{-}(CH_2CH{=}CH_2)_2)]^+$ TfO^- (E = S, PMe, PPh), formation of five-membered heterocycles (96–64%; crystal structure E = PMe); $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh((CH_2)_6CH{=}CH_2)_2)(L)]^{n+}$ nBF_4^- (L/n = CO/1, Cl/0), intramolecular macrocyclization (94–89%; crystal structure L = Cl); *fac*-$[(CO)_3Re(Br)(PPh_2(CH_2)_6CH{=}CH_2)_2]$ and *cis*-$[(Cl)_2Pt(PPh_2(CH_2)_6CH{=}CH_2)_2]$, intramolecular macrocyclizations (80–71%; crystal structures of each and a hydrogenation product); *cis*-$[(Cl)_2Pt(S(R)(CH_2)_6CH{=}CH_2)_2]$, intra-/intermolecular macrocyclization (R = Et, 55%/24%; *t*Bu, 72%/<4%); *trans*-$[(Cl)(L)M(PPh_2(CH_2)_6CH{=}CH_2)_2]$ (M/L = Rh/CO, Pt/C_6F_5) intramolecular macrocyclization (90–83%; crystal structure of hydrogenation product, M = Pt); *fac*-$[W(CO)_3(PPh((CH_2)_6CH{=}CH_2)_2)_3]$, intramolecular trimacrocyclization (83%) to a complex mixture of triphosphine, diphosphine/monophosphine, and tris(monophosphine) complexes, from which two isomers of the first type are crystallized. The macrocycle conformations, and basis for the high yields, are analyzed.

Keywords: Grubbs' catalyst · macrocycles · metathesis · *trans*-spanning ligands

Introduction

The olefin metathesis reaction is making a profound impact upon every branch of organic synthesis, and novel new applications are being developed at an astonishing pace.[1] However, there have been far fewer efforts in inorganic or organometallic synthesis—in other words, olefin metatheses in metal coordination spheres.[2–7] Scheme 1 illustrates representative examples. The first is one of several reported by Rudler and co-workers (Scheme 1A).[2] They were the earliest group active in this area, although turnover numbers with their tungsten/silane catalyst system were low (<4). Then followed applications in ADMET[3a] and ring-opening[3b,c] polymerizations of unsaturated ferrocenophanes (Scheme 1B). Sauvage subsequently described an elegant series of catenane syntheses (Scheme 1C).[4, 5] These processes, effected with modern alkylidene catalyst precursors, featured high yields and turnover numbers.

These auspicious beginnings nevertheless posed more questions than answers. For example, do coordinatively unsaturated substrates react as effectively as the eighteen-valence-electron educts in Scheme 1? Are a broad spectrum of ligands, and a range of formal charges, tolerated? Can non-catenated macrocycles be accessed in high yields? If all of these answers were to be yes, olefin metathesis would have immense utility in inorganic and organometallic synthesis. We could envision a number of specific applications to problems under investigation in our laboratory.

Towards these ends, we designed the series of test reactions in Scheme 2. In general, we sought to probe whether intermolecular reactions could be effected with simple

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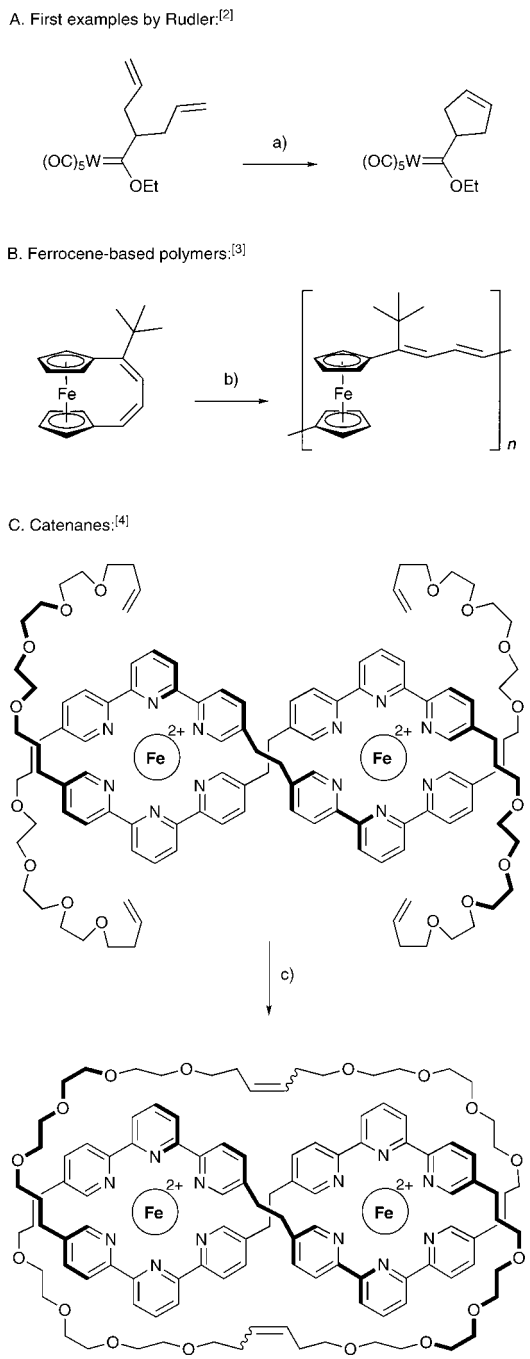
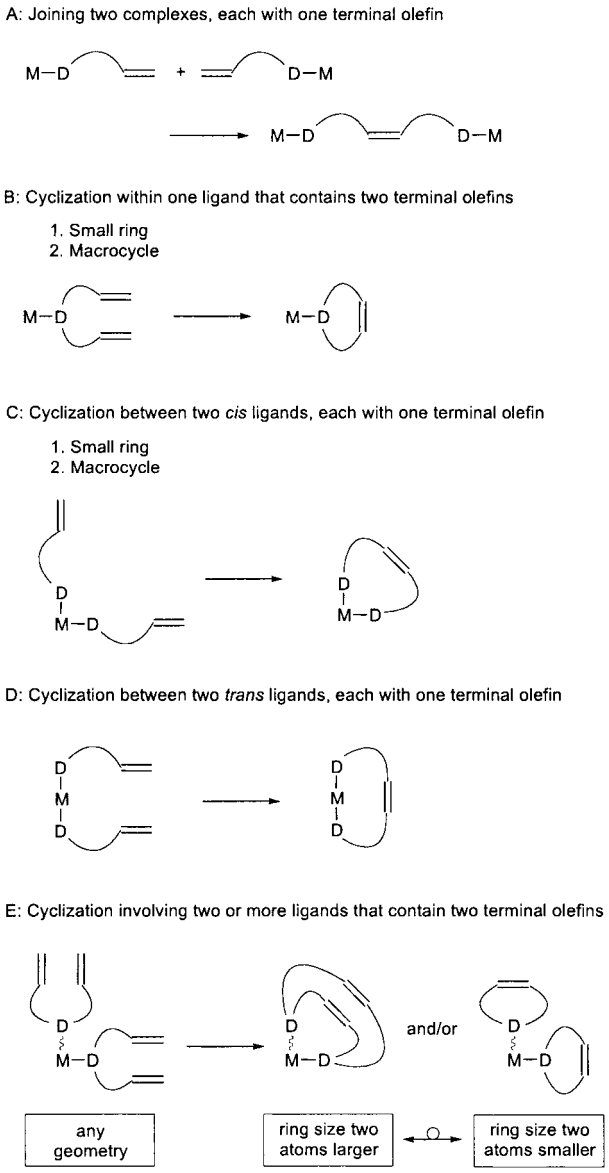


Scheme 1. Some previous examples of olefin metathesis in metal coordination spheres. a) $WOCl_4/Ph_2SiH_2$; b) [W(=CH-*o*-C_6H_4OMe)(OR_f)$_2$(=NPh)(THF)]; c) [Ru(=CHPh)(PCy_3)$_2$(Cl_2)] (**1**).



Scheme 2. Conceptual planning: selected categories of olefin metathesis reactions.

monoolefinic substrates as in Scheme 2A, the competition between ring closing metathesis and intermolecular reactions with the various diolefinic substrates in Scheme 2B–D, dependencies on substrate stereochemistry, such as with the *cis*/*trans* isomers in Scheme 2C–D, and selectivity issues of the type posed in Scheme 2E.

We selected Grubbs' catalyst, [Ru(=CHPh)(PCy_3)$_2$(Cl_2)] (**1**),[8] which was known to exhibit good functional group tolerance, when we began reaction screening in 1998. We enjoyed a very high rate of success from the outset, and selected data have been communicated.[6] This full paper provides a complete account of these and many previously unreported data, integrating and interpreting all results in the context of Scheme 2 and the metal/ligand compatibility questions posed above. While our work was in progress, new contributions appeared from other laboratories.[7] These are presented and analyzed in the Discussion section.

Results

Intermolecular reactions: For many of the metatheses in Scheme 2, we anticipated competition between intermolecular and intramolecular pathways. We thus began with a monoolefinic test substrate that could only give an intermolecular reaction (Scheme 2A). As shown in Scheme 3, the racemic chiral rhenium methyl complex [(η^5-C_5H_5)Re(NO)(PPh_3)(CH_3)] (**2**)[9] was treated with *n*BuLi to generate

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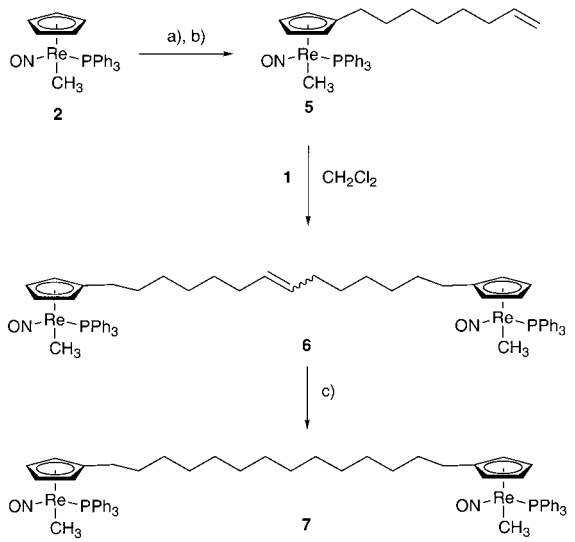


Scheme 3. An intermolecular metathesis reaction. a) *n*BuLi, THF, −30 °C; b) $Br(CH_2)_6CH{=}CH_2$ (**4**); c) H_2 (1 atm), cat. $[Rh(PPh_3)_3(Cl)]$, toluene.

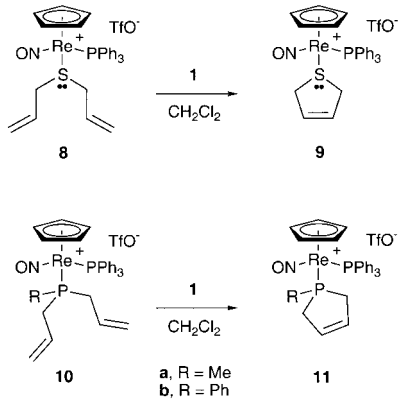
the known lithiocyclopentadienyl complex $[(\eta^5\text{-}C_5H_4Li)Re(NO)(PPh_3)(CH_3)]$ (**3**).[10] Then the commercially available α,ω-bromoolefin $Br(CH_2)_6CH{=}CH_2$ (**4**) was added. Workup gave the alkylcyclopentadienyl complex $[(\eta^5\text{-}C_5H_4(CH_2)_6CH{=}CH_2)Re(NO)(PPh_3)(CH_3)]$ (**5**) in 54% yield. Metathesis substrates were characterized by IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy, and gave correct microanalyses (Experimental Section). However, since close relatives lacking olefins have been characterized (e.g., the methylcyclopentadienyl analogue of **5**),[10] the spectroscopic data are not discussed.

A CH_2Cl_2 solution of **5** (0.0095 M) was treated with Grubbs' catalyst **1** (3 mol%). After 1.5 h at reflux, workup gave the metathesized dirhenium complex **6** shown in Scheme 3 in 95% yield as a 23:77 mixture of *Z*/*E* isomers. Stereochemistry was assigned on the basis of previously established ^{13}C NMR shielding trends.[11] Isomer ratios were measured by ^1H or ^{31}P NMR spectroscopy.[12] Metathesis products were characterized analogously to **5**, and unless noted gave correct microanalyses. However, no special attempts were made to separate *Z*/*E* isomers. We sought instead to effect hydrogenations, a process with good precedent in metal coordination spheres,[13] including Sauvage's catenanes.[4, 5]

Accordingly, **6** and H_2 (1 atm) were reacted in toluene in the presence of Wilkinson's catalyst. Workup gave the corresponding saturated dirhenium complex **7** shown in Scheme 3 in 93% yield. Complex **7** was characterized analogously to **5** and **6**. Although it would be expected to be a mixture of *meso*/*rac* configurational diastereomers, NMR spectra showed only a single set of signals. Other diastereomeric dirhenium complexes with comparable metal–metal distances behave similarly.[14]

Intramolecular reactions: **Cyclization within one ligand**. Metatheses of the type in Scheme 2B were examined next. Substrates that would give small rings were selected first, to avoid *Z*/*E* mixtures and lower the probability of intermolecular reaction. As shown in Scheme 4, a CH_2Cl_2 solution of the known cationic rhenium di(allyl) thioether complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(S(CH_2CH{=}CH_2)_2)]^+$ TfO^- (**8**, 0.0021 M)[15] was treated with **1** (2 mol%) at reflux. After 3 h, NMR spectra of the homogeneous mixture showed an essentially quantitative reaction. Workup gave the dihydrothiophene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(SCH_2CH{=}CHCH_2)]^+$ TfO^- (**9**) in 75% yield. Interestingly, ring closing metatheses of free di(allyl) thioether with catalysts similar to **1** fail or proceed in very low yield,[16] presumably due to strong sulfur binding to the alkylidene carbon or metal. Thioether ligands are easily detached from the rhenium Lewis acid in **8** and **9**.[15] Hence, the rhenium can serve as a protecting group for the metathesis of olefinic thioethers.

The cationic rhenium di(allyl) phosphine complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(PR(CH_2CH{=}CH_2)_2)]^+$ TfO^- (**10**, Scheme 4; R = **a**, Me; **b**, Ph) were synthesized by reactions of the free phosphines and the triflate complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OTf)]$, as reported for similar species



Scheme 4. Metatheses within a ligand: small ring syntheses.

earlier.[17] A CH_2Cl_2 solution of **10a** (0.0017 M) was treated with four portions of solid **1** (8 mol% total) over the course of 1 h at room temperature. Workup afforded the 2,5-dihydrophosphole complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(P(Me)CH_2CH{=}CHCH_2)]^+$ TfO^- (**11a**) in 96% yield. A similar reaction of **10b** (0.00087 M CH_2Cl_2, 4 mol% **1**) gave spectroscopically pure **11b** in 64% yield.[18] Other phosphorus heterocycles have been prepared by olefin metathesis,[19] but only in one study from unprotected phosphines. The crystal structure of **11a** was determined as described in the Experimental Section, and the structure of the cation is shown in Figure 1.

Metatheses with the potential to give macrocycles were examined next. Two new phosphine ligands were first prepared. As shown in Equation (i), the reaction of $LiPPh_2$[20a] or commercial $KPPh_2$ and the commercial olefinic bromide **4** gave the phosphine monoolefin $PPh_2(CH_2)_6CH{=}CH_2$ (**12**) as a viscous colorless liquid in 88% yield after workup. The phosphine diolefin $PPh((CH_2)_6CH{=}CH_2)_2$ (**13**) was obtained

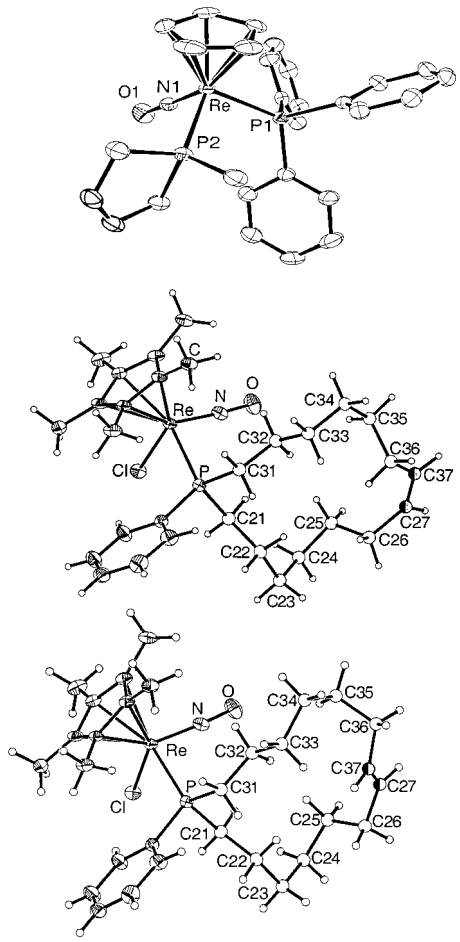


Figure 1. Structures of rhenium cyclic and macrocyclic monophoshine complexes **11a**·(CH_2Cl_2) (top, cation only), (*Z*)-**17** (middle), and (*E*)-**17** (bottom). Key bond lengths [Å] and angles [°], **11a**: Re–P1 2.3768(11), Re–P2 2.3594(11), Re–N1 1.764(3), P1-Re-P2 97.20(4), P1-Re-N1 91.18(9), P2-Re-N1 92.26(9); (*Z*)-**17** and (*E*)-**17**: Re–P 2.3836(14), Re–N 1.785(5), Re–Cl 2.429(2), P-Re-N 90.56(14), P-Re-Cl 87.71(5), N-Re-Cl 98.91(13).

in 78% yield from Li_2PPh[20b] and **4** [2.0 equiv; Equation (ii)].[21] Both can be stored indefinitely under inert atmospheres, but are air sensitive (**13** > **12**).

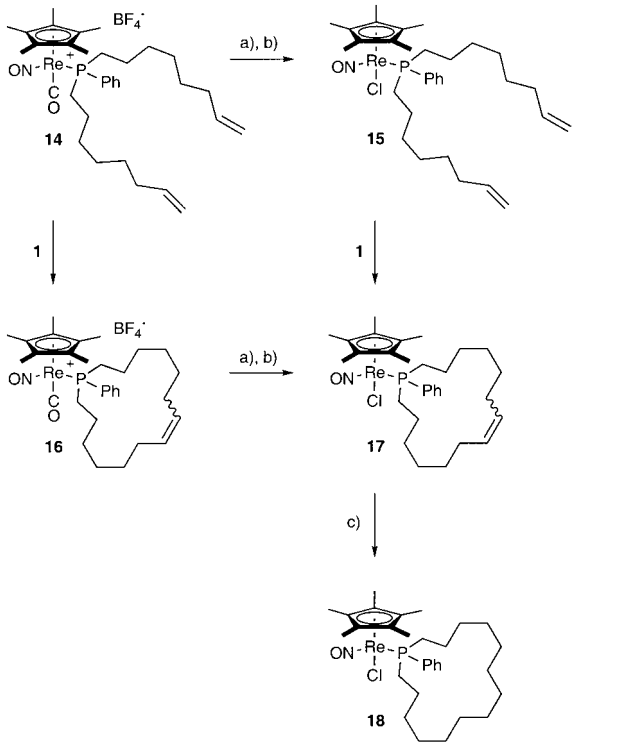
$Br(CH_2)_6CH{=}CH_2$ + MNu ⟶ $Nu(CH_2)_6CH{=}CH_2$ + MBr (i)

4; Nu = **12**, PPh_2; **27**, SEt; **28**, S*t*Bu

2 $Br(CH_2)_6CH{=}CH_2$ + Li_2PPh ⟶ $PPh((CH_2)_6CH{=}CH_2)_2$ + 2 LiBr (ii)

4; **13**

The acetonitrile ligand in the *pentamethyl*cyclopentadienyl complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(NCCH_3)(CO)]^+\ BF_4^-$ is displaced by numerous phosphines.[22] Reaction with the phosphine diolefin **13** gave the target complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh((CH_2)_6CH{=}CH_2)_2)(CO)]^+\ BF_4^-$ (**14**) in high spectroscopic yields. A chromatographic workup afforded analytically pure **14** in 41% yield. Related carbonyl complexes are reduced by $NaBH_4$ to the corresponding methyl complexes,[22] which react with strong acids HX to give species of the formula $[(\eta^5\text{-}C_5R_5)Re(NO)(PAr_3)(X)]$. As shown in Scheme 5, sequential reactions of **14** with $LiAlH_4$ and (after hydrolysis/extraction) aqueous HCl gave the



Scheme 5. Metatheses within a ligand: macrocycle syntheses. a) $LiAlH_4$/THF; b) aq. HCl/CH_2Cl_2; c) H_2 (4 atm), cat. $[Rh(PPh_3)_3(Cl)]$, toluene/ethanol.

chloride complex $[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh((CH_2)_6CH{=}CH_2)_2)(Cl)]$ (**15**) in 56% yield.

Next, CH_2Cl_2 solutions of **14** and **15** (0.00125 – 0.00070 M) were treated with **1** (4 – 5 mol%) at room temperature (Scheme 5). After 12 – 14 h, workups gave the fifteen-membered macrocyclic phosphine complexes $[(\eta^5\text{-}C_5Me_5)Re(NO)(P(Ph)(CH_2)_6CH{=}CH(CH_2)_6)(CO)]^+\ BF_4^-$ (**16**) and $[(\eta^5\text{-}C_5Me_5)Re(NO)(P(Ph)(CH_2)_6CH{=}CH(CH_2)_6)(Cl)]$ (**17**) in 94 – 89% yields. The former was a 44:56 mixture of C=C isomers, and the latter a 42:58 mixture, as assayed by ^1H NMR spectroscopy.[4b, 23] Hence, macrocyclization is spectacularly successful, both with cationic and neutral substrates, and in the absence of templating functionality that seems to be necessary for many ring closing metatheses of purely organic substrates.[11, 24]

Complex **17** could also be prepared from **16**, using the same $LiAlH_4$/HCl sequence used for the conversion of **14** to **15**.[25] Reaction of **17** and H_2 (ca. 5 atm) in the presence of Wilkinson's catalyst gave the corresponding saturated macrocycle $[(\eta^5\text{-}C_5Me_5)Re(NO)(P(Ph)(CH_2)_{14})(Cl)]$ (**18**) in 72% yield (Scheme 5). Of the preceding compounds, the most easily crystallized proved to be olefin **17**. The structure was determined as described in the Experimental Section. Refinement showed a 58:42 mixture of *Z*/*E* isomers in the lattice,[23] with identical atomic coordinates for all atoms except the macrocycle carbons. Both structures are given in Figure 1, and analyzed below.

Intramolecular reactions: **Cyclization between two *cis* ligands, each with one olefin**. The preceding metatheses involve similar chiral rhenium fragments that are known to tolerate

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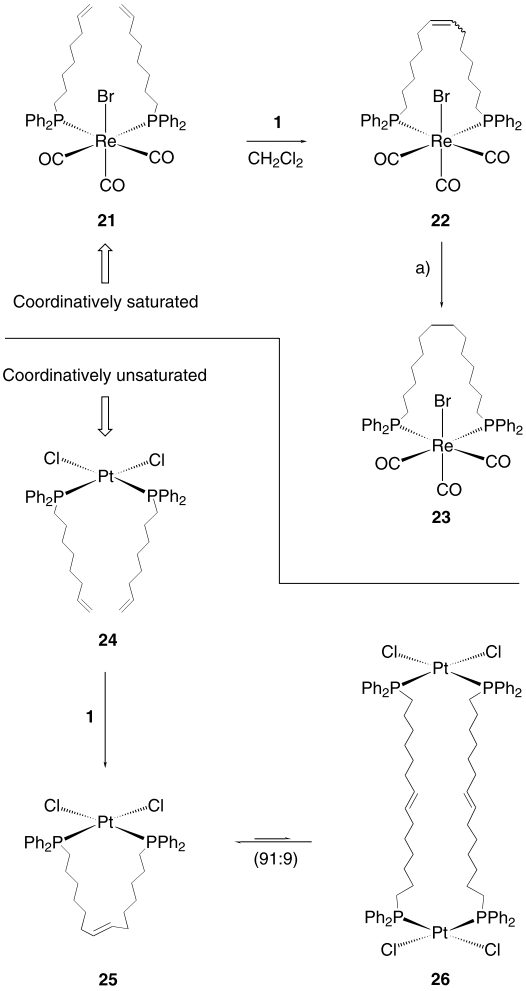
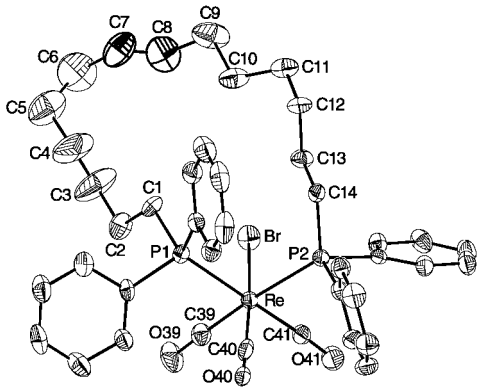
many types of reactions in their coordination spheres. We sought to evaluate a wider variety of metal/ligand assemblies. Thus, for the purposes of testing metatheses between two *cis* ligands (Scheme 2C), we turned to six-coordinate octahedral and four-coordinate square planar substrates. Only macrocyclic targets were investigated.

Reactions of pentacarbonyl rhenium halides and phosphorus donor ligands (> 2 equiv) give facially-substituted tricarbonyl complexes.[26] Accordingly, the reaction of $[(CO)_5Re(Br)]$ and the phosphine monoolefin **12** in refluxing $CHCl_3$ afforded the target complex *fac*-$[(CO)_3Re(Br)(PPh_2(CH_2)_6CH{=}CH_2)_2]$ (**21**) in 72% yield after workup. As shown in Scheme 6, a CH_2Cl_2 solution of **21** (0.0028 M) and **1** (2 mol%) was heated under reflux. Workup gave the seventeen-membered macrocyclic chelating diphosphine complex *fac*-$[(CO)_3Re(Br)(P(Ph)_2(CH_2)_6CH{=}CH(CH_2)_6P(Ph)_2)]$ (**22**) in an impressive 80% yield (17–20:83–80 *Z*/*E*). Hydrogenation (1 atm, Pd/C) afforded the saturated analogue *fac*-$[(CO)_3Re(Br)(P(Ph)_2(CH_2)_{14}P(Ph)_2)]$ (**23**) in 98% yield. The crystal structures of **22** and **23** were determined (Experimental Section), and ORTEP diagrams are given in Figure 2. The crystal of **22** examined contained only the *E* isomer, although NMR spectra of the bulk crystalline sample showed both *Z* and *E* isomers to be present.



Scheme 6. Metatheses between two *cis*-phosphine ligands: macrocyclic diphosphine chelates. a) H_2 (1 atm), cat. 10% Pd/C, toluene/ethanol.



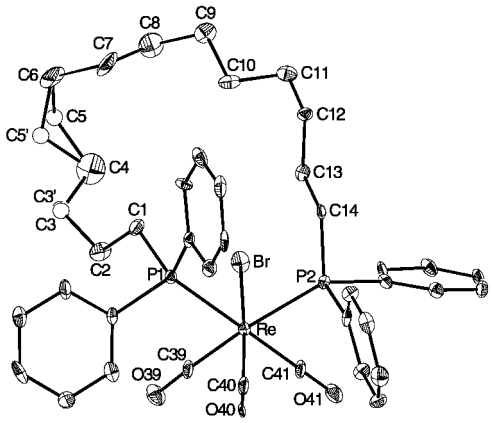


Figure 2. Structures of rhenium macrocyclic diphosphine complexes (*E*)-**22** (top) and **23** (bottom). Key bond lengths [Å] and angles [°], (*E*)-**22**/**23**: Re–P1 2.499(2)/2.487(3), Re–P2 2.534(2)/2.520(3), Re–Br 2.6614(14)/2.6540(12), Re–C39 1.899(10)/1.949(11), Re–C40 1.912(11)/2.054(13), Re–C41 1.901(8)/1.936(10), P1-Re-P2 97.48(7)/97.97(8), P1-Re-Br 90.90(6)/89.71(7), P1-Re-C39 88.2(3)/87.6(3), P1-Re-C40 90.0(3)/91.4(3), P1-Re-C41 178.8(3)/177.9(3), P2-Re-Br 94.04(6)/94.04(7), P2-Re-C39 174.2(3)/174.4(3), P2-Re-C40 91.8(3)/90.8(3), P2-Re-C41 82.7(3)/83.4(3).

Metatheses of coordinatively unsaturated substrates were investigated. A reaction of platinum cyclooctadiene complex $[(Cl)_2Pt(cod)]$ with **12** gave, in accord with much literature precedent,[27] the bis(phosphine) complex *cis*-$[(Cl)_2Pt(PPh_2(CH_2)_6CH{=}CH_2)_2]$ (**24**) in 70% yield. The stereochemistry of **24** and all platinum bis(phosphine) compounds below could be assigned from the diagnostic ^1J(P,Pt) values (*cis*: 3652–3627 Hz, *trans*: 2659–2685 Hz).[27] As shown in Scheme 6, a CH_2Cl_2 solution of **24** (0.0027 M) and **1** (2 mol%) was heated under reflux. Workup gave a substance whose microanalysis fit the target complex *cis*-$[(Cl)_2Pt(P(Ph)_2(CH_2)_6CH{=}CH(CH_2)_6P(Ph)_2)]$ (**25**) in 71% yield (<2:>98 *Z*/*E*). A second minor species could be detected by ^{31}P NMR (91:9 in $CDCl_3$ or acetone). Based upon observations with other $PtCl_2$ adducts of chelating diphosphines,[28] we suspected a monomer/dimer mixture, with the latter involving two mutually-*cis* bridging diphosphines (**26**, Scheme 6).

Indeed, FAB mass spectra showed strong ions with masses corresponding to (**25**-Cl)$^+$ and (**26**-Cl)$^+$ (63%, 46%). An

osmotic molecular weight determination established that the major species in solution was **25** (calcd: 830.8, found ($CHCl_3$): 844). A crystal structure (Figure 3, top) showed only (*E*)-**25**. The unit cell dimensions of six additional crystals were determined, and all were identical. Nonetheless, when crystals

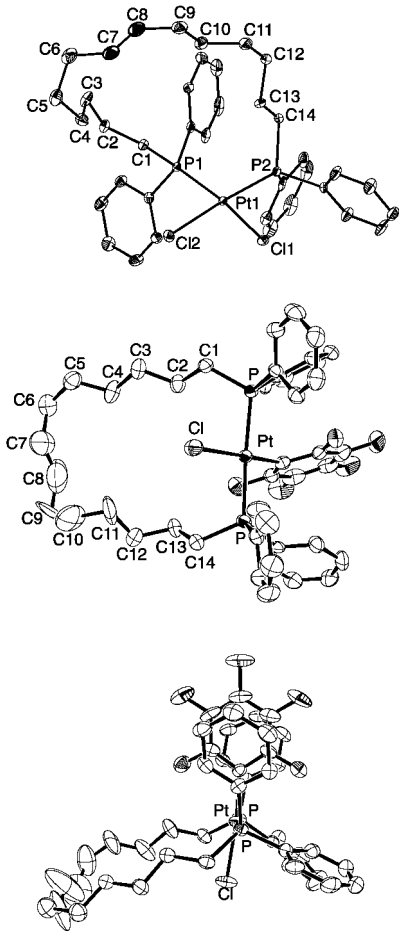
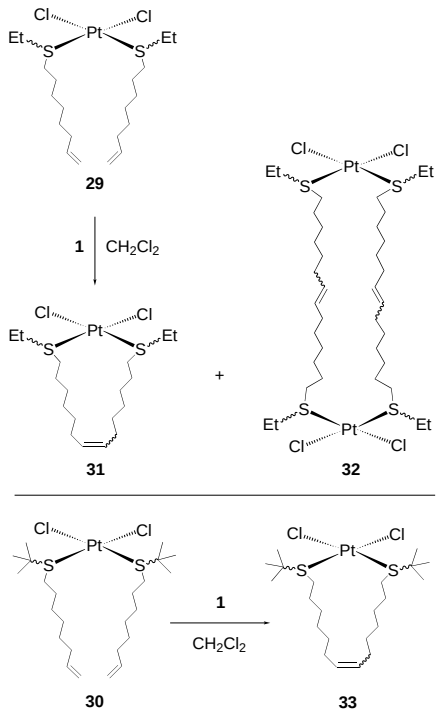


Figure 3. Structures of platinum macrocyclic diphosphine complexes (*E*)-**25** (top) and **39** (middle and bottom). Key bond lengths [Å] and angles [°], (*E*)-**25**: Pt–P1 2.261(2), Pt-P2 2.2492(13), Pt–Cl1 2.337(2), Pt–Cl2 2.3586(13), P1-Pt-P2 98.22(5), P1-Pt-Cl2 84.86(5), P1-Pt-Cl1 171.92(4), P2-Pt-Cl1 89.85(5), P2-Pt-Cl2 175.93(4), Cl1-Pt-Cl2 87.10(5); **39**: Pt–P1 2.306(2)l, Pt–P2 2.299(2), Pt–Cl 2.359(2), Pt–C21 1.996(7), P1-Pt-P2 172.00(7), Cl-Pt-C21 174.3(2), P1-Pt-Cl 88.67(7), P1-Pt-C21 91.4(2), P2-Pt-Cl 89.07(7), P2-Pt-C21 91.4(2).

were dissolved in acetone that had been cooled to $-80\,^{\circ}C$, and ^{31}P NMR spectra immediately recorded, both isomers were present. This indicates either a very rapid equilibrium, or a devious ability of **26** to disguise itself in the solid sample.

Similar reactions with sulfur donor ligands were investigated. The ethyl and *tert*-butyl thioethers $S(R)(CH_2)_6CH{=}CH_2$ (R = Et, **27**; R = *t*Bu, **28**) were first prepared by the standard procedures shown in Equation (i). Reactions with $K_2[PtCl_4]$ gave, as expected,[29] the bis(thioether) complexes *cis*-$[(Cl)_2Pt(S(R)(CH_2)_6CH{=}CH_2)_2]$ (R = Et, **29**; *t*Bu, **30**) in 84–50% yields. As is evident from Scheme 7, the ligating sulfur atoms in **29** and **30** are stereocenters. In agreement with an extensive literature of similar complexes,



Scheme 7. Metatheses between two *cis*-thioether ligands: macrocyclic dithioether chelates.

NMR spectra showed mixtures of *meso*/*rac* (*syn*/*anti*) diastereomers.[29–31]

A CH_2Cl_2 solution of **29** (0.0016 M) and **1** (2 mol%) was heated under reflux. As shown in Scheme 7, workup gave two chromatographically separable macrocycles, both of empirical formula $[(Cl)_2Pt(S(Et)(CH_2)_6CH{=}CH(CH_2)_6S(Et))]$. The mass spectrum of the more rapidly eluting complex showed it to be the monomer **31** (57%, *Z*/*E* 21:79). The mass spectrum of the second complex showed it to be the dimer **32** (24%),[18] containing a thirty-four membered macrocycle. Due to the many diastereomers resulting from the four sulfur stereocenters, the *Z*/*E* ratio was not quantified. Complexes **31** and **32** showed no tendency to interconvert in solution. Hence, the latter is presumed to be derived from an intermolecular metathesis.

A CH_2Cl_2 solution of the *tert*-butyl substituted thioether complex **30** (0.0012 M) and **1** (2 mol%) was heated under reflux. As shown in Scheme 7, workup gave only one macrocycle, the monoplatinum chelate *cis*-$[(Cl)_2Pt(S(tBu)(CH_2)_6CH{=}CH(CH_2)_6S(tBu))]$ (**33**), in 72% yield (*Z*/*E* 16:84).[18] Only a small amount (<4%) of a diplatinum complex could have gone undetected. Possible reasons for the higher selectivity with **30** are suggested below.

Intramolecular reactions: **Cyclization between two *trans* ligands, each with one olefin**. Ligands that span *trans* positions must by definition be macrocyclic. Most examples involve diphosphines, an important area that has been recently reviewed.[28a, 32] In the majority of cases, the diphosphines are "preformed" as opposed to generated by linking two monophosphines in a metal coordination sphere. We sought to attempt the synthesis of *trans*-spanning diphosphines by the

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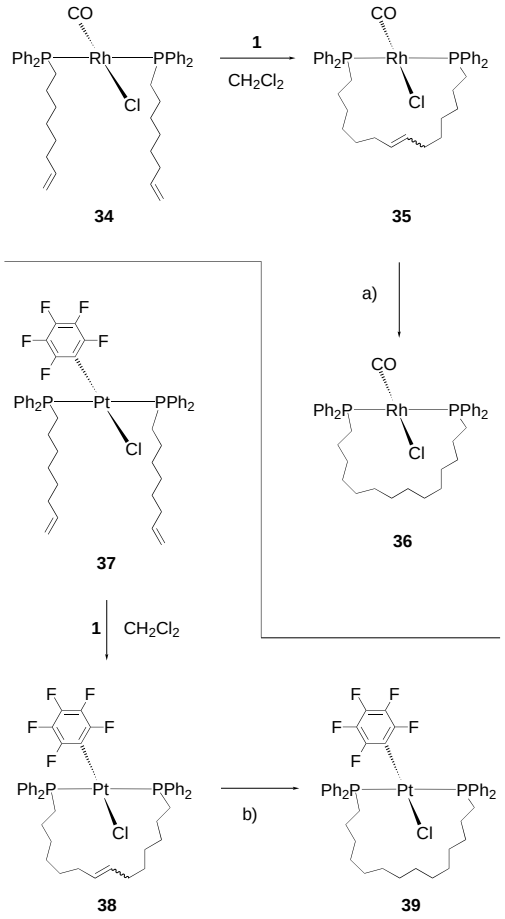
route in Scheme 2D. If successful, this would represent the first monophosphine-linking protocol yielding a hydrocarbon tether.

The phosphine monoolefin **12**, rhodium complex $[Rh(\mu\text{-}Cl)(COD)]_2$, and CO were combined under conditions known to give bis(phosphine) complexes *trans*-$[(Cl)(CO)Rh(L)_2]$.[33] Workup afforded *trans*-$[(Cl)(CO)Rh(PPh_2(CH_2)_6CH{=}CH_2)_2]$ (**34**) in 79% yield. As shown in Scheme 8, a CH_2Cl_2 solution of



Scheme 8. Metatheses between two *trans*-phosphine ligands: *trans*-spanning macrocyclic diphosphine chelates. a) H_2 (5 atm), cat. $[Rh(PPh_3)_3(Cl)]$, toluene; b) H_2 (1 atm), cat. 10% Pd/C, ethanol/$ClCH_2CH_2Cl$.

34 (0.0027 M) and **1** (5 mol%) was heated under reflux. Chromatography gave the target macrocycle *trans*-$[(Cl)(CO)Rh(P(Ph)_2(CH_2)_6CH{=}CH(CH_2)_6P(Ph)_2)]$ (**35**) in an astoundingly high 83% yield (*Z*/*E* 17:83). A reaction of **35** and H_2 (5 atm) in the presence of Wilkinson's catalyst afforded the saturated *trans*-spanning diphosphine complex *trans*-$[(Cl)(CO)Rh(P(Ph)_2(CH_2)_{14}P(Ph)_2)]$ (**36**) in high spectroscopic yields. However, due to several minor workup complications (see Experimental Section), analytically pure product could only be obtained in 55% yield.

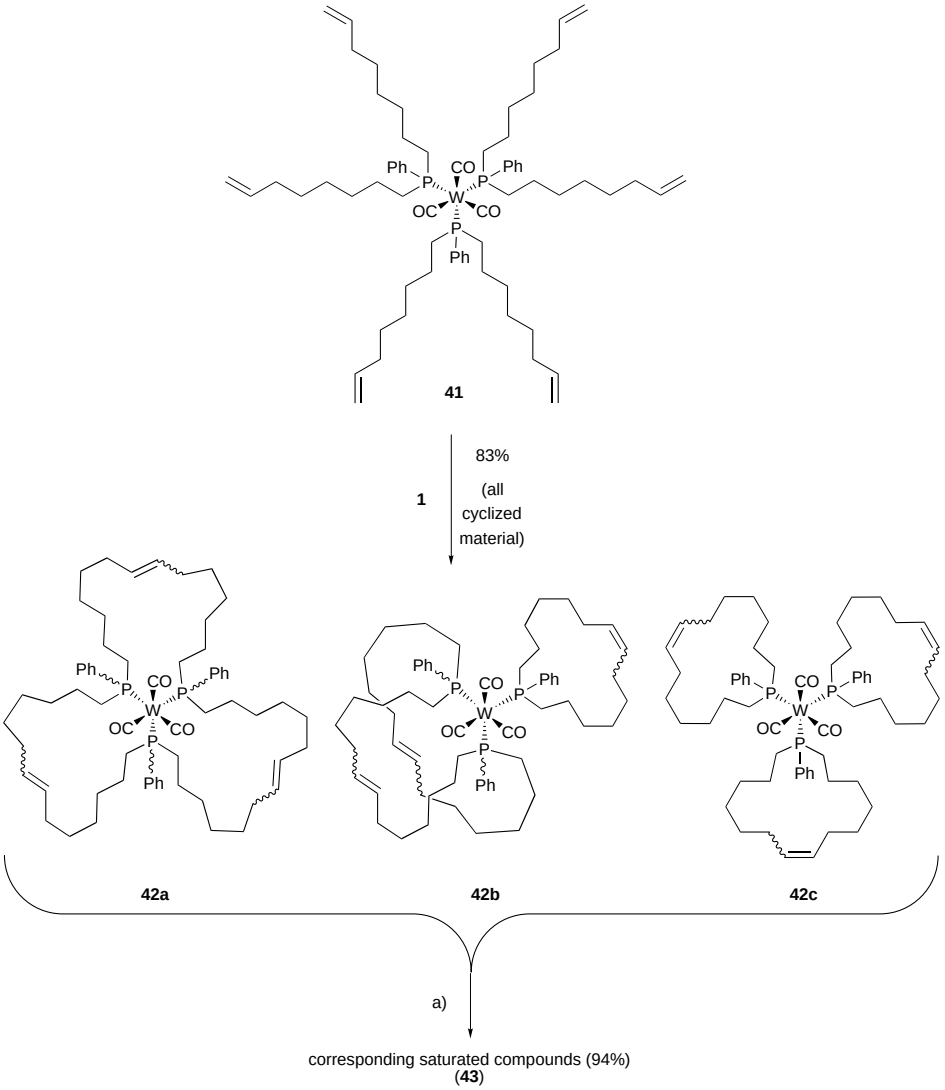
In an attempt to obtain a crystalline *trans*-spanning diphosphine complex, we returned to platinum compounds. First, the pentafluorophenyl platinum dihydrothiophene (SR_2) complex $[Pt(\mu\text{-}Cl)(C_6F_5)(SR_2)]_2$ and **12** were combined under conditions known to give bis(phosphine) complexes *trans*-$[(Cl)(C_6F_5)Pt(L)_2]$.[34, 35] Workup gave *trans*-$[(Cl)(C_6F_5)Pt(PPh_2(CH_2)_6CH{=}CH_2)_2]$ (**37**) in 79% yield. As shown in Scheme 8, a CH_2Cl_2 solution of **37** (0.0025 M) and **1** (6 mol%; added in two portions) was heated under reflux. Alumina filtration gave the target macrocycle *trans*-$[(Cl)(C_6F_5)Pt(P(Ph)_2(CH_2)_6CH{=}CH(CH_2)_6P(Ph)_2)]$ (**38**) in 90% yield (*Z*/*E* 17:83), which gave correct microanalyses. Depending upon how the filtration was conducted, samples contained up to 15% of a second species, as assayed by ^{31}P NMR spectroscopy. This was provisionally assigned to a diplatinum by-product derived from intermolecular metathesis.

Reactions of **38** and H_2 (1 atm) in the presence of 10% Pd/C catalyst gave the saturated macrocycle *trans*-$[(Cl)(C_6F_5)Pt(P(Ph)_2(CH_2)_{14}P(Ph)_2)]$ (**39**). Yields of analytically pure material ranged from 94% (with up to 15% of a by-product by ^{31}P NMR) to 72% (no by-product). A crystal structure was determined, and two views are given in Figure 3 (middle and bottom). The second highlights a stacking interaction involving the pentafluorophenyl ligand and a phenyl group on each phosphorus. It is now well established that π -C_6H_5/-C_6F_5 interactions are attractive and a driving force in many crystallizations.[36]

Intramolecular reactions: **Cyclization involving two or more ligands**, **each with two olefins**. We next sought to test the feasibility of *poly*macrocyclization reactions, as exemplified in Scheme 2E. The simplest version would involve two ligands that each contain two terminal olefins. One such metathesis has been communicated.[6b] This unexpectedly selective process exhibits so many fascinating nuances that it will be reported as a part of a separate, long-term study. Thus, we conclude this paper with a reaction at the next higher level of complexity—a substrate featuring three *facially* disposed ligands, each bearing two terminal olefins. In this case, an extensive mixture of trimacrocyclic products is obtained.

The reaction of tungsten propionitrile complex *fac*-$[(CO)_3W(NCCH_2CH_3)_3]$ (**40**)[37] and phosphine diolefin **13** gave, in accord with much literature precedent,[38] the tris(phosphine) complex *fac*-$[(CO)_3W(PPh((CH_2)_6CH{=}CH_2)_2)_3]$ (**41**) in 71% yield. As shown in Scheme 9, a CH_2Cl_2 solution of **41** (0.00042 M) and **1** (9 mol% or 3 mol% per product C=C) was heated under reflux. Chromatography gave a sample of empirical formula $[(CO)_3W(P(Ph)((CH_2)_6CH{=})_2)_3]$ (**42**) in 83% yield. NMR spectra indicated that all terminal olefins had been replaced by disubstituted olefins, and a mass spectrum showed an intense molecular ion (100%).[18] The pattern of the isotope envelope (*m*/*z* 1173–1179) agreed perfectly with that calculated. HPLC showed three overlapping regions of partially resolved peaks. Three limiting structures are given in Scheme 9: **42a**, with one triphosphine, **42b**, with one diphosphine and one monophosphine, and **42c**, with three monophosphines. We conjectured that these might correspond to the three HPLC regions. The mass spectrum showed ions for each type of ligand ($3 \times 10\%$).

Two complexes could be crystallized from this mixture. The crystal structures were determined, and are illustrated in Figure 4. Both feature a forty-five membered macrocyclic tridentate triphosphine with three *E*−C=C linkages (**42a′**, **42a″**). They differ in phosphorus stereochemistry. The first



Scheme 9. Metatheses between three *fac*-phosphine ligands: polymacrocyclizations. a) H_2 (6 atm), cat. $[Rh(PPh_3)_3(Cl)]$, toluene.

has all three PPh groups *anti* to the $W(CO)_3$ moiety, while the second has one PPh group *syn*. Considering all *Z*/*E* and *syn*/*anti* permutations, there are sixteen possible stereoisomers of **42a**. Complexes **42b** and **42c** can have as many as eighteen and four stereoisomers, respectively (the diphosphine in **42b** has three possible PPh orientations). The HPLC and ^{31}P NMR data suggested that a majority of these 38 species were present.

Complexes **42** and H_2 (ca. 6 atm) were reacted in the presence of Wilkinson's catalyst. Workup gave the corresponding mixture of saturated complexes (**43**) in 94% yield, as assayed by mass spectrometry and ^1H NMR spectroscopy. However, the HPLC trace and ^{31}P NMR spectrum remained complex, and further purification attempts were not successful. We note in passing that analogues of **42a** with much smaller ring sizes have been prepared by free radical cyclizations of $M(CO)_3$ (M = Cr, Mo, W) adducts of allyl or homoallyl monophosphines $H_2C{=}CH(CH_2)_nPH_2$.[39, 40] In some cases, the new tridentate triphosphines have been detached from the metal.[39c,d]

Discussion

Scope of title reaction: The preceding data establish the broad applicability of Grubbs' catalyst **1** for effecting olefin metatheses in metal coordination spheres. Our examples involve neutral and charged, coordinatively saturated and unsaturated, and octahedral and square-planar rhenium, platinum, rhodium, and tungsten complexes with cyclopentadienyl, phosphine, and thioether ligands that contain terminal olefins. The previously described metatheses in Scheme 1 feature olefin-containing Fischer carbene, ferrocene, and tripyridyl-based ligands. More recent reports that further expand synthetic utility are summarized in Scheme 10.

Scheme 10B depicts a family of cross-metatheses in ferrocene coordination spheres. Together with other examples,[3a] these can be viewed as conceptual extensions of the intermolecular homometatheses in Schemes 2A and 3. Schemes 10C, 10D, and 1A involve the formation of medium or small rings *within* ligands, thus constituting examples of Scheme 2B. We find the excellent yield with the highly

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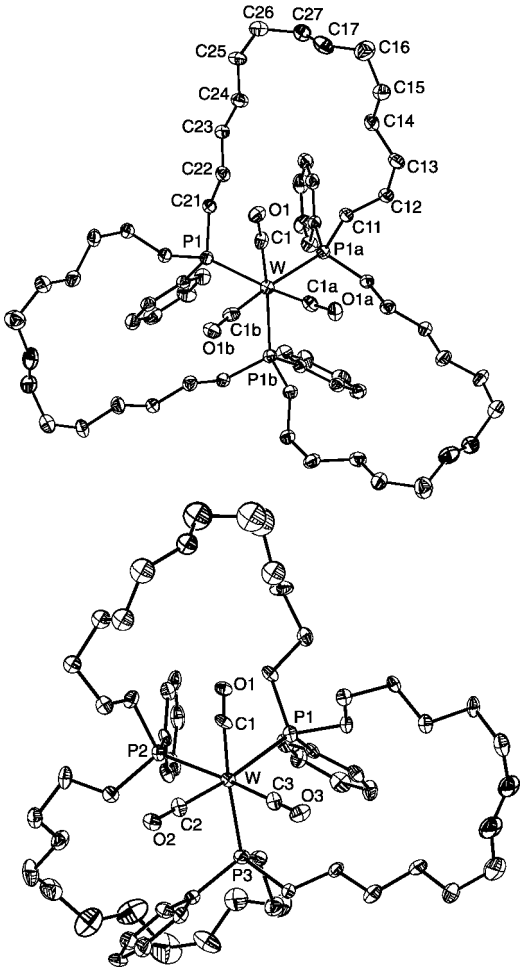
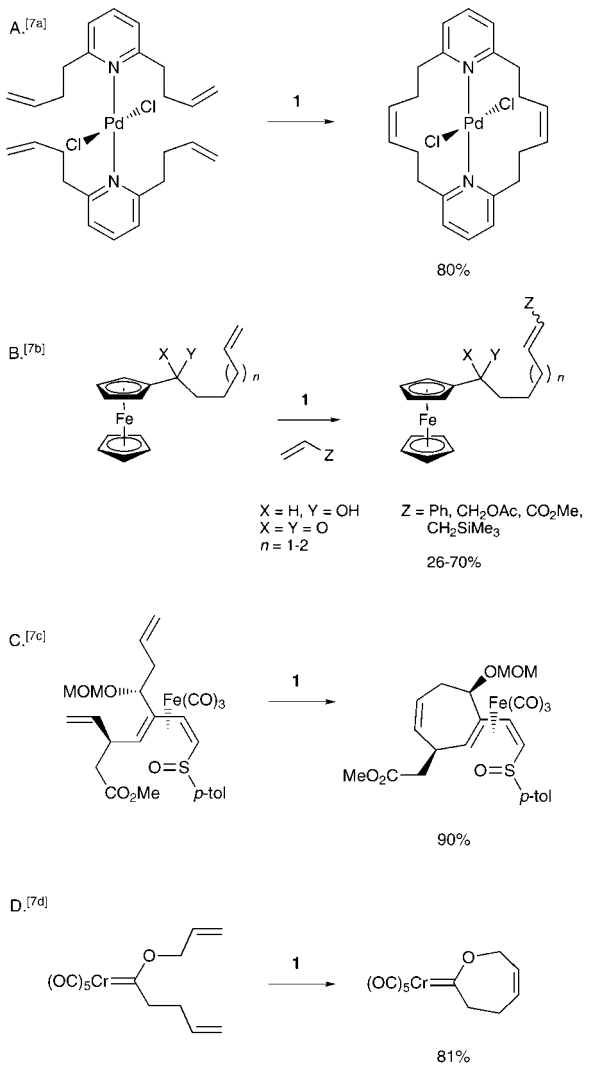


Figure 4. Structures of tungsten trimacrocyclic triphosphine complexes **42a′** (top) and **42a″** · $(C_6H_{14})_{0.5}$ (bottom, solvate omitted). Key bond lengths [Å] and angles [°], **42a′**: W–P 2.545(2), W–C1 1.938(10), P-W-P 99.29(7), P-W-C1 84.0(3), P-W-C1a 89.7(3), P-W-C1b 169.8(3); **42a″** · $(C_6H_{14})_{0.5}$: W–P1 2.537(3), W–P2 2.554(2), W–P3 2.556(3), W–C1 1.969(9), W–C2 1.982(10), W–C3 1.981(9), P1-W-P2 96.51(8), P1-W-P3 95.69(9), P1-W-C1 82.8(2), P1-W-C2 171.4(3), P1-W-C3 92.0(3), P2-W-P3 96.13(9), P2-W-C1 89.7(3), P2-W-C2 83.9(3), P2-W-C3 170.2(3), P3-W-C1 174.1(3), P3-W-C2 92.8(3), P3-W-C3 87.8(3).



Scheme 10. Additional examples of olefin metathesis in metal coordination spheres.

functionalized 1,3-diene iron tri(carbonyl) in Scheme 10C particularly noteworthy. The two-fold metathesis of the diolefinic pyridine ligands in Scheme 10A leads to a novel doubly *trans*-spanning macrocycle. This can be viewed as a conceptual extension of the monocyclizations in Schemes 2D and 8. However, this system is geometrically predisposed towards *trans* cyclization, unlike the substrates in Scheme 8, which are further analyzed below.

Although the yields of our metathesis reactions are high, they are in most cases unoptimized (particularly Schemes 3 to 7). The catalyst loadings are typical of those used with organic substrates. We view the apparent absence of side reactions involving the chain-carrying ruthenium alkylidene as remarkable. Deactivation was sometimes observed, but this could be remedied by the portion-wise addition of **1**. Some metatheses of rhodium complex **34** (Scheme 8) gave minor by-products (^{31}P NMR), which seem to be in part derived from the PCy_3 that dissociates from **1**. An independent reaction of **35** and PCy_3 (4 equiv, $CDCl_3$) gave the known compound *trans*-$[(Cl)(CO)Rh(PCy_3)_2]$.[41]

All of our reactions give internal olefins, which are much less reactive towards the chain-carrying ruthenium alkylidene than terminal olefins.[42] We therefore presume that they are under kinetic control. However, we did not monitor product *Z*/*E* ratios as a function of time, or attempt to anneal or equilibrate products by treating purified samples with **1**. This represents a possible approach to enhancing the selectivities, such as with the reaction in Scheme 9. Some of the new second-generation ruthenium catalysts appear particularly promising for such purposes.[8, 43, 44]

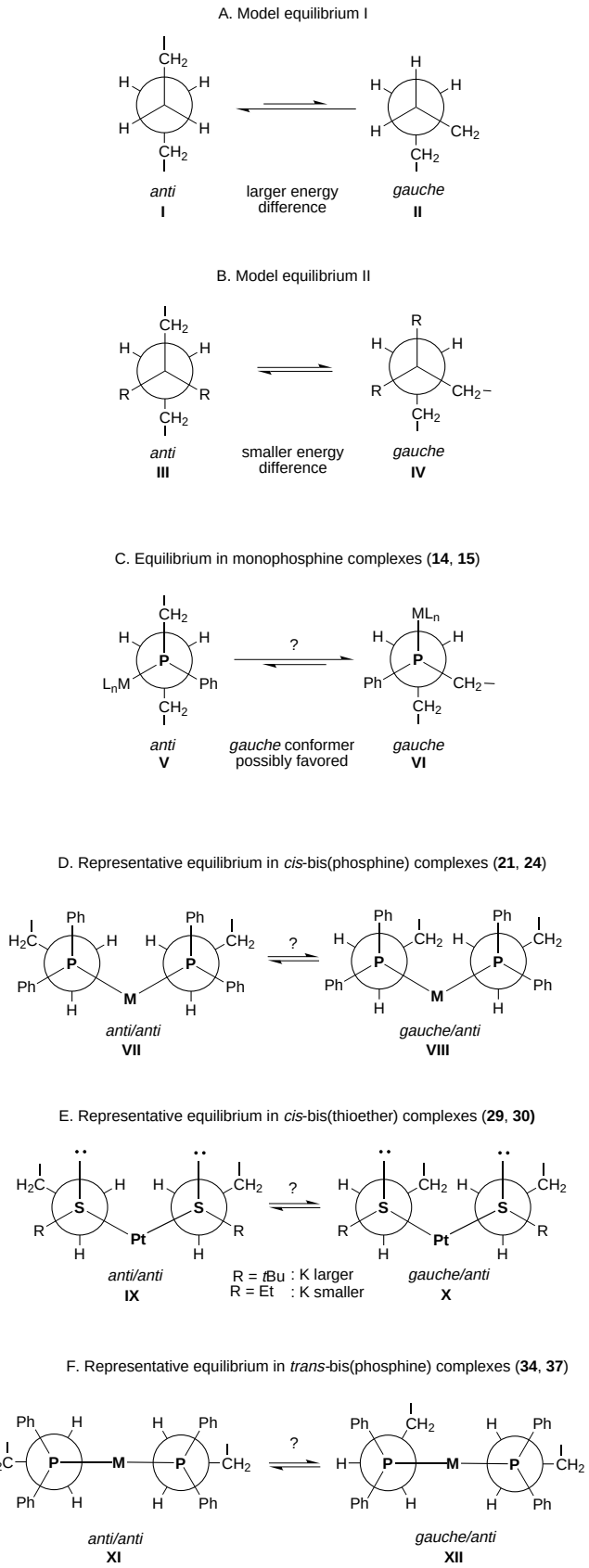
Why are the macrocyclizations so successful? The uniformly high yields of the many types of intramolecular macrocyclizations (Schemes 5 to 9) deserve analysis. Substrate concentrations range from 0.0028 M—in our view, not particularly dilute—to 0.00042 M, which corresponds to 0.131 g of **41** in 250 mL of CH_2Cl_2. Hence, factors or properties that enhance the competitiveness of intramolecular versus intermolecular reactions appear likely.

Fürstner has compared metatheses of α,ω-diolefins that lack functionality in the backbone to those with various Lewis-basic functional groups. To account for the much higher yields of simple monomeric macrocycles with the latter, transient binding of the chain-carrying ruthenium alkylidene was proposed.[25] In this context, consider the diolefins **14** and **15** in Scheme 5. Both lack binding sites in the intervening $(CH_2)_6P(CH_2)_6$ chain. External to this assembly, the nitrosyl, carbonyl, and chloride ligands are possible candidates. However, the first two are very feeble Lewis bases. Although the chloride ligand can bind a second metal,[45] **14** shows that it is not required for macrocyclization.

It is well known that when geminal dialkyl groups are introduced on a methylene chain (e.g., a $-CH_2C\boldsymbol{R}_2CH_2CH_2-$ moiety) intramolecular α,ω-cyclizations are promoted.[46, 47] The alkyl groups render the energies of *anti* and *gauche* conformations much closer, as illustrated in Scheme 11 A – B (**I/II** vs. **III/IV**). In all carbocycles (and the precursor transition states), *gauche* segments are mandatory, as easily identified in the above crystal structures. We propose that in **14** and **15**, the phenyl and rhenium groups on phosphorus play roles equivalent to those of geminal dialkyl groups in carbocyclic systems. As illustrated in Scheme 11 C, the energy of the macrocyclization-friendly *gauche* conformer **VI** (CH_2 *gauche* to phenyl and CH_2 groups) might even be lower than that of the *anti* isomer **V** (CH_2 *gauche* to phenyl and L_nM groups). An alternative but less precise formulation would be that bulky metal fragments restrict the conformational space and freedom of coordinated ligands, such that the terminal olefins in complexes such as **14** and **15** have a higher probability of being close to each other.

With the *cis*-bis(phosphine) complexes **21** and **24** (Scheme 6), the metal becomes part of the macrocyclic ring. Thus, conformations of the $MPPh_2CH_2CH_2$ segments must be analyzed, and two of many possibilities are depicted in Scheme 11 D. Relative to model compounds with $MPH_2CH_2CH_2$ or MCH_2-CH_2CH_2 segments, the phosphorus phenyl groups should increase the fraction of molecules with cyclization-favorable *gauche* conformations (e.g., **VIII**). Since **24** gives monoplatinum and diplatinum macrocycles that appear to be in equilibrium (**25**, **26**), we do not rigorously know if intramolecular metathesis is kinetically preferred. However, the *cis*-bis(thioether) complex **29** yields monoplatinum and diplatinum macrocycles that are not in equilibrium (**31**, **32**; Scheme 7). This shows that intramolecular macrocyclization of **29** is preferred. We presume that **24** exhibits analogous selectivity.

In contrast to **21** and **24**, the *cis*-bis(thioether) complexes **29** and **30** lack geminal groups. Since they give predominantly intramolecular macrocyclization (**30**, *t*Bu > **29**, Et), additional factors that promote ring formation are likely (and furthermore operative with **21** and **24**). We feel it would be premature to speculate about these at this time. However, the higher proportion of intramolecular metathesis with **30** can be rationalized. In an *anti* Pt-SR-CH_2-CH_2 conformation, the R group is *gauche* to a hydrogen atom and a methylene group (**IX**, Scheme 11 E). In a *gauche* conformation (**X**), the R group is *gauche* to two hydrogen atoms. Hence, a *tert*-butyl group should increase the fraction of molecules with *gauche* conformations.



Scheme 11. Conformational factors in macrocyclizations.

With the *trans*-bis(phosphine) complexes **34** and **37** (Scheme 8), the phenyl groups will (as with **21** and **24**) increase the fraction of *gauche* M-PPh_2-CH_2-CH_2 conforma-

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tions relative to those in suitable models. As shown in Scheme 11 F, conformer **XII** should gain at the expense of **XI**. However, there are many possible conformations about the metal–phosphorus bonds besides those shown, and the *trans* chains must localize on the same side of the metal square plane. A greater phosphorus–phosphorus bond length must be traversed than in the preceding examples, with increased potential for van der Waals interactions with the metal fragment. Thus, we find the success of these intramolecular macrocyclizations particularly surprising. With **37**, a $-C_6H_5$/$-C_6F_5$ stacking interaction as in crystalline **39** (Figure 3) might provide a preorganizational benefit.[36] However, this would be absent in **34**. As communicated earlier,[6b] it is furthermore possible to effect a double macrocyclization, akin to that of the preorganized *ortho*-disubstituted pyridine complex in the Scheme 10 A. Accordingly, the scope of and possible driving forces for such *trans*-macrocyclizations remain under active investigation.[48]

Macrocycle structures: The crystal structures in Scheme 1–4 exhibit a variety of macrocycle conformations, aspects of which are relevant to the analyses in the preceding section. For example, the *Z*- and *E* isomers of the fifteeen-membered macrocycle **17** (Figure 1) feature *gauche* conformations of the type **VI** (Scheme 11 C) about all four $CH_2P(Ph)(Re)CH_2CH_2$ segments. The overall C34-C33-C32-C31-P-C21-C22-C23-C24-C25-C26 conformations are quite similar, with *gauche* butane segments at C21-C22-C23-C24, C22-C23-C24-C25, and C23-C24-C25-C26. The C=C linkages (C27–C37) initiate four carbon sequences where the conformations are distinctly different.

The seventeen-membered macrocycles in (*E*)-**22** (Figure 2) and (*E*)-**25** (Figure 3) are—despite the difference in metal coordination numbers—very similar with respect to the P1-M-P2 and phosphorus phenyl ring conformations. The Pt-PPh_2-C14-C13 and Pt-PPh_2-C1-C2 conformations in (*E*)-**25** are analogous to the *gauche* and *anti* segments in **VIII** (Scheme 11 D), respectively. The Re-PPh_2-C14-C13 and Re-PPh_2-C1-C2 conformations in (*E*)-**22** are both *gauche*. The C14-C13-C12-C11-C10-C9 linkages are quite similar in (*E*)-**22** and (*E*)-**25** (*anti*, *gauche*, *anti* butanes). However, the C9–C8 conformations (the vinyl linkages) differ by approximately 180°, resulting in distinctly different return paths to phosphorus P1. The saturated macrocycle **23** is virtually identical to (*E*)-**22** over the C2-C1-P1-Re-P2-C14-C13-C12-C11-C10-C9 moiety.

Complex **42a′** (Figure 4) features a three-fold rotational symmetry axis, which renders the macrocyclic rings equivalent. The ring sizes and olefin geometries are the same as in (*E*)-**22** and (*E*)-**25**, but since there is only one phenyl group on each phosphorus, comparisons are not as meaningful. There is one *gauche* butane segment on one side of the olefin (C11-C12-C13-C14), *gauche* $=CH\text{-}\boldsymbol{C}H_2\text{-}\boldsymbol{C}H_2\text{-}CH_2$ conformations on each side of the olefin, and only *anti* butane segments on the path back to tungsten. Every macrocyclic ring in the lower-symmetry isomer **42a″** has a unique conformation. The saturated *trans*-spanning macrocycle in **39** (Figure 3) is disordered, but the major isomer exhibits a very symmetrical conformation with *anti*, *anti*, *anti*, and *gauche* butane segments as the methylene chain extends from each phosphorus. Both Pt-P-CH_2-CH_2 conformations are analogous to the *gauche* linkage in **XII** (Scheme 11 F).

When molecules are viewed at van der Waals radii, the macrocycles contain little "empty space". Another common feature is that there are no marked distortions in bond lengths or angles about the metals. For example, the *trans*-spanning ligand in **22** gives a P-Pt-P bond angle (172.00(7)°) close to 180°, and comparable to the Cl-Pt-C angle (174.3(2)°). Metal–ligand bonds have lower bending force constants than sp^3–sp^3 carbon–carbon bonds. Hence, this is consistent with little or no bond or angle strain within the seventeen-membered ring (normalized to the number of atoms). Since numerous non-macrocyclic structural models for all of the preceding compounds are readily obtained from the Cambridge crystallographic data base, we do not provide a list of references or otherwise discuss the routine metrical parameters summarized in the captions.

Summary and Prospective

We have demonstrated the viability of Grubbs' catalyst **1** for the construction of numerous types of acyclic, cyclic, and macrocyclic inorganic and organometallic compounds from easily accessed precursors. Intramolecular metatheses are always more efficient than intermolecular metatheses, even under only modestly dilute conditions. Many of the macrocycles are topologically novel, and most metatheses are remarkably selective. As one proceeds through the increasingly complex paradigm in Scheme 2, product mixtures are encountered only at the stage 2E. These are tractable in at least some cases.[6b] However, Scheme 9, which represents a still higher level of complexity, gives an intractable mixture of seemingly every possible isomer of **42a–c**, from which we were fortunate to acquire at least some meaningful data. Nonetheless, this constitutes an efficient synthesis of a combinatorial library, an area in which olefin metathesis is seeing increasing application.[49]

The preceding data also leave a number of open questions that will make attractive themes for future research. For example, how are the macrocyclizations in Schemes 5 to 9 affected by the lengths of the methylene chains and the presence of substitutents and/or heteroatoms? Do newer second-generation ruthenium metathesis catalysts effect significant improvements? Can chiral metathesis catalysts[50] effect kinetic resolutions of chiral organometallic substrates (Schemes 3–5), or enantioselective syntheses of chiral products from achiral substrates (e.g., certain isomers of **42a–b**)? Most importantly, the stage is now firmly set for the widespread and systematic application of olefin metathesis in the targeted synthesis of complex organometallic systems. Specific applications involving multistep sequences will be reported in the near future.[51]

Experimental Section

General data: All reactions except thioether syntheses were conducted under N_2 (or H_2) atmospheres. Chemicals were treated as follows: acetone, 2-butanone, and $CHCl_3$, distilled from anhydrous $CaSO_4$; THF, diethyl ether (ether), benzene, and toluene, distilled from Na/benzophenone;

CH_2Cl_2 and C_6H_5Cl distilled from CaH_2 and then P_2O_5; pentane and hexane, distilled from P_2O_5; $ClCH_2CH_2Cl$ (99%, Fluka), DMF (99%, Fluka), methanol and ethanol, used as received; $CDCl_3$, vacuum transferred from CaH_2 or P_2O_5; [D$_6$]benzene, vacuum transferred from Na; *n*BuLi (Acros, 2.5 or 1.6 M in hexanes), standardized;[52] K_2PtCl_4 (Strem), water-insoluble residue removed by filtration; $Br(CH_2)_6C{=}CH_2$ (**4**; 97%, Aldrich or Fluka), PPh_2H (Aldrich), $PPhH_2$ (97%, Fluka), $PPh(CH_2CH{=}CH_2)_2$ (95%, Aldrich), HSEt (Aldrich), NaS-*t*Bu (Aldrich), $LiAlH_4$ (97%, Fluka), TfOH (97%, Merck), [Ru(=CHPh)(PCy$_3$)$_2$(Cl)$_2$] (**1**, Strem), [Rh(PPh$_3$)$_3$(Cl)] (Strem), and Pd/C (10%, Lancaster or Acros), used as received.

IR spectra were recorded on Mattson Polaris FT or ASI React-IR 1000 spectrometers. NMR spectra were obtained on Varian 300 MHz or Jeol 400 MHz spectrometers. Mass spectra were recorded on Finnigan MAT 95 or Micromass Zabspec high resolution instruments. Microanalyses were conducted by Atlantic Microlab or with a Carlo Erba EA1110 instrument (in-house). Osmotic molecular weights were determined by Galbraith.

[(η^5-$C_5H_4(CH_2)_6CH{=}CH_2$)Re(NO)(PPh$_3$)(CH$_3$)] (5): A Schlenk flask was charged with [(η^5-C_5H_5)Re(NO)(PPh$_3$)(CH$_3$)] (**2**;[9] 0.553 g, 0.989 mmol) and THF (20 mL) and cooled to $-30\,^\circ$C. Then *n*BuLi (2.5 M, 1.10 mL, 2.7 mmol) was added dropwise with stirring over 5 min.[10] After 5 h, **4** (0.43 mL, 2.56 mmol) was added with stirring. After 18 h, solvent was removed by oil pump vacuum. The red oil was placed on top of a Celite/silica plug (2 cm each above a frit). The red material was rinsed through the plug with toluene. The sample was taken to dryness by oil pump vacuum. Column chromatography (silica gel, 20:1 *v*/*v* hexane/THF) gave two partially resolved bands (**5**, **2**). The forerun of the first was collected and dried by oil pump vacuum to give **5** as a red oil (0.358 g, 0.535 mmol, 54%). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 7.44-7.37$ (m, 15H, 3Ph), 5.78 (m, 1H, C*H*=), 5.21 (m, 1H of C_5H_4), 4.93 (m, 2H, =CH_2), 4.61, 4.56, 4.10 (3m, 3H of C_5H_4), 2.18 (m, 2H, $C_5H_4CH_2$), 2.00 (m, 2H, $CH_2CH{=}$), 1.54–1.21 (m, 8H, 4CH_2), 0.90 (d, ^3J(H,P) = 6 Hz, 3H, ReCH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 20 °C): $\delta = 139.1$ (s, *C*H=), 136.5 (d, ^1J(C,P) = 51 Hz, *i*-Ph), 133.6 (d, ^2J(C,P) = 11 Hz, *o*-Ph), 129.8 (d, ^4J(C,P) = 3 Hz, *p*-Ph), 128.1 (d, ^3J(C,P) = 10 Hz, *m*-Ph),[53] 114.2 (s, =*C*H$_2$), 112.6 (s, *i*C_5H_4R), 91.8, 88.8, 86.5, 84.1 (4s, other C_5H_4R), 33.7 (s, $CH_2CH{=}$), 30.9 (s, *C*H$_2$), 29.2 (s, *C*H$_2$), 28.9 (s, *C*H$_2$), 28.8 (s, *C*H$_2$), 28.0 (s, *C*H$_2$), −32.9 (d, ^2J(C,P) = 7 Hz, Re*C*H$_3$); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 20 °C): $\delta = 25.7$ (s); IR (KBr): $\tilde{\nu} = 1633$ (NO) cm^{-1}; MS (FAB, 3-NBA/CH_2Cl_2): *m*/*z* (%): 669 (100) $[M]^+$, 654 (17) $[M-CH_3]^+$; elemental analysis calcd (%) for $C_{32}H_{37}NOPRe$ (668.83): C 57.47, H 5.58; found: C 57.26, H 5.65.

[(H$_3$C)(Ph$_3$P)(ON)Re(η^5-$C_5H_4(CH_2)_6CH{=}CH(CH_2)_6$-$\eta^5$-$C_5H_4$)Re(NO)(PPh$_3$)(CH$_3$)] (6): A Schlenk flask was charged with **5** (0.380 g, 0.568 mmol), **1** (0.015 g, 0.018 mmol, 3 mol%), and CH_2Cl_2 (60 mL). The solution was heated under reflux (1.5 h). Solvent was removed by rotary evaporation. The brown foam was dissolved in a minimum of CH_2Cl_2. The solution was rinsed through a Celite/silica plug (1 and 2 cm above a frit). Solvent was removed by oil pump vacuum to give **6** as an orange solid (0.355 g, 0.271 mmol, 95%; *Z*/*E* 23:77[54, 55a]). M.p. 72 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 7.42-7.35$ (m, 30H, 6Ph), 5.35 (m, 2H, C*H*=C*H*), 5.21, 4.61, 4.56, 4.10 (4m, 4 × 2H, 2C_5H_4), 2.19 (m, 4H, 2$C_5H_4CH_2$), 1.94 (m, 4H, 2$CH_2CH{=}$), 1.54–1.21 (m, 16H, 8CH_2), 0.89 (d, ^3J(H,P) = 6 Hz, 6H, 2ReCH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 20 °C): $\delta = 136.5$ (d, ^1J(C,P) = 51 Hz, *i*-Ph), 133.6 (d, ^2J(C,P) = 11 Hz, *o*-Ph), 130.3 (s, *C*H=*C*H), 129.7 (d, ^4J(C,P) = 2 Hz, *p*-Ph), 128.1 (d, ^3J(C,P) = 10 Hz, *m*-Ph), 112.7 (s, *i*C_5H_4R), 91.7, 88.7, 86.4, 84.0 (4s, other C_5H_4R), 32.6 (s, *C*H$_2$CH=, *E*), 30.9 (s, *C*H$_2$), 29.5 (s, *C*H$_2$), 29.3 (s, *C*H$_2$), 28.9 (s, *C*H$_2$), 28.0 (s, *C*H$_2$), −32.9 (d, ^2J(C,P) = 7 Hz, Re*C*H$_3$); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 20 °C): $\delta = 26.0$ (s); IR (KBr): $\tilde{\nu} = 1621$ (NO) cm^{-1}; MS (FAB, 3-NBA/CH_2Cl_2): *m*/*z* (%): 1310 (6) $[M]^+$, 1295 (2) $[M-CH_3]^+$; elemental analysis calcd (%) for $C_{62}H_{70}N_2O_2P_2Re_2$ (1309.61): C 56.86, H 5.39; found: C 56.52, H 5.64.

[(H$_3$C)(Ph$_3$P)(ON)Re(η^5-$C_5H_4(CH_2)_{14}$-η^5-C_5H_4)Re(NO)(PPh$_3$)(CH$_3$)] (7): A Schlenk flask was charged with **6** (0.174 g, 0.133 mmol), [Rh(PPh$_3$)$_3$(Cl)] (0.020 g, 0.021 mmol, 15 mol%), and toluene (10 mL), flushed with H_2, and fitted with a balloon of H_2. The mixture was stirred for 24 h. Solvent was removed by oil pump vacuum. The residue was rinsed through a silica plug with CH_2Cl_2. Solvent was removed by oil pump vacuum to give **7** as an orange-red gum (0.162 g, 0.124 mmol, 93%). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 7.46-7.35$ (m, 30H, 6Ph), 5.23, 4.62, 4.57, 4.12 (4m, 4 × 2H, 2C_5H_4), 2.19 (m, 4H, 2$C_5H_4CH_2$), 1.50–1.22 (m, 24H, 12CH_2), 0.93 (d, ^3J(H,P) = 6 Hz, 6H, 2ReCH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 20 °C): $\delta = 136.5$ (d, ^1J(C,P) = 51 Hz, *i*-Ph), 133.6 (d, ^2J(C,P) = 11 Hz, *o*-Ph), 129.7 (d, ^4J(C,P) = 2 Hz, *p*-Ph), 128.1 (d, ^3J(C,P) = 10 Hz, *m*-Ph), 112.7 (s, *i*C_5H_4R), 91.7, 88.7, 86.4, 84.0 (4s, other C_5H_4R), 30.9 (s, *C*H$_2$), 29.6 (s, 2 × intensity, *C*H$_2$), 29.5 (s, *C*H$_2$), 29.4 (s, *C*H$_2$), 29.3 (s, *C*H$_2$), 28.1 (s, *C*H$_2$), −32.9 (d, ^2J(C,P) = 7 Hz, Re*C*H$_3$); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 20 °C): $\delta = 26.1$ (s); IR (KBr): $\tilde{\nu} = 1621$ (NO) cm^{-1}; MS (FAB, 3-NBA/CH_2Cl_2): *m*/*z* (%): 1312 (12) $[M]^+$; elemental analysis calcd (%) for $C_{62}H_{72}N_2O_2P_2Re_2$ (1311.64): C 56.78, H 5.53; found: C 56.87, H 5.70.

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(SCH$_2$CH=CHCH$_2$)]$^+$ TfO$^-$ (9): A Schlenk flask was charged with [(η^5-C_5H_5)Re(NO)(PPh$_3$)(S$(CH_2CH{=}CH_2)_2$)]$^+$ TfO$^-$ (**8**;[15] 0.242 g, 0.300 mmol) and CH_2Cl_2 (140 mL). Another Schlenk flask was charged with **1** (0.005 g, 0.006 mmol, 2 mol%) and CH_2Cl_2 (5 mL). The latter solution was added by cannula to the former with stirring. The mixture was heated under reflux (3 h) and turned light brown. A small amount of activated charcoal was added. The suspension was swirled and filtered through a Celite plug (2 cm). Solvent was removed by rotary evaporation. The residue was dissolved in acetone and layered with ether. After 48 h, red prisms of **9** were collected by filtration and dried under oil pump vacuum (0.175 g, 0.225 mmol, 75%). M.p. 191 °C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 7.57-7.54$ (m, 9H of 3Ph), 7.36–7.31 (m, 6H of 3Ph), 5.92 (brs, 2H, SCH$_2$C*H*), 5.60 (s, 5H, C_5H_5), 3.75 (m, 4H, 2SC*HH*′); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 20 °C): $\delta = 133.5$ (d, ^2J(C,P) = 11 Hz, *o*-Ph), 132.7 (d, ^1J(C,P) = 56 Hz, *i*-Ph), 132.0 (d, ^4J(C,P) = 2 Hz, *p*-Ph), 130.0 (d, ^3J(C,P) = 11 Hz, *m*-Ph), 127.6 (s, SCH$_2$*C*H), 93.4 (s, C_5H_5), 54.5 (s, S*C*H$_2$); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 20 °C): $\delta = 11.5$ (s); IR (CH_2Cl_2/Nujol): $\tilde{\nu} = 1711/1708$ (NO) cm^{-1}; MS (FAB, 3-NBA/CH_2Cl_2): *m*/*z* (%): 630 (100) $[M]^+$, 544 (59) $[M-SCH_2CH-CHCH_2]^+$; elemental analysis calcd (%) for $C_{28}H_{26}F_3NO_4PS_2Re$ (778.82) C 43.18, H 3.36; found: C 43.16, H 3.35.

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(PMe(CH$_2$CH=CH$_2$)$_2$)]$^+$ TfO$^-$ (10a): A Schlenk flask was charged with **2** (0.759 g, 1.36 mmol) and C_6H_5Cl (25 mL) and cooled to $-45\,^\circ$C. Then TfOH (0.120 mL, 1.36 mmol) was added with stirring. After 5 min, the cold bath was removed. After 20 min, PMe$(CH_2CH{=}CH_2)_2$ (ca. 4.0 mmol from a ca. 90% pure ether solution[56]) was added. After 16 h, the yellow solution was concentrated to about 15 mL by oil pump vacuum. Hexane (50 mL) was added dropwise giving an oil, which was stirred (0.5 h) and then triturated. The solid was collected by filtration, washed with pentane (50 mL), ether (50 mL), and pentane (10 mL), and dried by oil pump vacuum (3 d) to give **10a** as a bright yellow microcrystalline powder (1.021 g, 1.244 mmol, 92%). M.p. 177–180 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 7.55-7.25$ (m, 15H, 3Ph), 5.61 (m, 2H, 2C*H*=), 5.51 (s, 5H, C_5H_5), 5.30–4.92 (m, 4H, 2=CH_2), 2.94–2.33 (m, 4H, 2PC*HH*′), 1.33 (d, ^2J(H,P) = 9 Hz, 3H, PCH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 20 °C): $\delta = 134.1$ (d, ^1J(C,P) = 55 Hz, *i*-Ph), 133.2 (d, ^2J(C,P) = 11 Hz, *o*-Ph), 131.6 (d, ^4J(C,P) = 1 Hz, *p*-Ph), 129.2 (d, ^3J(C,P) = 11 Hz, *m*-Ph), 128.8 (d, ^2J(C,P) = 9 Hz, *C*H=), 128.7 (d, ^2J(C,P) = 9 Hz, *C*′H=), 121.3 (d, ^3J(C,P) = 6 Hz, =*C*H$_2$), 121.2 (d, ^3J(C,P) = 6 Hz, =*C*′H$_2$), 92.0 (s, C_5H_5), 36.0 (d, ^1J(C,P) = 33 Hz, P*C*H$_2$), 35.1 (d, ^1J(C,P) = 33 Hz, P*C*′H$_2$), 12.9 (d, ^1J(C,P) = 35 Hz, PCH$_3$); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 20 °C): $\delta = 12.2$ (d, ^2J(P,P) = 12 Hz, *P*Ph$_3$), −27.8 (d, ^2J(P,P) = 12 Hz, *P*MeR$_2$); IR (KBr): $\tilde{\nu} = 1709$ (NO) cm^{-1}; elemental analysis calcd (%) for $C_{31}H_{33}F_3NO_4P_2SRe$ (820.86): C 45.36, H 4.05; found: C 45.27, H 4.15.

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(PPh(CH$_2$CH=CH$_2$)$_2$)]$^+$ TfO$^-$ (10b): Complex **2** (1.507 g, 2.701 mmol), C_6H_5Cl (25 mL), TfOH (0.480 g, 3.20 mmol), and PPh$(CH_2CH{=}CH_2)_2$ (0.760 g, 4.00 mmol) were combined at $-15\,^\circ$C in a procedure analogous to that for **10a**. An identical workup (final product wash with pentane) gave **10b** as a bright yellow microcrystalline powder (1.221 g, 1.383 mmol, 51%). M.p. 138–140 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 32 °C): $\delta = 7.55-7.01$ (m, 20H, 4Ph), 5.53 (m, 2H, 2C*H*=), 5.43 (s, 5H, C_5H_5), 5.32–5.08 (m, 4H, 2=CH_2), 3.32–2.74 (m, 4H, 2PC*HH*′); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 32 °C): $\delta = 134.0$ (d, ^1J(C,P) = 55 Hz, *i*-PPh$_3$), 133.2 (d, ^2J(C,P) = 11 Hz, *o*-PPh$_3$), 133.0 (d, ^1J(C,P) = 56 Hz, *i*-PPhR$_2$), 130.3 (d, ^2J(C,P) = 11 Hz, *o*-PPhR$_2$), 131.5 (s, *p*-PPh$_3$), 130.8 (s, *p*-PPhR$_2$), 129.3 (d, ^3J(C,P) = 11 Hz, *m*-PPh$_3$), 129.0 (d, ^3J(C,P) = 11 Hz, *m*-PPhR$_2$), 128.5 (d, ^2J(C,P) = 8 Hz, *C*H=), 128.3 (d, ^2J(C,P) = 8 Hz, *C*′H=), 121.8 (d, ^3J(C,P) = 13 Hz, =*C*H$_2$), 121.7 (d, ^3J(C,P) = 13 Hz, =*C*′H$_2$), 92.7 (s, C_5H_5), 35.6 (d, ^1J(C,P) = 35 Hz, P*C*H$_2$), 31.4 (d, ^1J(C,P) = 35 Hz, P*C*′H$_2$); ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$, 32 °C): $\delta = 10.3$ (d, ^2J(P,P) = 10 Hz, *P*Ph$_3$), −19.0 (d, ^2J(P,P) = 10 Hz, *P*PhR$_2$); IR (solid): $\tilde{\nu} = 1702$ (NO) cm^{-1}; MS (FAB, 3-NBA): *m*/*z* (%): 734 (100) $[M]^+$ of cation; elemental analysis calcd (%)

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for $C_{36}H_{35}F_3NO_4P_2SRe$ (882.88): C 49.98, H 4.11, N 1.59; found: C 50.10, H 4.21, N 1.49.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(P(Me)CH_2CH{=}CHCH_2)]^+$ TfO^- (11a): A Schlenk flask was charged with **10a** (0.204 g, 0.249 mmol) and CH_2Cl_2 (150 mL). Solid **1** (0.016 g, 0.017 mmol, 8 mol%) was added in four portions over 1 h with stirring. After another hour, the mixture was filtered through a silica plug. Solvent was removed from the filtrate by oil pump vacuum. Column chromatography (silica gel, 10×2 cm, 95:5 *v*/*v* CH_2Cl_2/methanol) gave a yellow eluate which was dried by oil pump vacuum to give **11a** as a yellow foam (0.193 g, 0.244 mmol, 96%). M.p. 76 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 32 °C, TMS): $\delta = 7.55-7.26$ (m, 15H, 3Ph), 5.78 (m, 2H, C*H*=C*H*), 5.56 (s, 5H, C_5H_5), 2.63 (m, 3H of PC*HH*′ + PC′*HH*′), 2.17 (m, 1H of PC*HH*′ + PC′*HH*′), 1.62 (d, ^2J(H,P) = 10 Hz, 3H, PCH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 32 °C, TMS): $\delta = 133.9$ (d, ^1J(C,P) = 56 Hz, *i*-Ph), 133.2 (d, ^2J(C,P) = 11 Hz, *o*-Ph), 131.6 (d, ^4J(C,P) = 1 Hz, *p*-Ph), 129.3 (d, ^3J(C,P) = 11 Hz, *m*-Ph), 128.9 (s, *C*H=), 128.3 (s, *C*′H=), 91.9 (s, C_5H_5), 38.8 (d, ^1J(C,P) = 35 Hz, P*C*H$_2$), 35.3 (d, ^1J(C,P) = 33 Hz, P*C*′H$_2$), 17.4 (d, ^1J(C,P) = 34 Hz, PCH_3); ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$, 32 °C): $\delta = 13.8$ (d, ^2J(P,P) = 14 Hz, *P*Ph$_3$), −15.8 (d, ^2J(P,P) = 14 Hz, *P*MeR$_2$); IR (KBr): $\tilde{\nu} = 1695$ (NO) cm^{-1}; MS (FAB, 3-NBA/CH_2Cl_2): *m*/*z* (%): 644 (100) $[M]^+$ of cation; elemental analysis calcd (%) for $C_{29}H_{29}F_3NO_4P_2SRe$ (792.77): C 43.94, H 3.69, N 1.77; found: C 44.33, H 3.97, N 1.46.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(P(Ph)CH_2CH{=}CHCH_2)]^+$ TfO^- (11b): Complex **10b** (0.100 g, 0.130 mmol), CH_2Cl_2 (150 mL), and solid **1** (0.006 g, 0.005 mmol, 4 mol% in two portions) were combined in a procedure analogous to that given for **11a**. An identical workup gave **11b** as a yellow foam (0.071 g, 0.083 mmol, 64%). M.p. 80 °C;[18] ^{1}H NMR (400 MHz, $CDCl_3$, 32 °C, TMS): $\delta = 7.49-7.02$ (m, 20H, 4Ph), 5.74 (m, 2H, C*H*=C*H*), 5.43 (s, 5H, C_5H_5), 3.11–2.78 (m, 4H, 2PCH_2); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 32 °C, TMS): $\delta = 134.8$ (d, ^1J(C,P) = 49 Hz, *i*-PPhR$_2$), 133.7 (d, ^1J(C,P) = 56 Hz, *i*-PPh_3), 133.1 (d, ^2J(C,P) = 11 Hz, *o*-PPh_3/PPhR$_2$), 131.6 (d, ^4J(C,P) = 2 Hz, *p*-PPh_3), 130.8 (s, *p*-PPhR$_2$), 129.8 (d, ^3J(C,P) = 10 Hz, *m*-PPh_3), 129.2 (d, ^3J(C,P) = 10 Hz, *m*-PPhR$_2$), 129.1 (s, *C*H=), 129.0 (s, *C*′H=), 92.5 (s, C_5H_5), 39.9 (d, ^1J(C,P) = 34 Hz, P*C*H$_2$), 34.6 (d, ^1J(C,P) = 33 Hz, P*C*′H$_2$); ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$, 32 °C): $\delta = 11.7$ (d, ^2J(P,P) = 12 Hz, *P*Ph$_3$), −1.4 (d, ^2J(P,P) = 12 Hz, *P*PhR$_2$); IR (solid film): $\tilde{\nu} = 1695$ (NO) cm^{-1}; MS (FAB, 3-NBA): *m*/*z* (%): 706 (100) $[M]^+$ of cation.

$PPh_2(CH_2)_6CH{=}CH_2$ (12):[21] A Schlenk flask was charged with PPh_2H (3.210 g, 17.24 mmol) and THF (90 mL). Then *n*BuLi (2.5 M in hexanes; 7.2 mL, 18 mmol) was added dropwise with stirring. The solution turned orange-red.[20a] After 10 min, a solution of **4** (3.130 g, 16.38 mmol) in THF (10 mL) was added. The sample turned light yellow. After 3 h, solvent was removed by oil pump vacuum to give a white solid suspended in an oil. Hexane (30 mL) was added, and the mixture was passed through a silica plug (2 cm). Solvent was removed by oil pump vacuum. The residue was distilled under vacuum to give **12** as a viscous colorless liquid (4.515 g, 15.23 mmol, 88%). Procedures using $KPPh_2$ (Fluka, 0.5 M in THF) gave equivalent results. ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 7.45-7.32$ (m, 10H, 2Ph), 5.79 (m, 1H, C*H*=), 5.02–4.91 (m, 2H, =CH_2), 2.07–1.99 (m, 4H, CH_2CH= + PCH_2), 1.45–1.27 (m, 8H, 4CH_2); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 20 °C): $\delta = 139.3$ (s, *C*H=), 139.2 (d, ^1J(C,P) = 16 Hz, *i*-Ph), 132.9 (d, ^2J(C,P) = 19 Hz, *o*-Ph), 128.6 (d, ^3J(C,P) = 9 Hz, *m*-Ph), 128.6 (s, *p*-Ph), 114.4 (s, =CH_2), 34.0 (s, *C*H_2CH=), 31.3 (d, ^1J(C,P) = 13 Hz, P*C*H$_2$),[57] 29.0 (s, 2 × intensity, *C*H_2CH_2CH_2CH=CH$_2$), 28.2 (d, ^3J(C,P) = 11 Hz, PCH$_2$CH_2CH_2), 26.1 (d, ^2J(C,P) = 16 Hz, PCH_2CH_2); ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$, 32 °C): $\delta = -15.8$ (s); elemental analysis calcd (%) for $C_{20}H_{25}P$ (296.39): C 81.05, 8.50; found: C 81.02, H 8.44.

$PPh((CH_2)_6CH{=}CH_2)_2$ (13):[21] A Schlenk flask was charged with $PPhH_2$ (0.938 g, 8.52 mmol) and THF (40 mL) and was cooled to 0 °C. Then *n*BuLi (1.8 M in hexanes, 10.1 mL, 18 mmol) was added dropwise with stirring over 10 min.[20b] After another 10 min, a solution of **4** (3.260 g, 17.06 mmol) in THF (5 mL) was added. The cold bath was removed. After 2 h, solvent was removed by oil pump vacuum. The residue was filtered through a silica plug (3 cm) with hexane (3×20 mL). The filtrate was taken to dryness by oil pump vacuum. The residue was distilled (10^{-2} bar, 111–115 °C) to give **13** as a viscous colorless liquid (2.200 g, 6.657 mmol, 78%). ^{1}H NMR (400 MHz, $CDCl_3$, 32 °C): $\delta = 7.63$ (m, 1H of Ph), 7.49 (m, 2H of Ph), 7.34 (m, 2H of Ph), 5.79 (m, 2H, 2C*H*=), 4.90 (m, 4H, 2=CH_2), 1.98 (m, 4H, 2CH_2CH=), 1.69 (m, 4H, 2PCH_2), 1.42–1.08 (m, 16H, 8CH_2); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 32 °C): $\delta = 139.4$ (m, *i*-Ph), 139.1 (s, *C*H=), 132.6 (d, ^2J(C,P) = 18 Hz, *o*-Ph), 128.2 (d, ^3J(C,P) = 20 Hz, *m*-Ph), 128.4 (s, *p*-Ph), 114.2 (s, =CH_2), 34.0 (s, *C*H_2CH=), 31.3 (d, ^1J(C,P) = 11 Hz, P*C*H$_2$),[57] 29.0 (s, 2 × intensity, *C*H_2CH_2CH_2CH=CH$_2$), 28.5 (d, ^3J(C,P) = 11 Hz, PCH$_2$CH_2CH_2), 26.1 (d, ^2J(C,P) = 15 Hz, PCH_2CH_2); ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$, 32 °C): $\delta = -23.8$ (s); MS (FAB, 3-NBA/CH_2Cl_2): *m*/*z* (%): 331 (100) $[M]^+$; elemental analysis calcd (%) for $C_{22}H_{35}P$ (330.49): C 79.95, 10.67; found: C 79.95, H 9.90.

$[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh((CH_2)_6CH{=}CH_2)_2)(CO)]^+$ BF_4^- (14): A Schlenk flask was charged with $[(\eta^5\text{-}C_5Me_5)Re(NO)(NCMe)(CO)]^+$ BF_4^- (0.190 g, 0.374 mmol), **13** (0.103 g, 0.312 mmol), and $ClCH_2CH_2Cl$ (20 mL), and fitted with a condenser. The solution was heated under reflux (15 h). Solvent was removed by oil pump vacuum. Column chromatography (silica gel, 20×2 cm, CH_2Cl_2) gave a red by-product band. The eluent was changed to 97:3 *v*/*v* CH_2Cl_2/methanol (yellow band containing some **14**) and then 92:8 *v*/*v* CH_2Cl_2/methanol. Solvent was removed from the last series of fractions by oil pump vacuum to give spectroscopically pure **14** (0.101 g, 0.127 mmol, 41%). An analytical sample was obtained by further column chromatography (silica gel, 7:3 *v*/*v* CH_2Cl_2/acetone). ^{1}H NMR (400 MHz, $CDCl_3$, 32 °C, TMS): $\delta = 7.56-7.45$ (m, 5H, Ph), 5.74 (m, 2H, 2C*H*=), 4.92 (m, 4H, 2=CH_2), 2.37 (m, 4H, 2PCH_2), 2.01 (m, 4H, 2CH_2CH=), 1.93 (s, 15H, $C_5(CH_3)_5$), 1.45–1.25 (m, 16H, 8CH_2); ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]benzene, 32 °C): $\delta = 203.8$ (d, ^2J(C,P) = 8 Hz, Re*C*O), 139.0 (s, *C*H=), 131.7 (d, ^1J(C,P) = 53 Hz, *i*-Ph,), 129.9 (d, ^2J(C,P) = 11 Hz, *o*-Ph), 128.6 (d, ^3J(C,P) = 10 Hz, *m*-Ph), 127.8 (s, *p*-Ph), 114.5 (s, =*C*H$_2$), 106.1 (s, $C_5(CH_3)_5$), 34.0 (s, *C*H$_2$CH=), 30.6 (d, *J*(C,P) = 8 Hz, *C*H$_2$), 30.4 (d, *J*(C,P) = 11 Hz, *C*H$_2$), 28.9 (s, 2 × intensity, *C*H$_2$), 28.8 (s, *C*H$_2$), 24.0 (s, *C*H$_2$), 9.7 (s, $C_5(CH_3)_5$); ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$, 32 °C): $\delta = 0.4$ (s); IR (solid film): $\tilde{\nu} = 1984$ (CO), 1722 (NO) cm^{-1}; MS (FAB, 3-NBA/CH_2Cl_2): *m*/*z* (%): 710 (100) $[M]^+$ of cation; elemental analysis calcd (%) for $C_{33}H_{50}BF_4NO_2PRe$ (796.75): C 49.75, H 6.33, N 1.76; found: C 49.81, H 6.59, N 1.73.

$[(\eta^5\text{-}C_5Me_5)Re(NO)(PPh((CH_2)_6CH{=}CH_2)_2)(Cl)]$ (15): A Schlenk flask was charged with **14** (0.300 g, 0.377 mmol) and THF (20 mL). Then $LiAlH_4$ (0.047 g, 1.243 mmol) was added with stirring. After 2 h, small amounts of water were added until gas evolution ceased. Solvent was removed by oil pump vacuum. Then CH_2Cl_2 (ca. 20 mL) was added, and the sample filtered. Aqueous HCl (12 N; 0.20 mL, 2.4 mmol) was added with stirring. After 0.5 h, the sample was concentrated and filtered through a silica plug (3 cm). Solvent was removed from the filtrate by oil pump vacuum to give **15** as dark red solid (152 mg, 0.213 mmol, 56%). M.p. 162–174 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 32 °C, TMS): $\delta = 7.72-7.63$ (m, 2H of Ph), 7.15–7.00 (m, 3H of Ph), 5.83–5.66 (m, 2H, 2C*H*=), 5.06–4.92 (m, 4H, 2=CH_2), 2.76–2.38 (m, 4H, 2PCH_2), 2.00–1.84 (m, 4H, 2CH_2CH=), 1.53 (s, 15H, $C_5(CH_3)_5$), 1.37–1.00 (m, 16H, 8CH_2); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 32 °C, TMS): $\delta = 139.0$ (s, *C*H=), 131.7 (d, ^2J(C,P) = 12 Hz, *o*-Ph), 131.1 (partially obscured d, ^1J(C,P) = 50–56 Hz, *i*-Ph), 129.7 (s, *p*-Ph), 128.7 (d, ^3J(C,P) = 11 Hz, *m*-Ph), 114.6 (s, =CH_2), 99.4 (s, $C_5(CH_3)_5$), 34.0 (s, *C*H$_2$CH=), 31.3 (d, *J*(C,P) = 13 Hz, *C*H$_2$), 29.1 (d, *J*(C,P) = 9 Hz, *C*H$_2$), 28.8 (s, *C*H$_2$), 26.3 (s, *C*H$_2$), 23.2 (s, *C*H$_2$), 10.1 (s, $C_5(CH_3)_5$); ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$, 32 °C): $\delta = -6.9$ (s); IR (solid film): $\tilde{\nu} = 1637$ (NO) cm^{-1}; MS (FAB, 3-NBA): *m*/*z* (%): 717 (100) $[M]^+$; elemental analysis calcd (%) for $C_{32}H_{50}ClNOPRe$ (717.38): C 53.58, H 7.02, N 1.95; found: C 53.40, H 6.81, N 1.59.

$[(\eta^5\text{-}C_5Me_5)Re(NO)(P(Ph)(CH_2)_6CH{=}CH(CH_2)_6)(CO)]^+$ BF_4^- (16): A Schlenk flask was charged with **14** (0.150 g, 0.188 mmol), CH_2Cl_2 (150 mL) and **1** (0.0064 g, 0.0078 mmol, 4 mol%). The sample was stirred for 14 h, and filtered through a Celite plug (2 cm). Solvent was removed by oil pump vacuum to give **16** as a dark solid of >98% spectroscopic purity (0.142 g, 0.178 mmol, 94%; *Z*/*E* (tentative)[23] 44:56[55b,c]). Extensive attempts to obtain analytically pure samples were unsuccessful. M.p. 68 °C;[18] ^{1}H NMR (400 MHz, $CDCl_3$, 32 °C, TMS): $\delta = 7.56-7.45$ (m, 5H, Ph), 5.42–5.38/5.36–5.26 (2m, 2H, *E*/*Z* C*H*=C*H*, 56:44), 2.43 (m, 4H, 2PCH_2), 2.10 (m, 4H, 2CH_2CH=), 1.97/1.96 (2s, 15H, $C_5(CH_3)_5$), 1.50–1.21 (m, 16H, 8CH_2); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 32 °C, TMS): $\delta = 203.7$ (br s, Re*C*O) 137.3/137.0 (2s, *C*H=), 134.7–126.8 (PPh signals), 99.1/99.0 (2s, $C_5(CH_3)_5$), 36.0/35.4 (2s, *C*H$_2$CH=), 32.9–21.9 (*C*H$_2$ signals), 10.1/10.0 (2s, $C_5(CH_3)_5$); ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$, 32 °C): $\delta = -0.71/-0.85$ (2s, *Z*/*E*, 44:56); IR (solid film): $\tilde{\nu} = 1980$ (CO), 1718 (NO) cm^{-1}; MS (FAB, 3-NBA/CH_2Cl_2): *m*/*z* (%): 682 (100) $[M]^+$ of cation.

$[(\eta^5\text{-}C_5Me_5)Re(NO)(P(Ph)(CH_2)_6CH{=}CH(CH_2)_6)(Cl)]$ (17)

A: A Schlenk flask was charged with **15** (0.074 g, 0.105 mmol), **1** (0.0042 g, 0.0051 mmol, 5 mol%), and CH_2Cl_2 (150 mL). The sample was stirred for

12 h, concentrated by oil pump vacuum to ca. 5 mL, and filtered through a silica plug (3 cm). Solvent was removed by oil pump vacuum to give **17** as a dark red solid (0.065 g, 0.094 mmol, 89%).

B: Complex **16** (0.160 g, 0.208 mmol), THF (10 mL), $LiAlH_4$ (0.028 g, 0.735 mmol), CH_2Cl_2 (ca. 20 mL),[25] and aqueous HCl (12 N, 0.10 mL, 1.2 mmol) were combined in a procedure analogous to that given for **15**. An identical workup gave **17** as dark red solid (0.110 g, 0.160 mmol, 76%; *Z*/*E* (tentative, range for both syntheses)[23] 41–43:59–57[55b,c]). M.p. 165–172 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 32 °C, TMS): $\delta = 7.60-7.26$ (m, 5H, Ph), 5.34–5.30/5.29–5.21 (2m, 2H, *E*/*Z* C*H*=C*H*, 59:41), 2.65–2.10 (m, 4H, 2PCH_2), 2.05–1.81 (m, 4H, 2CH_2CH=), 1.56/1.55 (2s, 15H, $C_5(CH_3)_5$), 1.51–1.18 (m, 16H, 8CH_2); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 32 °C, TMS): $\delta = 131.3$ (2 overlapping d, *i*-Ph), 131.24/131.15 (*C*H=), 131.1 (d, ^2J(C,P) = 14 Hz, *o*-Ph), 129.6 (d, ^3J(C,P) = 16 Hz, *m*-Ph), 128.0 (s, *p*-Ph), 99.4 (s, $C_5(CH_3)_5$), 32.4/31.9 (2s, *C*H_2CH=), 29.7–24.0 (*CH*$_2$ signals), 9.9/9.8 (2s, $C_5(CH_3)_5$); ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$, 32 °C): $\delta = -8.42/-8.81$ (2s, *Z*/*E*, 43:57); IR (solid film): $\tilde{\nu} = 1637$ (NO) cm^{-1}; MS (FAB, 3-NBA/CH_2Cl_2): *m*/*z* (%): 689 (100) $[M]^+$; elemental analysis calcd (%) for $C_{30}H_{46}ClNOPRe$ (689.33): C 52.27, H 6.73, N 2.03; found: C 52.17, H 7.05, N 1.90.

[(η^5-C_5Me_5)Re(NO)(P(Ph)(CH$_2$)$_{14}$)(Cl)] (18): A Fischer–Porter bottle was charged with **17** (0.075 g, 0.108 mmol), freshly degassed ethanol/toluene (30 mL, 1:1 *v*/*v*), and $[Rh(PPh_3)_3(Cl)]$ (0.0074 g, 0.005 mmol, 7 mol%). The mixture was stirred under H_2 (60 psig, 36 h). Solvent was removed by oil pump vacuum, and CH_2Cl_2 (12 mL) was added. The sample was filtered through a silica plug (2 cm) and concentrated to about 1 mL. Hexane was added, and solvent was removed by oil pump vacuum to give **18** as a red powder (0.053 g, 0.077 mmol, 72%). M.p. 180–182 °C (DSC, 183.6 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 32 °C, TMS): $\delta = 7.61-7.24$ (m, 5H, Ph), 2.49–2.02 (m, 4H, 2PCH_2), 1.61 (s, 15H, $C_5(CH_3)_5$), 1.51–1.16 (m, 24H, 12CH_2); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 32 °C, TMS): $\delta = 134.2$ (d, ^2J(C,P) = 10 Hz, *o*-Ph), 131.2 (d, ^3J(C,P) = 23 Hz, *m*-Ph), 130.3 (m, *i*-Ph), 128.1 (s, *p*-Ph), 99.4 (s, $C_5(CH_3)_5$), 29.7–22.0 (unresolved and diastereotopic *C*H$_2$ signals), 9.9 (s, $C_5(CH_3)_5$); ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$, 32 °C): $\delta = -8.35$ (s); IR (solid film): $\tilde{\nu} = 1640$ (NO) cm^{-1}; MS (FAB, 3-NBA): *m*/*z* (%): 691 (100) $[M]^+$, 386 (90) $[M-(PPh(CH_2)_{14})]^+$; elemental analysis calcd (%) for $C_{30}H_{48}ClNOPRe$ (691.35): C 52.12, H 7.00, N 2.03; found: C 52.17, H 7.05, N 1.90.

***fac*-[(CO)$_3$Re(Br)(PPh$_2$(CH$_2$)$_6$CH=CH$_2$)$_2$] (21)**: A Schlenk flask was charged with **12** (0.750 g, 2.530 mmol), $CHCl_3$ (20 mL), and $[(CO)_5Re(Br)]$ (0.514 g, 1.266 mmol),[58] and fitted with a condenser. The mixture was heated under reflux (56 h; monitored by IR). Solvent was removed by rotary evaporation. Column chromatography (silica gel, 1:1 *v*/*v* CH_2Cl_2/hexane) gave a product band which was taken to dryness by rotary evaporation. The colorless oil solidified over the course of one week, and was dried by oil pump vacuum to give **21** as a white powder (0.863 g, 0.915 mmol, 72%). M.p. 101–102 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 7.44-7.34$ (m, 20H, 4Ph), 5.76 (m, 2H, 2C*H*=), 4.99–4.90 (m, 4H, 2=CH_2), 2.56 (m, 2H, 2PCH*H*′), 2.00–1.88 (m, 6H, 2CH_2CH=+2PC*H*H′), 1.59–0.89 (m, 16H, 8CH_2); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 20 °C): $\delta = 190.2$, 189.5 (2t, 1:2, ^2J(C,P) = 25 Hz, Re*C*O), 139.2 (*C*H=), 134–132 (complex, *i*-Ph), 133.3, 133.0 (2 virtual t, *J*(C,P) = 5 Hz,[59] *o*-Ph), 130.2 (s, *p*-Ph), 128.5 (m, *m*-Ph), 114.5 (s, =*C*H$_2$), 33.8 (s, *C*H$_2$CH=), 30.9 (virtual t, *J*(C,P) = 6 Hz, *C*H$_2$), 28.9 (s, *C*H$_2$), 28.7 (s, *C*H$_2$), 26.5 (virtual t, *J*(C,P) = 14 Hz, *C*H$_2$), 24.1 (br s, *C*H$_2$); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 20 °C): $\delta = -8.4$ (s); IR ($CDCl_3$/Nujol): $\tilde{\nu} = 2035/2029$, 1952/1948, 1906/1906 (CO) cm^{-1}; MS (FAB, 3-NBA/CH_2Cl_2): *m*/*z* (%): 942 (8) $[M]^+$, 914 (50) $[M-CO]^+$, 886 (28) $[M-2CO]^+$, 863 (100) $[M-Br]^+$, 835 (43) $[M-Br-CO]^+$; elemental analysis calcd (%) for $C_{43}H_{50}BrO_3P_2Re$ (942.92): C 54.77, 5.34; found: C 54.62, H 5.36.

***fac*-[(CO)$_3$Re(Br)(P(Ph)$_2$(CH$_2$)$_6$CH=CH(CH$_2$)$_6$P(Ph)$_2$)] (22)**: A Schlenk flask was charged with **21** (0.286 g, 0.303 mmol) and CH_2Cl_2 (110 mL). Another Schlenk flask was charged with **1** (0.005 g, 0.006 mmol; 2 mol%) and CH_2Cl_2 (10 mL). The latter solution was added by cannula to the former with stirring. The mixture was heated under reflux (3 h). Solvent was removed by rotary evaporation. Column chromatography (silica gel, CH_2Cl_2) gave a product band which was taken to dryness by rotary evaporation to give **22** as a white powder (0.221 g, 0.242 mmol, 80%; *Z*/*E* 17–20:83–80[54, 55a]). M.p. 184–185 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 7.62-7.23$ (m, 20H, 4Ph), 5.39 (m, 2H, C*H*=C*H*), 2.77 (m, 2H, 2PCH*H*′), 2.07 (m, 6H, 2PC*H*H′+2CH_2CH=), 1.56–1.18 (m, 16H, 8CH_2); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 20 °C, *E* isomer unless noted): $\delta = 190.0$, 189.3 (2t, 1:2, ^2J(C,P) = 28 Hz, Re*C*O), 131.1 (*C*H=*C*H), 134–133 (complex, *i*-Ph), 133.2, 132.8 (2 virtual t, *J*(C,P) = 5 Hz,[59] *o*-Ph), 130.1, 130.1 (2s, *p*-Ph), 128.7, 128.3 (2 virtual t, *J*(C,P) = 4 Hz, *m*-Ph), 32.3 (s, *C*H$_2$CH=(*E*)), 30.5 (virtual t, *J*(C,P) = 6 Hz, *C*H$_2$), 29.5 (s, *C*H$_2$CH=(*Z*)) 29.2 (s, *C*H$_2$, *Z* at 28.0), 28.7 (s, *C*H$_2$, *Z* at 27.0), 25.5 (virtual t, *J*(C,P) = 12 Hz, *C*H$_2$), 24.4 (br s, *C*H$_2$); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 20 °C): δ = -8.2 (s); IR ($CDCl_3$/Nujol): $\tilde{\nu} = 2033/2031$, 1950/1952, 1904/1900 (CO) cm^{-1}; MS (FAB, 3-NBA/CH_2Cl_2): *m*/*z* (%): 914 (17) $[M]^+$, 886 (70) $[M-CO]^+$, 858 (42) $[M-2CO]^+$, 835 (100) $[M-Br]^+$, 807 (25) $[M-Br-CO]^+$; elemental analysis calcd (%) for $C_{41}H_{46}BrO_3P_2Re$ (914.87): C 53.83, 5.07; found: C 53.81, H 5.10.

***fac*-[(CO)$_3$Re(Br)(P(Ph)$_2$(CH$_2$)$_{14}$P(Ph)$_2$)] (23)**: A Schlenk flask was charged with **22** (0.035 g, 0.038 mmol), 10% Pd/C (0.004 g, 0.004 mmol), and toluene/ethanol (20 mL, 1:1 *v*/*v*), flushed with H_2, and fitted with a balloon of H_2. The suspension was stirred overnight. Solvent was removed by oil pump vacuum. The residue was extracted with CH_2Cl_2. Column chromatography (silica gel, CH_2Cl_2) gave a product band which was taken to dryness by rotary evaporation to give **23** as a white powder (0.034 g, 0.037 mmol, 98%). M.p. 186–188 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 7.67-7.22$ (m, 20H, 4Ph), 2.87–2.83 (m, 2H, 2′), 2.13–2.06 (m, 2H, 2PC*H*H′), 1.38–1.19 (m, 24H, 12CH_2); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 20 °C): $\delta = 190.1$, 189.6 (2t, 1:2, ^2J(C,P) = 28.7, Re*C*O), 134–133 (complex, *i*-Ph), 133.3, 132.7 (2 virtual t, *J*(C,P) = 5 Hz,[59] *o*-Ph), 130.2, 130.1 (2s, *p*-Ph), 128.7, 128.3 (2 virtual t, *J*(C,P) = 5 Hz, *m*-Ph), 30.5 (virtual t, *J*(C,P) = 6 Hz, *C*H$_2$), 27.82 (s, *C*H$_2$), 27.79 (s, *C*H$_2$), 27.5 (s, *C*H$_2$), 26.8 (s, *C*H$_2$), 25.9 (virtual t, *J*(C,P) = 12 Hz, *C*H$_2$), 23.8 (br s, *C*H$_2$); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 20 °C): $\delta = -8.2$ (s); IR ($CDCl_3$/Nujol): $\tilde{\nu} = 2032/2036$, 1951/1958, 1904/1903 (CO) cm^{-1}; MS (FAB, 3-NBA/CH_2Cl_2): *m*/*z* (%): 916 (13) $[M]^+$, 888 (96) $[M-CO]^+$, 860 (79) $[M-2CO]^+$, 837 (100) $[M-Br]^+$, 809 (53) $[M-Br-CO]^+$; elemental analysis calcd (%) for $C_{41}H_{48}BrO_3P_2Re$ (916.88): C 53.71, 5.28; found: C 53.76, H 5.30.

***cis*-[(Cl)$_2$Pt(PPh$_2$(CH$_2$)$_6$CH=CH$_2$)$_2$] (24)**: A Schlenk flask was charged with $[(Cl)_2Pt(COD)]$ (0.160 g, 0.432 mmol)[60] and CH_2Cl_2 (10 mL). A solution of **12** (0.260 g, 0.877 mmol) in CH_2Cl_2 (5 mL) was added via cannula with stirring. After 5 h, the mixture was filtered through a Celite plug (3 cm). Solvent was removed by oil pump vacuum. The oily residue was washed with hexane (3 × 5 mL). Column chromatography (alumina, benzene) gave a product band which was taken to dryness by oil pump vacuum to give **24** as a white powder (0.257 g, 0.299 mmol, 70%). M.p. 98–100 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 7.51-7.22$ (m, 20H, 4Ph), 5.75 (m, 2H, 2C*H*=), 4.99–4.89 (m, 4H, 2=CH_2), 2.30–2.10 (m, 4H, 2PCH_2), 1.99–1.92 (m, 4H, 2CH_2CH=), 1.60–1.45 (m, 4H, 2PCH$_2$CH_2), 1.27–1.15 (m, 12H, 6CH_2); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 20 °C): $\delta = 139.1$ (*C*H=), 133.6 (virtual t, *J*(C,P) = 5 Hz, *o*-Ph), 131.0 (s, *p*-Ph), 129.8 (d, ^1J(C,P) = 64 Hz, *i*-Ph), 128.4 (virtual t, *J*(C,P) = 5 Hz, *m*-Ph), 114.5 (s, =*C*H$_2$), 33.8 (s, *C*H$_2$CH=), 30.8 (virtual t, *J*(C,P) = 8 Hz, *C*H$_2$), 28.8 (2s, 2*C*H$_2$), 28.6 (br s, *C*H$_2$), 25.2 (s, *C*H$_2$); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 20 °C): $\delta = 7.6$ (s, ^1J(P,Pt) = 3652 Hz);[61] MS (FAB, 3-NBA/CH_2Cl_2): *m*/*z* (%): 858 (2) $[M]^+$, 823 (100) $[M-Cl]^+$, 489 (80) $[M-2Cl-Ph_2P(CH_2)_6CH=CH_2]^+$; elemental analysis calcd (%) for $C_{40}H_{50}Cl_2P_2Pt$ (858.77): C 55.94, 5.87; found: C 55.77, H 5.82.

***cis*-[(Cl)$_2$Pt(P(Ph)$_2$(CH$_2$)$_6$CH=CH(CH$_2$)$_6$P(Ph)$_2$)] (25)**: A Schlenk flask was charged with **24** (0.257 g, 0.299 mmol) and CH_2Cl_2 (110 mL). Another Schlenk flask was charged with **1** (0.005 g, 0.006 mmol, 2 mol%) and CH_2Cl_2 (10 mL). The latter solution was added by cannula to the former with stirring. The mixture was heated under reflux (3 h), concentrated to about 3 mL, and purified by chromatography on a short silica gel column (CH_2Cl_2). Solvent was removed by oil pump vacuum to give **25** as a white powder (0.177 g, 0.213 mmol, 71%; *Z*/*E* < 2: > 98[54, 55a]). M.p. 246–248 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 7.44-7.20$ (m, 20H, 4Ph), 5.44 (m, 2H, C*H*=C*H*), 2.16–2.06 (m, 8H, 2PCH_2+2CH_2CH=), 2.03–1.92, 1.60–1.35 (2m, 16H, 8CH_2); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 20 °C): $\delta = 133.3$ (virtual t, *J*(C,P) = 5 Hz, *o*-Ph), 133.6–133.1 (complex, *i*-Ph), 131.5 (*C*H=*C*H), 130.9 (s, *p*-Ph), 128.3 (virtual t, *J*(C,P) = 5 Hz, *m*-Ph), 32.2 (s, *C*H$_2$CH=(*E*)), 30.6 (virtual t, *J*(C,P) = 9 Hz, *C*H$_2$), 29.3 (virtual t, *J*(C,P) = 10 Hz, *C*H$_2$), 29.1 (s, *C*H$_2$), 28.4 (s, *C*H$_2$), 27.3 (br s, *C*H$_2$); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 20 °C): $\delta = 7.9$ (s, 9%, ^1J(P,Pt) = 3631 Hz,[61] assigned to dimeric compound **26** as described in the text), 7.7 (s, 91%, ^1J(P,Pt) = 3627 Hz);[61] MS (FAB, 3-NBA/CH_2Cl_2): *m*/*z* (%): 1625 (46) $[M-Cl]^+$ for **26**, 795 (63) $[M-Cl]^+$ for **25**, 757 (100); osmometry ($CHCl_3$): calcd for **25**

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830.8; found 844; elemental analysis calcd (%) for $C_{38}H_{46}Cl_2P_2Pt$ (830.71): C 54.94, 5.58; found: C 54.91, H 5.57.

S(Et)(CH$_2$)$_6$CH=CH$_2$ (27): A flask was charged with NaOH (0.600 g, 15.0 mmol), water (ca. 4 mL, to give a solution), ethanol (15 mL), and HSEt (0.930 g, 15.0 mmol), fitted with a condenser, and cooled in an ice bath. A solution of **4** (2.850 g, 14.91 mmol) in ethanol (5 mL) was added with stirring over 20 min. The suspension was heated under reflux (4 h) and stirred at room temperature (12 h). Water (5 mL) and ether (15 mL) were added. The phases were separated, and the aqueous phase extracted with ether (2×10 mL). The combined organic phases were dried (Na_2SO_4). Solvent was removed by rotary evaporation and the residue vacuum distilled (48–51 °C) to give **27** as a colorless liquid (2.270 g, 13.17 mmol, 88 %). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 5.79$ (m, 1H, C*H*=), 4.92 (m, 2H, =CH_2), 2.51 (q, ^3J(H,H) = 7.5 Hz, 2H, SCH_2CH$_3$), 2.50 (t, ^3J(H,H) = 8.1 Hz, 2H, SCH_2CH$_2$), 2.02 (m, 2H, CH_2CH=), 1.57 (m, 2H, CH_2), 1.34 (m, 6H, 3CH_2), 1.23 (t, ^3J(H,H) = 7.5 Hz, 3H, CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 20 °C): $\delta = 138.9$ (s, *C*H=), 114.2 (s, =*C*H$_2$), 33.6 (s, *C*H$_2$CH=), 31.6 (s, SCH_2), 29.5 (s, SC′H$_2$), 28.7 (s, 2 × intensity, CH_2), 28.6 (s, CH_2), 25.8 (s, CH_2), 14.7 (s, CH_3); MS (80 eV, EI): *m*/*z* (%): 172 (25) $[M]^+$, 143 (100), $[M - CH_2CH_3]^+$; elemental analysis calcd (%) for $C_{10}H_{20}S$ (172.33): C 69.70, H 11.70; found: C 69.72, H 11.58.

S(*t*Bu)(CH$_2$)$_6$CH=CH$_2$ (28): A flask was charged with NaS-*t*Bu (0.920 g, 8.20 mmol) and DMF (20 mL) and cooled to 0 °C. A solution of **4** (1.110 g, 5.808 mmol) in DMF (5 mL) was added with stirring over 20 min. The mixture was heated to 100 °C (1 h) and cooled to room temperature. Water (15 mL) was added with stirring. The phases were separated, and the aqueous phase extracted with ether (3×15 mL). The combined organic phases were washed with water (5×10 mL) and dried (Na_2SO_4). Solvent was removed by rotary evaporator and the oil vacuum distilled (79–82 °C) to give **28** as a colorless liquid (0.812 g, 4.05 mmol, 70 %). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 5.78$ (m, 1H, C*H*=), 4.94 (m, 2H, =CH_2), 2.49 (t, ^3J(H,H) = 7.5 Hz, 2H, SCH_2), 2.02 (m, 2H, CH_2CH=), 1.53 (m, 2H, CH_2), 1.37 (m, 6H, 3CH_2), 1.30 (s, 9H, C(CH_3)$_3$); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 20 °C): $\delta = 139.0$ (s, *C*H=), 114.2 (s, =*C*H$_2$), 41.8 (s, *C*(CH$_3$)$_3$), 33.7 (s, *C*H$_2$CH=), 31.0 (s, C(*C*H$_3$)$_3$), 29.8 (s, *C*H$_2$), 29.1 (s, *C*H$_2$), 28.8 (s, 2 × intensity, *C*H$_2$), 28.3 (s, *C*H$_2$); MS (80 eV, EI): *m*/*z* (%): 200 (11) $[M]^+$, 185 (19) $[M - CH_3]^+$, 143 (47) $[M - C(CH_3)_3]^+$, 57 (100) $[C(CH_3)_3]^+$; elemental analysis calcd for $C_{12}H_{24}S$ (200.38): C 71.93, H 12.07; found: C 71.94, H 12.24.

***cis*-[(Cl)$_2$Pt(S(Et)(CH$_2$)$_6$CH=CH$_2$)$_2$] (29)**:[31] A flask was charged with **27** (0.364 g, 2.11 mmol), methanol (3 mL), and a solution of $K_2[PtCl_4]$ (0.385 g, 0.928 mmol) in water (5 mL). The mixture was stirred (14 h), and a yellow-brown oil separated. Solvent was removed by rotary evaporation. The residue was washed with ethanol (2×5 mL), dried by oil pump vacuum, dissolved in CH_2Cl_2 (2 mL), and added to a small amount of silica. Solvent was removed by oil pump vacuum, and the yellow powder added to the top of a dry silica column. The column was rinsed with hexane and hexane/THF (gradient ending at 60:40 *v*/*v*). A yellow band was dried by oil pump vacuum to give **29** as a yellow oil (0.479 g, 0.784 mmol, 84 %). ^{1}H NMR (300 MHz, $CDCl_3$, 30 °C): $\delta = 5.76$ (m, 2H, 2C*H*=), 4.97 (m, 4H, 2=CH_2), 3.24/3.10–2.40 (2m, 2H + 6H, 2SC*HH*′R + 2SC*HH*′R′), 2.02 (m, 4H, 2CH_2CH=), 1.83 (m, 4H, 2SCH$_2$CH_2), 1.55–1.33 (m, 18H, 6CH_2 + 2CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 20 °C, *syn*/*anti* isomers): $\delta = 138.9/138.7$ (2s, *C*H=), 114.5/114.4 (2s, =*C*H$_2$), 37.6 (br s, SCH_2), 35.7 (br s, SC′H$_2$), 33.61/33.57 (2s, *C*H$_2$CH=), 30.6 (s, 2 × intensity, *C*H$_2$), 28.6/28.5 (2s, 1 and 2 × intensity, *C*H$_2$), 27.6/27.5 (2s, *C*H$_2$), 12.76/12.72 (2s, *C*H$_3$); MS (FAB, glycerol/2-NPOE/CH_2Cl_2): *m*/*z* (%): 611 (6) $[M+H]^+$, 575 (12) $[M - Cl]^+$, 353 (36) $[M - 2Cl - RSR']^+$; elemental analysis calcd (%) for $C_{20}H_{40}Cl_2S_2Pt$ (610.65): C 39.34, H 6.60; found: C 39.60, H 6.61.

***cis*-[(Cl)$_2$Pt(S(*t*Bu)(CH$_2$)$_6$CH=CH$_2$)$_2$] (30)**:[31] A flask was charged with **28** (0.462 g, 2.31 mmol), methanol (8 mL), and a solution of $K_2[PtCl_4]$ (0.326 g, 0.793 mmol) in water (10 mL). The mixture was stirred (48 h) and then centrifuged. The supernatant was removed from a yellow oily precipitate by pipette. Column chromatography (silica gel, twice: first 3:1 *v*/*v* hexane/THF; second 1:1 *v*/*v* hexane/CH_2Cl_2) gave a yellow band which was dried by oil pump vacuum to give **30** as a yellow waxy solid (0.261 g, 0.392 mmol, 50 %). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 5.76$ (m, 2H, 2C*H*=), 4.94 (m, 4H, 2=CH_2), 3.39 (br m, 2H, 2SC*H*H′), 2.18 (br m, 2H, 2SCH*H*′), 2.02 (m, 4H, 2CH_2CH=), 1.96–1.61 (br m, 4H, 2SCH$_2$CH_2), 1.54 (s, 18H, 2C(CH_3)$_3$), 1.51–1.29 (m, 12H, 6CH_2); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 20 °C): $\delta = 138.9$ (s, *C*H=), 114.3 (s, =*C*H$_2$), 51.5 (s, *C*(CH$_3$)$_3$), 33.7 (s, *C*H$_2$CH=), 30.0 (s, C(*C*H$_3$)$_3$), 29.6 (s, SC*H*$_2$), 28.7 (s, 2 × intensity, *C*H$_2$), 28.6 (s, *C*H$_2$), 27.2 (s, *C*H$_2$); MS (FAB, 3-NBA/CH_2Cl_2): *m*/*z* (%): 666 (12) $[M]^+$, 631 (22) $[M - Cl]^+$, 394 (50) $[M - 2Cl - RSR']^+$, 394 (93) $[M - 2Cl - RSR' - C(CH_3)_3]^+$, 57 (100) $[C(CH_3)_3]^+$; elemental analysis calcd (%) for $C_{24}H_{48}Cl_2S_2Pt$ (666.76): C 43.23, H 7.26; found: C 43.21, H 7.32.

***cis*-[(Cl)$_2$Pt(S(Et)(CH$_2$)$_6$CH=CH(CH$_2$)$_6$S(Et))] (31)**:[31] A Schlenk flask was charged with **29** (0.200 g, 0.327 mmol) and CH_2Cl_2 (200 mL) and fitted with a condenser. The solution was heated under reflux, and a solution of **1** (0.006 g, 0.007 mmol, 2 mol %) in CH_2Cl_2 (200 mL) was added. After 2 h, the sample was concentrated to 5 mL and filtered through a silica plug (3 cm). A small amount of silica was added to the filtrate. Solvent was removed by oil pump vacuum and the yellow powder added to the top of a dry silica column. The column was rinsed with hexane/THF (gradient: start, 90:10 *v*/*v*; end, 60:40 *v*/*v*). Two yellow bands were collected and dried by oil pump vacuum, giving **31** (faster moving; 0.104 g, 0.179 mmol, 55 %; *Z*/*E* 21:79[54, 55a]) and **32** (0.045 g, 0.039 mmol, 24 %)[18] as yellow gums.

Data for **31**: ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 5.34$ (m, 2H, C*H*=C*H*), 3.24 (m, 2H, 2SC*H*H′), 3.05–2.40 (br m, 6H, remaining SC*HH*′), 1.94 (m, 4H, 2CH_2CH=), 1.82 (m, 4H, 2SCH$_2$CH_2), 1.55–1.33 (m, 18H, 6CH_2+2CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 20 °C, *syn*/*anti* isomers not assigned): $\delta = 130.4$, 130.2, 130.1 (3s, *C*H=*C*H), 37.5, 35.7 (2s, SCH_2), 32.1 (s, *C*H$_2$CH=(*E*)), 30.6, 30.2 (2s, *C*H$_2$), 29.3 (s, *C*H$_2$CH=(*Z*, tentative)), 28.6, 28.5 (2s, *C*H$_2$), 27.5, 27.1 (2s, *C*H$_2$), 12.7 (s, *C*H$_3$); MS (FAB, 3-NBA/CH_2Cl_2): *m*/*z* (%): 582 (13) $[M]^+$, 547 (19) $[M - Cl]^+$, 509 (18) $[M - 2Cl]^+$, 480 (14) $[M - 2Cl - CH_2CH_3]^+$, 447 (22) $[M - 2Cl - SCH_2CH_3]^+$; elemental analysis calcd (%) for $C_{18}H_{36}Cl_2S_2Pt$ (582.52): C 37.11, H 6.23; found: C 37.41, H 6.28.

Data for **32**: ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 5.29$ (m, 4H, 2C*H*=C*H*), 3.21 (m, 4H, 2SC*H*H′), 3.05–2.40 (br m, 12H, remaining SC*HH*′), 1.95 (m, 8H, 4CH_2CH=), 1.83 (m, 8H, 4SCH$_2$CH_2), 1.66–1.33 (m, 36H, 12CH_2+4CH_3); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 20 °C, *syn*/*anti* isomers present but unassigned): $\delta = 130.3$, 130.2, 130.0, 129.8, 129.7, 129.5 (6s, *C*H=*C*H), 37.5, 35.7, 34.1 (3s, SCH_2), 32.4, 32.1 (2s, *C*H$_2$CH=(*E*)), 30.6, 30.2 (2s, *C*H$_2$), 29.4, 29.3 (2s, *C*H$_2$CH=(*Z*, tentative)), 28.6 (s, 2 × intensity, *C*H$_2$), 28.5, 27.6, 27.5, 27.0 (4s, *C*H$_2$), 12.8 (s, 2 × intensity, *C*H$_3$); MS (FAB, 3-NBA/CH_2Cl_2): *m*/*z* (%): 1128 (10) $[M - Cl]^+$.

***cis*-[(Cl)$_2$Pt(S(*t*Bu)(CH$_2$)$_6$CH=CH(CH$_2$)$_6$S(*t*Bu))] (33)**:[31] A Schlenk flask was charged with **30** (0.154 g, 0.231 mmol) and CH_2Cl_2 (200 mL) and fitted with a condenser. The solution was heated under reflux, and a solution of **1** (0.005 g, 0.006 mmol, 2 mol %) in CH_2Cl_2 (5 mL) was added. After 2 h, the sample was concentrated to 3 mL and filtered through a silica plug (3 mL). Column chromatography (silica gel, CH_2Cl_2) gave a yellow band which was dried by oil pump vacuum to give **33** as a yellow gum (0.106 g, 0.166 mmol, 72 %; *Z*/*E* 16:84[54, 55a]).[18] ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 5.30$ (m, 2H, C*H*=C*H*), 3.38 (br m, 2H, 2SC*H*H′), 2.05–1.98 (m, 6H, 2SCH*H*′+2CH_2CH=), 1.54 (s, 18H, 2C(CH_3)$_3$), 1.32 (m, 16H, 8CH_2); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C): $\delta = 130.3$ (s, *C*H=*C*H), 51.5 (s, *C*(CH$_3$)$_3$), 32.5 (s, *C*H$_2$CH=(*E*)), 30.3 (s, SCH_2), 30.1 (s, C(*C*H$_3$)$_3$), 29.6 (s, *C*H$_2$CH=(*Z*, tentative)), 29.4 (s, *C*H$_2$), 28.8 (s, *C*H$_2$), 28.7 (s, *C*H$_2$), 27.3 (s, *C*H$_2$); MS (80 eV, EI): *m*/*z* (%): 638 (3) $[M]^+$, 508 (4) $[M - 2Cl - C(CH_3)_3]^+$, 452 (5) $[M - 2Cl - 2C(CH_3)_3]^+$, 420 (3) $[M - 2Cl - SC(CH_3)_3 - C(CH_3)_3]^+$, 315 (14) $[M - PtCl_2 - C(CH_3)_3]^+$, 259 (38) $[M - PtCl_2 - 2C(CH_3)_3]^+$, 57 (100) $[C(CH_3)_3]^+$.

***trans*-[(Cl)(CO)Rh(PPh$_2$(CH$_2$)$_6$CH=CH$_2$)$_2$] (34)**: A Schlenk tube was charged with **12** (1.000 g, 3.37 mmol), CH_2Cl_2 (13 mL), hexane (13 mL), and $[Rh(\mu\text{-}Cl)(COD)]_2$ (0.415 g, 0.842 mmol).[62] Then CO was bubbled through the deep orange solution (50 min; volatilized solvent periodically replaced; color change to deep yellow). Solvent was removed by oil pump vacuum. Column chromatography (silica gel, 7 × 2.5 cm, CH_2Cl_2) gave a yellow band which was dried by rotary evaporation. Pentane (4 mL) was added, and the sample kept at −24 °C. After 2 d, a yellow powder was collected by filtration and dried by oil pump vacuum to give **34** (1.008 g, 1.33 mmol, 79 %). M.p. 64–66 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 32 °C, TMS): $\delta = 7.73–7.68$ (m, 8H of 4Ph), 7.38–7.34 (m, 12H of 4Ph), 5.82–5.72 (m, 2H, 2C*H*=), 4.98–4.89 (m, 4H, 2=CH_2), 2.55–2.51 (m, 4H, 2PCH_2), 2.02–1.96 (m, 4H, 2CH_2CH=), 1.62–1.58 (m, 4H, 2PCH$_2$CH_2), 1.43–1.25 (m, 12H, 6CH_2); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 32 °C, TMS): $\delta = 187.8$ (dt, ^1J(C,Rh) = 80, ^2J(C,P) = 15 Hz, *C*O), 139.1 (s, *C*H=), 134.0 (virtual t, J(C,P) = 21 Hz,[59] *i*-Ph), 133.4 (virtual t, J(C,P) = 6 Hz, *o*-Ph), 129.8 (s, *p*-Ph), 128.2 (virtual t, J(C,P) = 6 Hz, *m*-Ph), 114.2 (s, =CH_2), 33.7 (s,

-CH_2CH=), 31.1 (virtual t, J(C,P) = 6 Hz, CH_2), 28.73 (s, CH_2), 28.69 (s, CH_2), 27.2 (virtual t, J(C,P) = 14 Hz, CH_2), 24.9 (s, CH_2); $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$, 32 °C): δ = 25.1 (d, ^1J(P,Rh) = 125.1 Hz) and (161 MHz, [D$_6$]DMSO, 32 °C): δ = 25.9 (d, ^1J(P,Rh) = 122.9 Hz) and (161 MHz, C_6H_5Cl, 32 °C) 22.3 (d, ^1J(P,Rh) = 125.0 Hz); IR ($CDCl_3$): $\tilde{\nu}$ = 1970 (CO) cm^{-1}; MS (FAB, 3-NBA): m/z (%): 760 (3) $[M+H]^+$, 730 (85) $[M-CO]^+$, 723 (30) $[M-Cl]^+$, 695 (42) $[M-CO-Cl]^+$, 397 (90) $[Rh(Ph_2P(CH_2)_6CH{=}CH_2)]^+$, 297 (100) $[Ph_2P(CH_2)_6CH{=}CH_2]^+$; elemental analysis calcd (%) for $C_{41}H_{50}ClOP_2Rh$ (759.1): C 64.87, H 6.64; found: C 64.74, H 6.34.

***trans*-[(Cl)(CO)Rh(P(Ph)$_2$(CH$_2$)$_6$CH=CH(CH$_2$)$_6$P(Ph)$_2$)] (35)**: A Schlenk flask was charged with **34** (0.080 g, 0.105 mmol), CH_2Cl_2 (39 mL) and **1** (ca. half of 0.0043 g, 0.0052 mmol, 5 mol %), and fitted with a condenser. The solution was heated under reflux. After 2 h, the remaining **1** was added. After 2 h, solvent was removed by rotary evaporation. Column chromatography (silica gel, 14 × 2.5 cm, 3:1 v/v CH_2Cl_2/hexane) gave a yellow band which was dried by oil pump vacuum to give **35** as a yellow powder (0.064 g, 0.088 mmol, 83 %; Z/E 17:83[54, 55b]). M.p. 145 – 146 °C (decomp); ^1H NMR (400 MHz, $CDCl_3$, 32 °C, TMS): δ = 7.81 – 7.76 (m, 8H of 4Ph), 7.37 – 7.24 (m, 12H of 4Ph), 5.38 – 5.35/5.34 – 5.30 (2m, 2H, Z/E CH=CH, 17:83),[55b] 2.56 – 2.53 (m, 4H, 2PCH_2), 2.01 (m, 4H, 2CH_2CH=), 1.90 (m, 4H, 2PCH$_2$CH_2), 1.42 – 1.23 (m, 12H, 6CH_2) and ([D$_6$]benzene, analogous conditions/assignments) 7.90 – 7.86 (m, 8H), 7.13 – 7.07 (m, 12H), 5.59 – 5.54/5.54 – 5.50 (2m, 2H, Z/E 11:89), 2.76 – 2.71 (m, 4H), 2.20 – 2.15 (m, 8H), 1.48 – 1.32 (m, 12H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 32 °C, TMS): δ = 187.6 (d, ^1J(C,Rh) = 73 Hz, CO), 134.6 (virtual t, J(C,P) = 21 Hz,[59] i-Ph), 133.2 (virtual t, J(C,P) = 7 Hz, o-Ph), 131.0 (s, $CH{=}CH$), 129.8 (s, p-Ph), 128.2 (virtual t, J(C,P) = 5 Hz, m-Ph), 31.9 (s, $CH_2CH{=}(E)$), 31.6 (virtual t, J(C,P) = 7 Hz, CH_2), 29.2 (s, $CH_2CH{=}(Z)$), 28.9 (s, CH_2), 28.5 (s, CH_2), 27.8 (virtual t, J(C,P) = 15 Hz, CH_2), 26.7 (s, CH_2); $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$, 32 °C): δ = 26.3/25.5[64] (2d, ^1J(P,Rh) = 125.0/125.0 Hz, 16:84); IR (solid film): $\tilde{\nu}$ = 1961 (CO) cm^{-1}; MS (FAB, 3-NBA): m/z (%): 731 (4) $[M]^+$, 702 (50) $[M-CO]^+$, 695 (40) $[M-Cl]^+$, 665 (30) $[M-CO-Cl]^+$, 565 (4) $[Ph_2P(CH_2)_6CH{=}CH(CH_2)_6PPh_2]^+$; elemental analysis calcd (%) for $C_{39}H_{46}ClOP_2Rh$ (731.1): C 64.07, H 6.34; found: C 64.33, H 6.51.

***trans*-[(Cl)(CO)Rh(P(Ph)$_2$(CH$_2$)$_{14}$P(Ph)$_2$)] (36)**: A Fischer – Porter bottle was charged with **35** (0.144 g, 0.156 mmol), $[Rh(PPh_3)_3(Cl)]$ (0.021 g, 0.0023 mmol, 14 mol %), and toluene (23 mL), and flushed several times with H_2. The mixture was stirred under H_2 (75 psig, 20 h). Solvent was removed by oil pump vacuum. Column chromatography (silica gel, 8 × 2.5 cm, 3:1 v/v CH_2Cl_2/hexane) gave a yellow band which was dried by oil pump vacuum to give **36** as a yellow powder (0.063 g, 0.086 mmol, 55 %). In some cases, an oil was obtained which solidified when stored in a refrigerator. If spectra showed small amounts of **35**, the hydrogenation was repeated (10 % Pd/C in toluene/ethanol gave comparable results). ^1H NMR (400 MHz, [D$_6$]benzene, 32 °C, TMS): δ = 7.83 – 7.75 (m, 8H of 4Ph), 7.14 – 6.96 (m, 12H of 4Ph), 2.66 – 2.63 (m, 4H, 2PCH_2), 1.97 (m, 4H, 2PCH$_2$CH_2), 1.70 – 1.22 (m, 20H, 10CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 32 °C, TMS): δ = 134.4 (virtual t, J(C,P) = 20 Hz,[59] i-Ph), 133.1 (virtual t, J(C,P) = 6 Hz, o-Ph), 129.8 (s, p-Ph), 128.2 (virtual t, J(C,P) = 5 Hz, m-Ph), 30.7 (virtual t, J(C,P) = 7 Hz, CH_2), 29.7 (s, CH_2), 27.8 (s, CH_2), 27.6 (s, CH_2), 27.2 (s, CH_2), 26.8 (s, CH_2), 25.1 (s, CH_2); $^{31}P\{^1H\}$ NMR (161 MHz, [D$_6$]benzene, 32 °C): δ = 26.22/26.19[64] (2d, ^1J(P,Rh) = 125.5/124.9 Hz); IR (solid film): $\tilde{\nu}$ = 1968 (CO) cm^{-1}; MS (FAB, 3-NBA): m/z (%): 734 (10) $[M+H]^+$, 704 (40) $[M-CO]^+$, 697 (35) $[M-Cl]^+$, 665 (50) $[M-CO-Cl]^+$, 567 (100) $[Ph_2P(CH_2)_{14}PPh_2]^+$; elemental analysis calcd (%) for $C_{39}H_{48}ClOP_2Rh$ (733.1): C 63.90, H 6.60; found: C 63.80/63.69, H 7.00/6.23 (same sample).

***trans*-[(Cl)(C$_6$F$_5$)Pt(PPh$_2$(CH$_2$)$_6$CH=CH$_2$)$_2$] (37)**: A Schlenk flask was charged with $[Pt(\mu\text{-}Cl)(C_6F_5)(SR_2)]_2$ (0.478 g, 0.493 mmol; SR_2 = tetrahydrothiophene),[34] **12** (0.720 g, 2.43 mmol) and CH_2Cl_2 (30 mL). The mixture was stirred (16 h) and filtered through a Celite plug (1 cm) and a decolorizing charcoal plug (2 cm). Solvent was removed by oil pump vacuum to yield **37** as a colorless oil (0.769 g, 0.776 mmol, 79 %) which was spectroscopically pure and used for further chemistry. For the analytical sample, the Celite/carbon filtrations were replaced by column chromatography (alumina, 10 × 2.5 cm, CH_2Cl_2; 71 % yield). ^1H NMR (400 MHz, $CDCl_3$, 32 °C, TMS): δ = 7.50 – 7.46 (m, 8H of 4Ph), 7.32 – 7.22 (m, 12H of 4Ph), 5.84 – 5.74 (m, 2H, 2CH=), 5.01 – 4.90 (m, 4H, 2=CH_2), 2.60 – 2.54 (m, 4H, 2PCH_2), 2.05 – 2.00 (m, 4H, 2CH_2CH=), 1.97 – 1.85 (m, 4H, 2PCH$_2$CH_2), 1.44 – 1.30 (m, 12H, 6CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 32 °C, TMS)[63] δ = 138.9 (s, CH=), 133.0 (virtual t, J(C,P) = 6 Hz,[59] o-Ph), 130.8 (virtual t, J(C,P) = 28 Hz, i-Ph) 130.2 (s, p-Ph) 128.0 (virtual t, J(C,P) = 6 Hz, m-Ph), 114.3 (s, $=CH_2$), 33.7 (s, CH_2CH=), 31.3 (virtual t, J(C,P) = 7 Hz, CH_2), 28.8 (s, 2 × intensity, CH_2), 26.0 (virtual t, J(C,P) = 17 Hz, CH_2), 25.6 (s, CH_2); $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$, 32 °C): δ = 16.6 (s, ^1J(P,Pt) = 2659 Hz);[61] IR (neat oil): $\tilde{\nu}$ = 3080, 2930, 2856, 1502, 1463, 1436, 1104, 1061, 1000, 953, 911, 803, 741, 690 cm^{-1}; MS (FAB, 3-NBA): m/z (%): 989 (3) $[M]^+$, 954 (30) $[M-Cl]^+$, 785 (20) $[M-Cl-C_6F_5]^+$, 489 (80) $[Pt(Ph_2P(CH_2)_6CH{=}CH_2)]^+$, 297 (100) $[Ph_2P(CH_2)_6CH{=}CH_2]^+$; elemental analysis calcd (%) for $C_{46}H_{50}ClF_5P_2Pt$ (990.4): C 55.79, H 5.09; found: C 55.87, H 5.17.

***trans*-[(Cl)(C$_6$F$_5$)Pt(P(Ph)$_2$(CH$_2$)$_6$CH=CH(CH$_2$)$_6$P(Ph)$_2$)] (38)**: A two-necked flask was charged with CH_2Cl_2 (60 mL), **1** (ca. half of 0.008 g, 0.009 mmol, 7 mol %), and **37** (0.150 g, 0.151 mmol), and fitted with a condenser. The solution was heated under reflux. After 2 h the remaining **1** was added. After 3 h, solvent was removed by rotary evaporation. The residue was filtered through an alumina plug (5 cm) with CH_2Cl_2. Solvent was removed by oil pump vacuum to give **38** as a pale pink solid (0.131 g, 0.136 mmol, 90 %; Z/E 17:83[54, 55b]). M.p. 193 – 195 °C; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.46 – 7.40 (m, 8H of 4Ph), 7.30 – 7.26 (m, 12H of 4Ph), 5.38 – 5.27 (m, 2H, CH=CH), 2.66 – 2.59 (m, 4H, 2PCH_2), 2.25 (m, 4H, 2CH_2CH=), 2.05 (m, 4H, 2PCH$_2$CH_2), 1.48 – 1.42 (m, 12H, 6CH_2) and ([D$_6$]benzene, analogous conditions/assignments) 7.67 – 7.60 (m, 8H), 7.03 – 6.99 (m, 12H), 5.56 – 5.53/5.52 – 5.49 (2m, 2H, Z/E 17:83), 2.73 – 2.69 (m, 4H), 2.49 (m, 4H), 2.19 – 2.18 (m, 4H), 1.57 – 1.38 (m, 12H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 32 °C, TMS)[63] δ = 132.7 (virtual t, J(C,P) = 6 Hz,[59] o-Ph), 131.8 (virtual t, J(C,P) = 28 Hz, i-Ph), 131.1 (s, $CH{=}CH$), 130.1 (s, p-Ph), 128.0 (virtual t, J(C,P) = 6 Hz, m-Ph), 32.0 (s, $CH_2CH{=}(E)$), 31.9 (s, CH_2), 28.9 (s, CH_2), 28.6 (s, CH_2), 27.2 (s, CH_2), 26.8 (virtual t, J(C,P) = 17 Hz, CH_2); $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$, 32 °C): δ = 17.3/16.3[64] (2s, ^1J(P,Pt) = 2679/2685 Hz);[61] IR (solid film): $\tilde{\nu}$ = 3057, 2926, 2853, 1502, 1459, 1436, 1104, 1058, 957, 803, 737, 690 cm^{-1}; MS (FAB, 3-NBA): m/z (%): 961 (3) $[M]^+$, 926 (55) $[M-Cl]^+$, 757 (20) $[M-Cl-C_6F_5]^+$, 566 (35) $[Ph_2P(CH_2)_6CH{=}CH(CH_2)_6PPh_2]^+$; elemental analysis calcd (%) for $C_{44}H_{46}ClF_5P_2Pt$ (962.3): C 54.92, H 4.82; found: C 55.19, H 5.00.

***trans*-[(Cl)(C$_6$F$_5$)Pt(P(Ph)$_2$(CH$_2$)$_{14}$P(Ph)$_2$)] (39)**

A. A Schlenk flask was charged with **38** (0.100 g, 0.104 mmol), 10 % Pd/C (0.011 g, 0.010 mmol Pd), $ClCH_2CH_2Cl$ (6 mL), and ethanol (6 mL), flushed with H_2, and fitted with a balloon of H_2. The mixture was stirred for 72 h. Solvent was removed by rotary evaporation, and the residue filtered through an alumina plug (1.5 cm) with CH_2Cl_2. Solvent was removed by oil pump vacuum to give **39** as a white powder (0.094 g, 0.098 mmol, 94 %). M.p. 162 – 164 °C; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.47 – 7.42 (m, 8H of 4Ph), 7.31 – 7.27 (m, 12H of 4Ph), 2.67 – 2.61 (m, 4H, 2PCH_2), 2.13 – 2.10 (m, 4H, 2PCH$_2$CH_2), 1.50 – 1.23 (m, 20H, 10CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 32 °C, TMS)[63] δ = 132.8 (virtual t, J(C,P) = 6 Hz,[59] m-Ph), 131.4 (virtual t, J(C,P) = 28 Hz, i-Ph), 130.1 (s, p-Ph), 127.9 (virtual t, J(C,P) = 5 Hz, m-Ph), 31.0 (virtual t, J(C,P) = 7 Hz, CH_2), 27.7 (s, CH_2), 27.6 (s, CH_2), 27.2 (s, CH_2), 26.5 (s, CH_2), 26.2 (virtual t, J(C,P) = 17 Hz, CH_2), 25.7 (s, CH_2); $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$, 25 °C): δ = 17.1/16.7[64] (2s, ^1J(P,Pt) = 2670/2663 Hz);[61] IR (solid film): $\tilde{\nu}$ = 3057, 2926, 2856, 1502, 1459, 1436, 1104, 1061, 957, 803, 741, 691 cm^{-1}; MS (FAB, 3-NBA): m/z (%): 964 (14) $[M]^+$, 928 (100) $[M-Cl]^+$, 760 (50) $[M-Cl-C_6F_5]^+$, 565 (16) $[Ph_2P(CH_2)_{14}PPh_2]^+$; elemental analysis calcd (%) for $C_{44}H_{48}ClF_5P_2Pt$ (964.3): C 54.80, H 5.02; found: C 54.91, H 5.23.

B. Complex **38** (0.237 g, 0.246 mmol), 10 % Pd/C (0.026 g, 0.024 mmol Pd), $ClCH_2CH_2Cl$ (13 mL), ethanol (13 mL), and H_2 were combined as in procedure A. Column chromatography of the reaction residue (alumina, 11 × 2.5 cm, 1:1 v/v CH_2Cl_2/hexane) gave a product band which was dried by oil pump vacuum to give **39** as a white powder (0.185 mg, 0.191 mmol, 72 %). The ^1H NMR and mass spectra were identical with those above. The ^{31}P NMR spectrum showed only one signal. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$/[D$_6$]benzene 25/32 °C): δ = 17.0/17.1 (s, ^1J(P,Pt) = 2672/2673 Hz).[61]

***fac*-[(CO)$_3$W(PPh((CH$_2$)$_6$CH=CH$_2$)$_2$)$_3$] (41)**: A Schlenk flask was charged with $[(CO)_3W(NCCH_2CH_3)_3]$ (**40**; 0.310 g, 0.716 mmol),[37] **13** (0.727 g, 2.20 mmol), and CH_2Cl_2 (50 mL). The mixture was stirred (2 h). Solvent removed by oil pump vacuum. Column chromatography (silica gel, 5:1 v/v pentane/CH_2Cl_2) gave a yellow band which was dried by oil pump vacuum to give **41** as a yellow solid (0.642 g, 0.510 mmol, 71 %). M.p. 58 – 61 °C;

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Table 1. General crystallographic data.

	11 · CH_2Cl_2	**17**	(*E*)-**22**	**23**
formula	$C_{29}H_{29}F_3NO_4P_2ReS \cdot CH_2Cl_2$	$C_{30}H_{46}ClNOPRe$	$C_{41}H_{46}BrO_3P_2Re$	$C_{41}H_{48}BrO_3P_2Re$
M_W	877.66	689.33	914.83	916.84
diffractometer	Nonius MACH3	Kuma KM4	Nonius CAD-4	Nonius MACH3
T [K]	173(2)	120(2)	291(2)	173(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a [Å]	9.324(2)	12.113(5)	18.788(6)	18.692(4)
b [Å]	13.835(3)	19.950(6)	10.092(3)	10.078(2)
c [Å]	13.896(3)	13.158(6)	20.495(7)	20.105(4)
α [°]	65.30(3)	90	90	90
β [°]	86.26(3)	109.20(4)	96.83(3)	97.09(3)
γ [°]	85.47(3)	90	90	90
V [Å^3]	1622.5(6)	3002.8(21)	3859(2)	3758.3(13)
Z	2	4	4	4
ρ_{calcd} [Mg m^{-3}]	1.796	1.525	1.575	1.620
μ [mm^{-1}]	4.127	4.21	4.304	4.419
$F(000)$	864	1392	1824	1832
crystal size [mm^3]	0.30 × 0.30 × 0.30	0.2 × 0.2 × 0.2	0.40 × 0.31 × 0.22	0.20 × 0.15 × 0.05
θ limit [°]	2.65 to 24.97	2.04 to 25.00	2.00 to 25.00	2.26 to 24.97
index ranges (h, k, l)	−11 to 11; −16 to 16; −16 to 16	−14 to 1; 0 to 23; −15 to 15	0 to 22; 0 to 11; −24 to 24	0 to 22; −11 to 0; −23 to 23
reflections collected	11874	6212	6971	6801
independent reflections	5683	5285	6753	6587
reflections [$I > 2\sigma(I)$]	5299	3468	5094	4164
data/restraints/parameters	5683/0/513	5285/27/308	6753/1/434	6587/28/429
GOF on F^2	0.997	1.170	1.000	1.211
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0202$, $wR2 = 0.0485$	$R1 = 0.0754$, $wR2 = 0.0584$	$R1 = 0.0537$, $wR2 = 0.1389$	$R1 = 0.0501$, $wR2 = 0.1123$
R indices (all data)	$R1 = 0.0231$, $wR2 = 0.0497$	$R1 = 0.0248$, $wR2 = 0.0645$	$R1 = 0.0822$, $wR2 = 0.1486$	$R1 = 0.1167$, $wR2 = 0.1347$
Δp (max) [e Å^{-3}]	0.893	1.128	1.443	1.679

^{1}H NMR (400 MHz, [D$_6$]benzene, 32 °C): $\delta = 7.27$, 7.14, 6.52 (3m, 15H, 3Ph), 5.76 (m, 6H, 6C*H*=), 4.98 (m, 12H, 6=CH_2), 2.21 (m, 12H, 6CH_2CH=), 1.91 (m, 12H, 6PCH_2), 1.62–0.94 (m, 48H, 24CH_2); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 32 °C): $\delta = 212.2$ (d, ^2J(C,P) = 53 Hz, W(*C*O)$_3$), 140.7 (m, *i*-Ph), 139.1 (s, *C*H=), 130.4 (s, *p*-Ph), 128.3 (m, *o*-Ph), 127.9 (m, *m*-Ph), 114.2 (s, =*C*H$_2$), 33.7 (s, *C*H$_2$CH=), 31.0 (s, *C*H$_2$), 29.0 (br, tentative, *C*H$_2$), 28.8 (s, *C*H$_2$), 28.7 (s, *C*H$_2$), 23.5 (s, *C*H$_2$); ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$, 32 °C): $\delta = -7.6$ (s, ^1J(P,W) = 215 Hz);[61] IR (solid film): $\tilde{\nu} = 1915$, 1810 (CO) cm^{-1}; MS (FAB, 3-NBA/CH_2Cl_2): *m*/*z* (%): 1259 (10) [*M*]$^+$, 1231 (2) [*M* − CO]$^+$, 1120 (5) [*M* − CO − C_8H_{15}]$^+$, 926 (10) [*M* − PhP(CH$_2$)$_6$CH=CH$_2$)$_2$]$^+$, 332 (100) [PhP(CH$_2$)$_6$CH=CH$_2$)$_2$]$^+$; elemental analysis calcd (%) for $C_{69}H_{105}O_3P_3W$ (1259.36): C 65.81, H 8.40; found: C 65.81, H 8.60.

***fac*-[(CO)$_3$W{P(Ph)((CH$_2$)$_6$CH=)$_2$}$_3$]** (**42**; mixture of macrocycles **a**, **b**, **c** in Scheme 9): A Schlenk flask was charged with **41** (0.131 g, 0.104 mmol) and CH_2Cl_2 (250 mL), and fitted with a condenser. The solution was heated under reflux, and about half of a solution of **1** (0.008 g, 0.009 mmol, 9 mol% or 3 mol% per product C=C) in CH_2Cl_2 (4 mL) was added. After 2 h, the remaining **1** was added. After another 2 h, solvent was removed by rotary evaporation. The residue was filtered through a silica plug (2 cm) with CH_2Cl_2. The filtrate was concentrated to a yellow solid. Column chromatography (silica gel, 3:1 *v*/*v* pentane/CH_2Cl_2) gave a yellow band which was dried by oil pump vacuum to give **42** as a yellow powder (0.098 g, 0.083 mmol, 83%). M.p. 205 °C (decomp);[18] ^{1}H NMR (400 MHz, $CDCl_3$, 32 °C): $\delta = 7.3$–6.4 (m, 15H, 3Ph), 5.30 (m, 6H, 3C*H*=C*H*), 2.04 (m, 12H, 6CH_2CH=), 2.00–1.80 (m, 12H, 6PCH_2), 1.60–0.94 (m, 48H, 24CH_2); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 32 °C): $\delta = 131.2$–127.8 (Ph and *C*H= signals), 34.0–23.2 (*C*H$_2$ signals); ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$, 32 °C): $\delta = -3.0$ to −8.0 (m); IR (solid film): $\tilde{\nu} = 1922$, 1818 (CO) cm^{-1}; MS (FAB, 3-NBA/CH_2Cl_2): *m*/*z* (%): 1174 (100) [*M*]$^+$, 1146 (40) [*M* − CO]$^+$, 1118 (15) [*M* − 2CO]$^+$, 905 (10) [(P(Ph)(CH$_2$)$_6$CH=CH(CH$_2$)$_6$)$_3$]$^+$, 814 (10) [*M* − (P(Ph)(CH$_2$)$_6$CH=CH(CH$_2$)$_6$)$_2$ − 2CO]$^+$, 605 (10) [(P(Ph)(CH$_2$)$_6$CH=CH(CH$_2$)$_6$)$_2$]$^+$, 303 (25) [P(Ph)(CH$_2$)$_6$CH=CH(CH$_2$)$_6$]$^+$.

***fac*-[(CO)$_3$W{P(Ph)((CH$_2$)$_6$CH$_2$)$_2$}$_3$]** (**43**; mixture of macrocycles): A Fisher–Porter bottle was charged with **42** (0.110 g, 0.094 mmol), [Rh(PPh$_3$)$_3$(Cl)] (0.005 g, 0.005 mmol, 5 mol%), and toluene (10 mL). The mixture was stirred under H_2 (90 psig; 2 d), concentrated to 1 mL, and rinsed through a silica plug (2 cm) with CH_2Cl_2. The filtrate was dried by oil pump vacuum to give **43** as a yellow powder (0.104 g, 0.088 mmol, 94%). M.p. 159 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$, 32 °C): $\delta = 7.40$–6.35 (m, 15H, 3Ph), 2.02–1.79 (m, 12H, 6PCH_2), 1.50–1.00 (m, 72H, 36CH_2); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 32 °C): $\delta = 131.0$–128.1 (Ph signals), 34.0–23.2 (CH$_2$ signals); ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$, 32 °C): $\delta = -3.0$ to −8.0 (m); IR (solid film): $\tilde{\nu} = 1915$, 1816 (CO) cm^{-1}; MS (FAB, 3-NBA/CH_2Cl_2): *m*/*z* (%): 1180 (70) [*M*]$^+$, 1152 (20) [*M* − CO]$^+$, 1124 (10) [*M* − 2CO]$^+$; elemental analysis calcd (%) for $C_{63}H_{99}O_3P_3W$ (1181.22): C 64.06, H 8.45; found: C 63.99, H 8.48.

Crystallography: A CH_2Cl_2 solution of **11** was layered with hexane and kept at 4 °C. After 2 d, yellow prisms of **11** · (CH_2Cl_2) were collected by filtration. Red prisms of **17** were grown by slow evaporation of a CH_2Cl_2 solution (room temperature). One was polished with xylene to a spherical shape. Colorless prisms of (*E*)-**22** and (*E*)-**25** were obtained by slow evaporation of CH_2Cl_2/hexane solutions (days, room temperature). Colorless prisms of **23** were obtained by slow evaporation of a CH_2Cl_2/ethanol solution (weeks, room temperature). A toluene solution of **39** was layered with ethanol and kept at −20 °C. After two days, a colorless prism was removed. Colorless needles of **42a′** were grown by slow evaporation of a CH_2Cl_2 solution (room temperature). The sample was not homogeneous (powder and other crystal morphologies were present), and was recrystallized from CH_2Cl_2/hexane to give another heterogeneous sample, from which a colorless prism of **42a″** · (C_6H_{14})$_{0.5}$ was extracted.

Data were collected as summarized in Table 1. Cell parameters were determined and refined from 15 reflections for **11** · (CH_2Cl_2), **23**, and **25**, 73 reflections for **17**, 25 reflections for (*E*)-**22**, and 50 reflections for **42a′** and **42a″** · (C_6H_{14})$_{0.5}$. Cell parameters for **39** were obtained from 10 frames using a 10° scan and refined with 9668 reflections. Space groups were

Table 1 cont.

	(*E*)-**25**	**39**	**42a′**	**42a″**·$(C_6H_{14})_{0.5}$
formula	$C_{38}H_{46}Cl_2P_2Pt$	$C_{44}H_{48}ClP_2F_5Pt$	$C_{63}H_{93}O_3P_3W$	$C_{63}H_{93}O_3P_3W \cdot 0.5\,C_6H_{14}$
M_W	830.68	964.33	1175.13	1218.22
diffractometer	Nonius MACH3	Nonius KappaCCD	Kuma KM4	Kuma KM4
T [K]	173(2)	173(2)	95(2)	100(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
crystal system	triclinic	monoclinic	hexagonal	triclinic
space group	$P\bar{1}$	$C2/c$	$P\bar{3}$	$P\bar{1}$
a [Å]	10.105(2)	31.7963(7)	18.900(8)	10.659(4)
b [Å]	13.837(3)	10.7342(3)	18.900(8)	16.353(5)
c [Å]	14.100(3)	24.9213(6)	9.842(3)	20.183(7)
α [°]	71.32(3)	90	90	109.78(3)
β [°]	85.11(3)	102.2800(10)	90	97.90(3)
γ [°]	71.25(3)	90	120	103.00(3)
V [Å^3]	1768.1(6)	8311.2(4)	3045(2)	3136.9(19)
Z	2	8	2	2
ρ_{calcd} [Mg m^{-3}]	1.560	1.541	1.282	1.290
μ [mm^{-1}]	4.235	3.570	2.017	1.960
$F(000)$	832	3856	1228	1278
crystal size [mm^3]	0.30 × 0.30 × 0.20	0.2 × 0.2 × 0.1	0.20 × 0.15 × 0.05	0.15 × 0.06 × 0.04
θ limit [°]	2.44 to 24.97	1.31 to 27.50	2.99 to 26.99	3.32 to 27.50
index ranges (h, k, l)	−12 to 11; −16 to 15; −16 to 0	−41 to 41; −12 to −13; −32 to −32	−25 to 12; 0 to 25; 0 to 12	−11 to 13; −21 to 21; −23 to 23
reflections collected	6481	15944	14105	21612
independent reflections	6206	9273	3555	13477
reflections [$I > 2\sigma(I)$]	5423	4884	3224	6634
data/restraints/parameters	6206/0/388	9273/44/486	3555/0/211	13477/64/658
GOF on F^2	1.034	0.998	1.277	0.994
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0274$, $wR2 = 0.0656$	$R1 = 0.0435$, $wR2 = 0.0913$	$R1 = 0.1018$, $wR2 = 0.1576$	$R1 = 0.0833$, $wR2 = 0.0875$
R indices (all data)	$R1 = 0.0375$, $wR2 = 0.0705$	$R1 = 0.1207$, $wR2 = 0.1278$	$R1 = 0.1196$, $wR2 = 0.1647$	$R1 = 0.1695$, $wR2 = 0.1041$
Δp (max) [e Å^{-3}]	1.631	1.885	1.374	1.451

determined from systematic absences and subsequent least-squares refinements. Lorentz, polarization, and empirical absorption corrections were applied (**11**·(CH_2Cl_2), (*E*)-**22**, **23**, and (*E*)-**25**, ϕ scans; **17**, **42a′**, and **42a″**·$(C_6H_{14})_{0.5}$, numerical by use of SHELX-76[65]; **39**, other[66]).

The structures of **11**·(CH_2Cl_2), **23**, and (*E*)-**25** were solved by direct methods (SHELXS-86). The parameters were refined with all data by full-matrix-least-squares on F^2 (SHELXL-93).[67] Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed in idealized positions (riding model). Two atoms of **23** showed displacement disorder (C3/C3′ and C5/C5′), which could be solved and refined to a 87:13 occupancy ratio. The structure of **39** was similarly solved and refined (SHELXS-97, SHELXL-97).[68] Two atoms showed displacement disorder (C10/C10′ and C11/C11′), which could be solved and refined to a 55:45 occupancy ratio. The immediately adjacent atoms gave larger thermal ellipsoids, but two distinct positions could not be resolved.

The structures of **17**, **42a′**, and **42a″**·$(C_6H_{14})_{0.5}$ were solved by standard heavy atom techniques (SHELXS-97) and refined with SHELXL-97. Non-hydrogen atoms were refined with anisotropic thermal parameters, except the following which showed non-positive definition: C21−C27, C31−C37, C21A−C27A, and C31A−C37A of **17** (cocrystallizing *Z*/*E* isomers that refined to a 58:42 ratio); C(14A), C(15A), C(16A), C(17A), C(27A), C(26A), C(25A), C(24A), and C(23A) of **42a″**·$(C_6H_{14})_{0.5}$. The hydrogen atoms were fixed in idealized positions (riding model). The structure of (*E*)-**22** was similarly solved and refined (MOLEN VAX package[69] and SHELX-97).

Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from literature.[70]

All data (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre in association with earlier communications ((*E*)-**22**,[6a] **23**,[6a] (*E*)-**25**,[6a] **39**,[6b] **42a′**[6b]) or as supplementary publications CCDC-148294 (**11**·(CH_2Cl_2)), CCDC-148297 (**17**), and CCDC-148298 (**42a″**·$(C_6H_{14})_{0.5}$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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