ELSEVIER

Syntheses of gyroscope-like molecules via three-fold ring closing metatheses of bis(phosphine) complexes $trans$-$L_yM(P((CH_2)_nCH{=}CH_2)_3)_2$, and extensions to bis(phosphite) complexes $trans$-$Fe(CO)_3(P(O(CH_2)_nCH{=}CH_2)_3)_2$

Katrin Skopek [a], John A. Gladysz [a,b,*]

[a] *Institut für Organische Chemie and Interdisciplinary Center for Molecular Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestraße 42, 91054 Erlangen, Germany*
[b] *Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, TX 77842-3012, USA*

Abstract

The synthesis of trigonal bipyramidal, square planar, and octahedral bis(phosphine) complexes of the formula $trans$-$L_yM(P((CH_2)_nCH{=}CH_2)_3)_2$, and their conversion to gyroscope-like molecules $trans$-$L_yM(P((CH_2)_{2n+2})_3P)$ via three-fold intramolecular alkene metathesis/hydrogenation sequences, is reviewed. New data involving bis(phosphite) complexes are then described. Reactions of $P(NMe_2)_3$ and $HO(CH_2)_nCH{=}CH_2$ ($n =$ **a**, 3; **b**, 4; **c**, 5; **d**, 6; **e**, 8; **f**, 9) afford the ligands $P(O(CH_2)_nCH{=}CH_2)_3$ (**26a–f**, 79–96%). Reactions of **26a,b,e,f** and $Fe(BDA)(CO)_3$ (BDA = benzylideneacetone) give $trans$-$Fe(CO)_3(P(O(CH_2)_nCH{=}CH_2)_3)_2$ (**27a,b,e,f**) as yellow or green oils in 17–64% yields after workup. Two representative complexes (**27b,e**) are treated with Grubbs' catalyst (2×6.5 mol%). NMR analyses of the resulting crude $trans$-$Fe(CO)_3(P(O(CH_2)_nCH{=}CH(CH_2)_nO)_3P)$ (**28b,e**) suggest mixtures of Z/E isomers and perhaps oligomers. Subsequent $ClRh(PPh_3)_3$-catalyzed hydrogenations afford the title molecules $trans$-$Fe(CO)_3(P(O(CH_2)_{2n+2})_3P)$ (**29b,e**) as oils of 82–83% purity by ^{31}P NMR. Although various properties of **29b,e** can be compared to **27b,c**, they could not be induced to solidify or crystallize, hampering purification.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Alkene/olefin metathesis; Hydrogenation; Iron; Carbonyl complexes; Phosphite complexes; Gyroscope

1. Introduction

In 1998, our research group began fundamental studies of alkene metatheses in metal coordination spheres [1], a subject that we comprehensively reviewed a few years ago [2]. This paper, which is derived from a presentation given at a symposium entitled "Frontiers in Organometallic Chemistry" (234th American Chemical Society National Meeting, August, 2007), is based upon the portion of this work leading to gyroscope-like molecules [3–5]. In the first sections, syntheses and reactions of diphosphine-based complexes are reviewed. In later sections, new data involving diphosphite-based species are presented.

In the initial stages of our efforts, we were interested in developing routes to complexes that can be regarded as "insulated molecular wires" [6]. As exemplified by **2** in Scheme 1, these feature sp carbon or polyynediyl chains suspended between platinum endgroups, which are in turn encased by double helices derived from the sp³ carbon chains of termini-spanning α,ω-diphosphines [7]. A speculative approach employing ring closing alkene metathesis

* Corresponding author. Address: Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, TX 77842-3012, USA. Tel.: +979 845 1399; fax: +979 845 5629.
*E-mail address:* gladysz@mail.chem.tamu.edu (J.A. Gladysz).
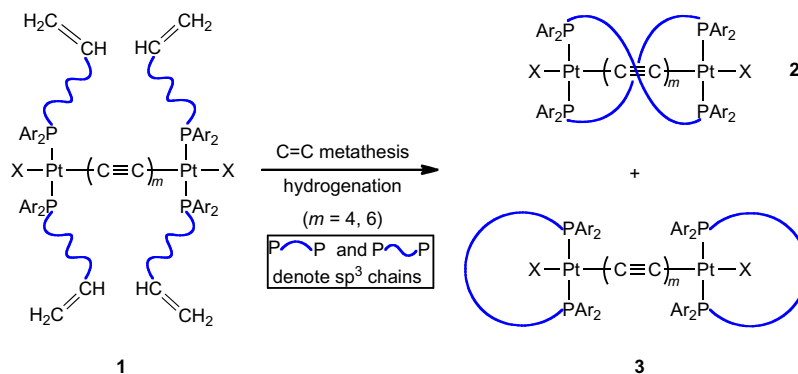
Scheme 1. Limiting modes for ring closing metathesis of **1**.

of precursors of the type **1**, followed by hydrogenation, was considered [7b,7c]. However, as shown in Scheme 1, an alternative cyclization mode is possible. This would afford **3**, with two *trans*-spanning diphosphine ligands. We sought to investigate the feasibility of the latter with model compounds.

The complexes **4b–f**, shown in Scheme 2 (top), contain *trans* monophosphine ligands bearing a single $(CH_2)_nCH=CH_2$ substituent. These were treated with Grubbs' catalyst at only moderate dilution. Subsequent hydrogenations afforded 13–23-membered macrocycles (**5b–f**) in 43–82% overall yields [8]. Thus, such ring closing metatheses are exceedingly general; no upper bound on the ring size is yet apparent. Interestingly, when substrates of the type **1** (Scheme 1) are similarly reacted, products of the type **2** almost always dominate [7b,7c].

We then prepared similar complexes **6b–e** in which each monophosphine ligand contains two $(CH_2)_nCH=CH_2$ substituents [9]. As shown in Scheme 2 (bottom), these can undergo either *inter*ligand metathesis to give **7b–e**, or *intra*-ligand metathesis to give **8b–e**. Surprisingly, only the former reaction mode is observed. In the case of **8d**, an authentic sample was synthesized, but none could be detected by ^{31}P NMR in the crude product. We have no explanation at present for this selectivity, or the preference for **2** in Scheme 1. However, we doubt that all possible metathesis products are thermodynamically sampled under the reaction conditions. Hence, catalysts that promote additional turnovers may afford different selectivities. As shown for **7b** in Scheme 2, Grubbs' second generation (H_2IMes) catalyst often gives improved yields of thirteen-membered macrocycles.

In any event, the yields of the dimacrocyclic diphosphine complexes **7b–e** are lower than those of the monomacrocyclic diphosphine complexes **5b–f**. Higher dilutions are necessary, and mass spectra suggest the presence of diplatinum byproducts. Despite this inauspicious trend, we wondered whether it might be possible to realize detectable quantities of three-fold intramolecular metathesis products from similar substrates in which the monophosphine ligands contain three $(CH_2)_nCH=CH_2$ substituents. Under the chromatographic conditions employed, such species would elute first.
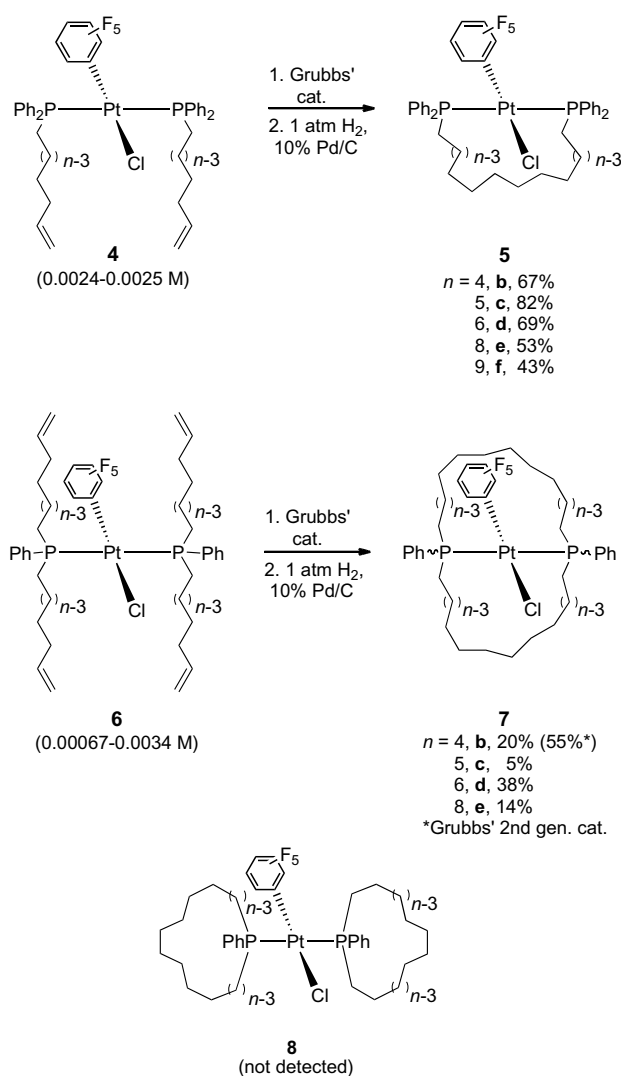
Scheme 2. Metathesis/hydrogenation sequences with pentafluorophenyl platinum complexes with *trans* phosphine ligands that contain one or two $(CH_2)_nCH=CH_2$ groups.

Thus, complexes of the type **9b–d** (Scheme 3) were similarly synthesized and reacted [10]. However, no trace of the target trimacrocyclic diphosphine complexes could be found
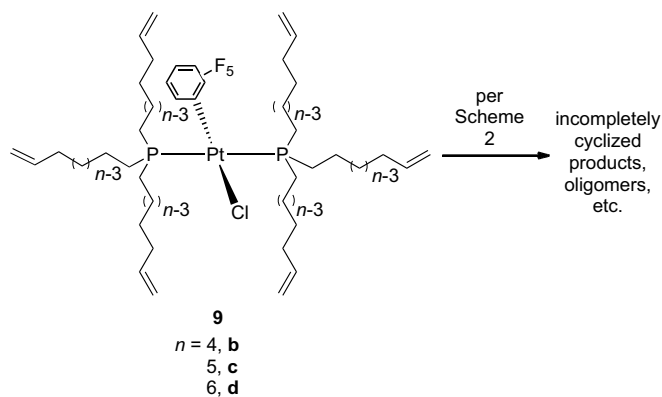
Scheme 3. Attempted metatheses of pentafluorophenyl platinum complexes with *trans* phosphine ligands that contain three $(CH_2)_nCH=CH_2$ groups.

in the crude reaction mixtures. Before hydrogenation, unreacted vinyl groups were evident.

2. Molecular gyroscopes

While investigating the preceding reactions, we became aware of work in the Garcia-Garibay laboratory directed at the synthesis of molecular compasses and gyroscopes [3,5]. These represent subsets of what can be termed molecular rotors [11]. Such assemblies are commonly dissected into rotators and stators. Since relative motion depends upon the frame of reference, the latter is assigned to the component with the greater moment of inertia. Representative compounds investigated by Garcia-Garibay are depicted in Scheme 4 (top; 10–12). Although the rotators are not "enclosed" by some type of superstructure, they are clearly sterically protected by the bulky endgroups. As illustrated with 12, the endgroups can be enlarged by introducing substituents.

Garcia-Garibay also drew attention to the utility of polar rotators, i.e. rotators that feature a permanent dipole moment (see 10). In principal, these can be exploited to orient the rotator in a static electric field (compass-like behavior), or compel unidirectional rotation in a rotating electric field. The latter is conceptually analogous to "pulling the string" of a toy gyroscope. The underlying physics – including limiting relationships involving the energy barrier for rotation and the frequency of the rotating field – has been reviewed in detail [11].

In the course of synthesizing the complexes in Scheme 2, we became attracted to the idea of transition-metal-based rotors. These would feature L′-M-L′ axes defined by two *trans* ligands, and L_yM rotators comprised of ancillary ligands. Indeed, the NMR properties of 5d indicated rapid passage of the chloride ligand through the seventeen-membered macrocycle on the NMR time scale, even at very low temperatures – a dynamic process for which a barrier could be measured with the smaller macrocycle 5c ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$: 6.0 kcal/mol and −13.9 eu), but proved impossible to observe in the case of 5b.
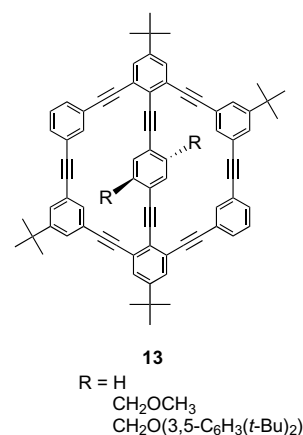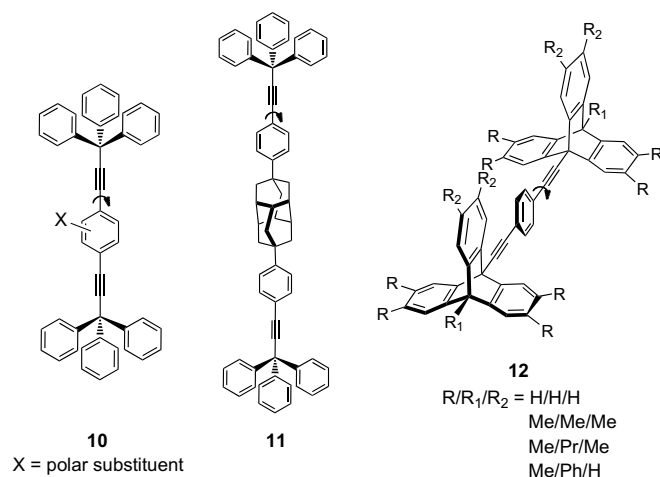
Scheme 4. Representative molecular rotors under investigation in the Garcia-Garibay group (top), and a turnstile-like molecule (bottom).

Despite the lack of encouraging results with 9b–d in Scheme 3, we thought that three-fold alkene metathesis still held promise as a route to "encapsulated" rotators. Importantly, macroscopic gyroscopes, which have a variety of technological applications, are to our knowledge always enclosed in protective housings to shield them from their environments. We therefore sought additional types of substrates for evaluation. We were particularly attracted to assemblies that would exhibit functional axes of rotation, and closely model the connectivities and symmetries of common toy gyroscopes. The latter implies D_{nh} symmetry, most logically with $n = 2–4$.

Before returning to our results, it should be noted that the descriptor 'gyroscope" has been applied to other types of organic and organometallic molecules in the literature [4]. Most of these are not relevant to this presentation. However, Moore has developed a series of macrocycles that he terms "turnstiles", as exemplified by 13 in Scheme 4 (bottom) [12]. The rotor is functional (provided the substituents R are small) and nearly of D_{2h} symmetry when R = H. Also, the rotor is sterically protected. In our view, these represent a sub-family of gyroscope-like molecules, and hold much promise for future research.
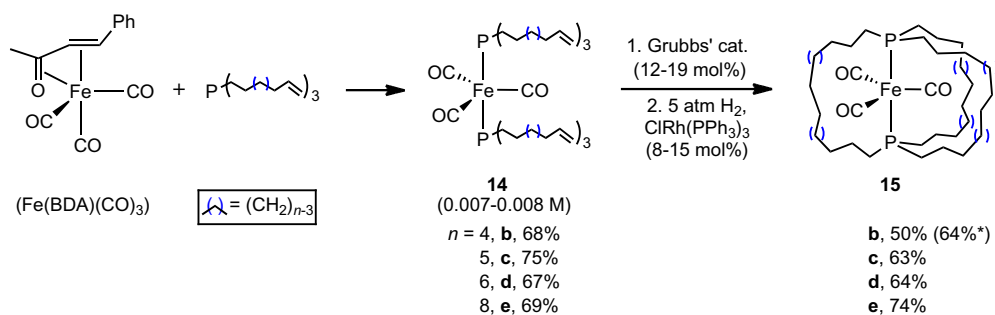
3. Three series of experiments from our group

This section treats all gyroscope-like molecules that we have synthesized by three-fold alkene metatheses of complexes with *trans* phosphine ligands of the type $P((CH_2)_nCH=CH_2)_3$ [13–16]. Triarylphosphine-based systems that feature much larger macrocycles with semi-rigid segments are detailed elsewhere [17].

3.1. Trigonal bipyramidal substrates

As shown in Scheme 5, the substitution-labile iron tricarbonyl complex $Fe(BDA)(CO)_3$ (BDA = benzylideneacetone) [18] was treated with a series of phosphines $P((CH_2)_nCH=CH_2)_3$. Workups gave the trigonal bipyramidal adducts *trans*-$Fe(CO)_3$ $(P((CH_2)_nCH=CH_2)_3)_2$ (**14b–e**) in 68–75% yields. These were subjected to metathesis conditions similar to those employed in Scheme 2, followed by $ClRh(PPh_3)_3$-catalyzed hydrogenations. To our delight, the target gyroscope-like complexes **15b–e** could be isolated in 50–74% overall yields [13,19]. Several could be crystallographically characterized.

Why are the three-fold alkene metatheses of **14b–e** so much more successful than those of **9b–d**? We believe that part of the answer involves the probable ground state conformation **I** depicted in Fig. 1. Since both the iron fragment $Fe(CO)_3$ and the phosphines possess three-fold symmetry axes, the CO ligands and $(CH_2)_nCH=CH_2$ groups can adopt perfectly staggered arrangements. This results in eclipsed $(CH_2)_nCH=CH_2$ groups on the two phosphines, which are directed into the same OC–Fe–CO interstice. Consequently, **14b–e** can be viewed as preorganized for three-fold metatheses.

The gyroscope-like complexes **15b–e** can be protonated [13,20], and one carbonyl ligand is easily replaced by NO^+. Nitrosylation affords a dipolar rotator, and lowers the symmetry such that the barrier to $Fe(CO)_2(NO)^+$ rotation can be probed by variable temperature ^{13}C NMR spectroscopy. The rotator in the complex with thirteen-membered macrocycles (**15b**) is locked. However, the barrier decreases in the higher homologs, and is easily quanti-
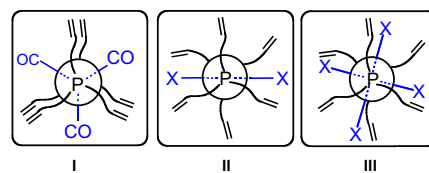

Fig. 1. Conformational energy minimum for trigonal bipyramidal complexes **14** and **27** (**I**), and representative conformations for square planar (**II**) and octahedral (**III**) analogs.

fied with the nitrosyl derivative of **15d** ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$: 9.5 kcal/mol and −6.5 eu).

3.2. Square planar substrates

We sought insight regarding the unsuccessful reactions with **9b–d** in Scheme 3. Thus, analogous square planar $PdCl_2$ and $PtCl_2$ adducts were prepared by standard methods [14]. As shown in Scheme 6 (top), similar metathesis/hydrogenation sequences starting with **16d** and **17d** afforded the gyroscope-like complexes **18d** and **19d** in 37–43% overall yields. Although the yields of these seventeen-mem-
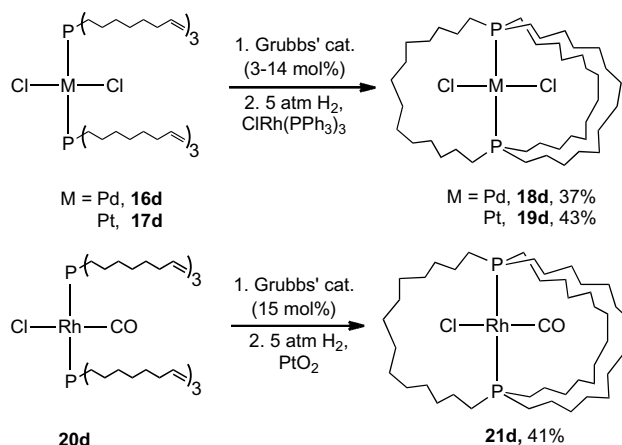
Scheme 6. Three-fold ring closing metathesis/hydrogenation sequences for square planar palladium, platinum, and rhodium complexes with *trans* phosphine ligands $P((CH_2)_6CH=CH_2)_3$.

Scheme 5. Three-fold ring closing metathesis/hydrogenation sequences for trigonal bipyramidal iron complexes with *trans* phosphine ligands $P((CH_2)_nCH=CH_2)_3$.
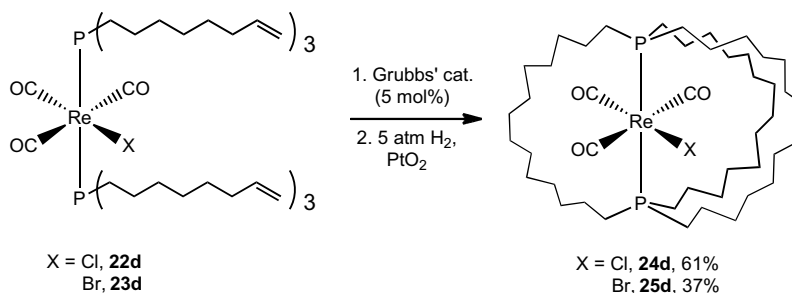
Scheme 7. Three-fold ring closing metathesis/hydrogenation sequences for octahedral rhenium complexes with *trans* phosphine ligands P((CH$_2$)$_6$CH=CH$_2$)$_3$.

bered macrocycles are lower than for the iron tricarbonyl analog **15d**, the syntheses are scaleable and gram quantities can be prepared. However, yields with dibromide complexes analogous to **16d** and **17d** were much lower. Furthermore, substrates with shorter methylene chains (e.g., **16b,c**) have afforded only oligomers under all conditions assayed to date. Substrates with longer methylene chains give gyroscope-like complexes, but in much lower yields than for iron analogs [21].

Thus, the replacement of the pentafluorophenyl ligand in **9d** (Scheme 3) by the smaller chloride ligand in **17d** allows access to a gyroscope-like complex. Given the lower yields with analogous dibromide complexes, we conclude that ligand size also plays a key role in the success of these sequences. Although we have not yet been able to obtain crystals of **16d**, **17d**, or related species that are suitable for structure determinations, one would expect a host of local conformational minima (e.g., **II** in Fig. 1), none of which are preorganized for three-fold alkene metathesis.

The two chloride ligands in **18d** and **19d** are easily substituted by bromide, iodide, and cyanide ligands. Interestingly, low temperature ^{13}C NMR spectra show that MX$_2$ rotation in all of these complexes is rapid on the NMR time scale in solution. However, the introduction of longer thiocyanide, isothiocyanide, or phenyl ligands "brakes" the rotation. Many crystal structures have been determined, from which the radii of the rotators and other metrical parameters relevant to these phenomena can be calculated [14,21].

We wanted to test these generalizations with another square planar system. Thus, as shown in Scheme 6 (bottom), the rhodium carbonyl chloride complex **20d** was synthesized [15]. Metathesis and hydrogenation proceeded in similar overall yield to give **21d**, which features a dipolar rotator. The chloride ligand was easily substituted by iodide. The crystal structure of the latter showed a 89:11 disorder involving two rotator orientations. Low temperature ^{13}C NMR spectra indicated rapid rotation of the Cl–Rh–CO and I–Rh–CO rotators in solution. Interestingly, the latter could be "braked" by adding gaseous CO, which afforded a slower-rotating IRh(CO)$_2$ species. Under a nitrogen atmosphere, the I–Rh–(CO) system was regenerated.

3.3. Octahedral substrates

Emboldened by the results in Scheme 6, we decided to try to extend this methodology to octahedral complexes. The *mer* rhenium halide complexes **22d** and **23d** shown in Scheme 7 are easily synthesized [16]. To our surprise, intramolecular three-fold alkene metathesis readily occurred. Following hydrogenation, the chloride and bromide complexes **24d** and **25d** were isolated in 61% and 37% overall yields. The crystal structures of both seventeen-membered macrocycles were determined. Low temperature ^{13}C NMR spectra showed the rapid rotation of the XRe(CO)$_3$ moieties on the NMR time scale.

The substrates **22d** and **23d** clearly do not qualify as preorganized, as illustrated by the arbitrary conformation **III** in Fig. 1. However, the ligands on the rotator are relatively small, and as with the other complexes above, the halide ligands are easily substituted. In work not yet submitted for publication, we have extended these reactions to a variety of other octahedral chromium, molybdenum, tungsten, rhenium and osmium complexes, all with various combinations of carbonyl, nitrosyl, chloride, and bromide ligands [22]. We have not yet begun to vary the macrocycle size. Given the unexpected breadth of this chemistry, we were also curious regarding possible variations of the phosphorus donor ligand. This led to the series of experiments in the following section.

4. New results: extension to phosphite ligands

An obvious question is to what extent the stator in the above types of gyroscope-like complexes can be varied. One straight-forward extension would involve systems based upon dibridgehead diphosphites, thereby introducing six additional heteroatoms. This would in turn require the monophosphite ligands P(O(CH$_2$)$_n$CH=CH$_2$)$_3$ (**26**). Given the ready commercial availability of α,ω-alkenols HO(CH$_2$)$_n$CH=CH$_2$, it should be a simple matter to access an extended family of such species. The ligands **26a** ($n = 3$) [23] and **26b** ($n = 4$) [24] have been previously synthesized. One was prepared by the condensation of P(NMe$_2$)$_3$ and excess α,ω-alkenol; for the other, no details or characterization were given.

As shown in Scheme 8, the six monophosphites **26a–f** were similarly synthesized on ca. 10 g scales in 79–97% yields after distillations (**26a–d**) or other workups (**26e,f**). The colorless oils were characterized by ^1H, ^{13}C, and ^{31}P NMR as described in the experimental section. The ^{13}C spectra showed, in accord with much literature data [25], phosphorus coupled POCH$_2$CH$_2$ signals, with $^2J_{CP} > {}^3J_{CP}$ (11.0–10.9 Hz and 5.0–4.9 Hz). The ^1H NMR spectrum of **26b** agreed with that previously reported [24]. All other features were routine.

We first sought to apply these ligands to Fe(CO)$_3$-based systems, which as shown in Scheme 5 are the most versatile with respect to macrocycle size. There is also an extensive literature involving bis(phosphite) complexes *trans*-Fe(CO)$_3$(P(OR)$_3$)$_2$ [26–28]. As shown in Scheme 9, Fe(BDA)(CO)$_3$ and **26a,b,e,f** (2.7 equiv.) were combined in toluene. The reactions were monitored by ^{31}P NMR. After 8–14 d, chromatographic workups gave the target complexes *trans*-Fe(CO)$_3$(P(O(CH$_2$)$_n$CH=CH$_2$)$_3$)$_2$ (**27a,b, e,f**) as yellow or green oils in 17–64% yields. In contrast to the phosphine homologs in Scheme 5, and other iron phosphite complexes [28], they could not be induced to solidify or crystallize. This complicated their purification,
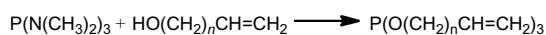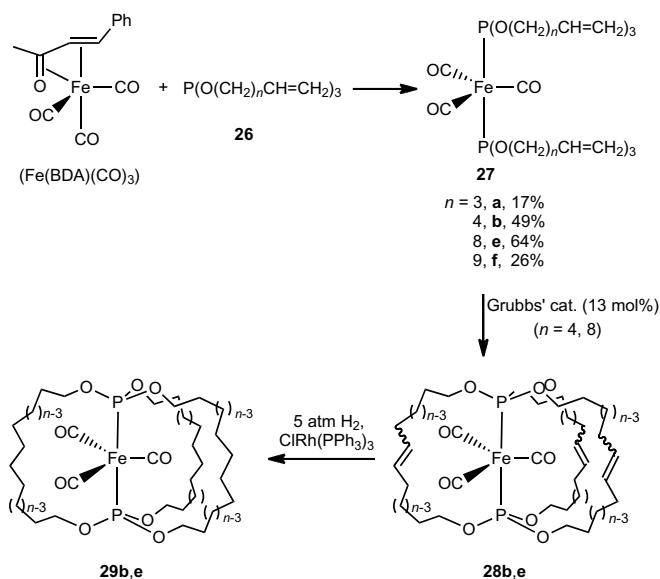
and only in the case of **27e** could an acceptable microanalyses be realized [29].

Complexes **27a,b,e,f** were characterized by NMR (^1H, ^{13}C, ^{31}P) and IR spectroscopy, and mass spectrometry. The ^1H and ^{13}C NMR spectra showed the customary vinyl signals, and POCH$_2$ signals at 4.26–3.90 and 65.1–66.1 ppm. In contrast to the free phosphites, the latter were not detectably coupled to phosphorus. Other researchers have noted both broad singlets and resolved doublets for the POCH$_2$CH$_2$ signals of phosphite complexes [30]. The ^{13}C NMR spectra also showed a single peak for the CO ligands (212.2–213.0 ppm), in two cases with resolved phosphorus coupling ($^2J_{CP}$ = 39.8–39.5 Hz). The ^{31}P signals (185.7–185.1 ppm) were as expected downfield of those of the free ligands (140.0–140.5 ppm), and very close to that of *trans*-Fe(CO)$_3$(P(O(CH$_2$)$_3$CH$_3$)$_3$)$_2$ (182.3 ppm) [27]. The IR spectra exhibited a strong ν_{CO} band at 1893–1895 cm^{-1}. The mass spectra showed weak molecular ions, and weak ions corresponding to the loss of three CO ligands. The most intense ion always had the composition FeP(O(CH$_2$)$_n$CH=CH$_2$)$_3$.

Metatheses of two representative complexes, **27b** and **27e**, were investigated. As shown in Scheme 9, reactions with Grubbs' catalyst (2 × 6.5 mol%) gave the crude metathesis products *trans*-Fe(CO)$_3$(P(O(CH$_2$)$_n$CH=CH(CH$_2$)$_n$O)$_3$P) (**28b,e**) as yellow oils in 52% and 45% yields. Complex **28b** contained approximately 12% of material with unreacted vinyl groups, as assayed by ^1H NMR. The mass spectra of **28b,e** now showed base peaks (100%) corresponding to the loss of three carbonyl ligands, supporting the formation of diphosphine cages. Molecular ions were also apparent. The ^{31}P NMR spectra showed several signals, consistent with a mixture of Z/E isomers, and likely oligomers.

Complexes **28b,e** were hydrogenated under conditions similar to those used in Scheme 5. A variety of chromatographic workups were investigated in hopes of obtaining spectroscopically pure products. However, all efforts were thwarted, in part due to the oily nature of the products, and in part due to decomposition during extended chromatography. Despite these difficulties, the target complexes *trans*-Fe(CO)$_3$(P(O(CH$_2$)$_{2n+2}$O)$_3$P) (**29b,e**) clearly comprised 82–83% of the isolated material (92% crude yield, **29e**). The mass spectra showed substantial molecular ions (10–20%), as well as base peaks corresponding to the loss of three carbonyl ligands. The ^1H and ^{13}C NMR spectra exhibited OCH$_2$ signals at 4.18–4.20 and 65.6–66.3 ppm, essentially unchanged from the "open" analogs **27a,b,e,f**. The CO signals were shifted slightly upfield (203.7 vs. 212.2–213.0 ppm), but the IR ν_{CO} bands were unchanged (1895 vs. 1893–1895 cm^{-1}). Hence, there is little if any "cage effect" on the spectroscopic properties.

Despite extensive efforts, **29b,e** proved resistant to crystallization [20]. Given the obvious importance of highly pure samples for many of our objectives, this series of complexes was therefore abandoned. However, the phosphite

P(N(CH$_3$)$_2$)$_3$ + HO(CH$_2$)$_n$CH=CH$_2$ ⟶ P(O(CH$_2$)$_n$CH=CH$_2$)$_3$

26

n = 3, **a**, 79%
4, **b**, 88%
5, **c**, 90%
6, **d**, 85%
8, **e**, 97%
9, **f**, 96%

Scheme 8. Syntheses of phosphite ligands.

26

(Fe(BDA)(CO)$_3$)

27

n = 3, **a**, 17%
4, **b**, 49%
8, **e**, 64%
9, **f**, 26%

Grubbs' cat. (13 mol%)
(n = 4, 8)

5 atm H$_2$,
ClRh(PPh$_3$)$_3$

29b,e   **28b,e**

Scheme 9. Syntheses and three-fold ring closing metathesis/hydrogenation sequences for trigonal bipyramidal iron complexes with *trans* phosphite ligands P(O(CH$_2$)$_n$CH=CH$_2$)$_3$.

ligands **26a–f** have been introduced into other metal fragments, from which crystalline polycyclized metathesis products – although not of the types in Fig. 8 – can be derived [31]. These will be reported in future publications. We note in passing that complexes of the type **2** (Scheme 1) that feature ether linkages in the flexible sp³ chain readily crystallize [4c]. Perhaps analogs of the gyroscope-like Fe(CO)₃ complex **15** with ether linkages will be more tractable than **29b,e**.

5. Summary

This article has reviewed existing syntheses of gyroscope-like complexes of the formula *trans*-L_yM(P((CH₂)$_{2n+2}$)₃P), where L_y denotes the ancillary ligands of a trigonal bipyramidal (L_3), square planar (L_2), or octahedral (L_4) species. These are accessible by threefold intramolecular alkene metatheses of precursors *trans*-L_yM(P((CH₂)$_n$CH=CH₂)₃)₂, followed by hydrogenations. Small ancillary ligands (e.g., CO, Cl) are essential, and yields are highest for trigonal bipyramidal Fe(CO)₃ complexes, which are preorganized for intramolecular metathesis in their ground state conformations. Analogous diphosphite adducts *trans*-Fe(CO)₃(P(O(CH₂)$_{2n+2}$O)₃P) can be synthesized by similar sequences, but are poorly tractable oils that resist purification.

6. Experimental

6.1. General

Reactions were carried out under dry N₂ atmospheres unless noted. Chemicals were treated as follows: toluene, pentane, and THF, distilled from Na/benzophenone; CH₂Cl₂, distilled from CaH₂; other solvents, distilled by rotary evaporation; HO(CH₂)₃CH=CH₂ (97%, Acros), HO(CH₂)₄CH=CH₂ (⩾90%, Fluka), HO(CH₂)₅CH=CH₂, HO(CH₂)₆CH=CH₂ (2 × TCI, ⩾96%), HO(CH₂)₈-CH=CH₂, HO(CH₂)₉CH=CH₂ (2 × Acros, 98–99%), P(N(CH₃)₂)₃ (⩾97.0%, Fluka), Grubbs' catalyst Ru(=CHPh)(PCy₃)₂(Cl)₂ (Aldrich), and ClRh(PPh₃)₃ (97%, Lancaster), used as received.

NMR spectra were obtained on a 400 MHz spectrometer and referenced as follows: ¹H NMR, residual CHCl₃ (7.24 ppm), C₆D₅H (7.15 ppm), CDHCl₂ (5.32 ppm), or CD₂HCN (1.93 ppm); ¹³C NMR, internal CDCl₃ (77.0 ppm), C₆D₆ (128.0 ppm), CD₃CN (118.7 ppm), or CD₂Cl₂ (53.5 ppm); ³¹P, external H₃PO₄ (0.00 ppm). IR and mass spectra were recorded on ASI React-IR 1000 and Micromass Zabspec instruments, respectively.

6.2. P(O(CH₂)₃CH=CH₂)₃ (**26a**) [23]

A flask was charged with P(N(CH₃)₂)₃ (5.919 g, 36.27 mmol) and HO(CH₂)₃CH=CH₂ (10.003 g, 116.14 mmol), fitted with a water cooled condenser, and heated at 100 °C until HN(CH₃)₂ no longer evolved. The residue was distilled (90 °C, 1.1 × 10⁻² mbar) to give **26a** as a colorless oil (8.100 g, 28.29 mmol, 79%).

NMR (CDCl₃, δ/ppm): ¹H, 5.81–5.71 (m, 3H, C*H*=), 4.96–4.74 (m, 6H, =C*H₂*), 3.79–3.74 (m, 6H, OC*H₂*), 2.12–2.07 (m, 6H, C*H₂*CH=), 1.70–1.63 (m, 6H, OCH₂C*H₂*); ¹³C{¹H}, 138.2 (s, *C*H=), 116.0 (s, =*C*H₂), 62.0 (d, ²J_{CP} = 10.9 Hz, O*C*H₂), 30.7 (d, ³J_{CP} = 5.0 Hz, OCH₂*C*H₂), 30.4 (s, *C*H₂CH=); ³¹P{¹H}, 140.0 (s).

6.3. P(O(CH₂)₄CH=CH₂)₃ (**26b**) [24]

P(N(CH₃)₂)₃ (6.042 g, 37.02 mmol) and HO(CH₂)₄CH=CH₂ (11.831 g, 118.12 mmol) were reacted in a procedure analogous to that used for **26a**. A similar workup (distillation at 130 °C, 8.0 × 10⁻² mbar) gave **26b** as colorless oil (10.670 g, 32.488 mmol, 88%).

NMR (CDCl₃, δ/ppm): ¹H, 5.70 (ddt, 3H, ³$J_{HHtrans}$ = 17.1 Hz, ³J_{HHcis} = 10.3 Hz, ³J_{HH} = 6.7 Hz, C*H*=), 4.99 (dd, 3H, ³$J_{HHtrans}$ = 17.1 Hz, ²J_{HH} = 1.6 Hz, =CH$_E$*H$_Z$*), 4.94 (br d, 3 H, ³J_{HHcis} = 10.0 Hz, =C*H$_E$*H$_Z$), 3.80 (m, 6H, OC*H₂*), 2.05 (m, 6H, C*H₂*CH=), 1.41–1.70 (m, 12H, OCH₂*C*H₂*C*H₂); ¹³C{¹H}, 139.0 (s, *C*H=), 115.0 (s, =*C*H₂), 62.5 (d, ²J_{CP} = 10.9 Hz, O*C*H₂), 33.8 (s, *C*H₂CH=), 31.0 (d, ³J_{CP} = 5.1 Hz, OCH₂*C*H₂), 25.5 (s, *C*H₂); ³¹P{¹H}, 140.4 (s).

6.4. P(O(CH₂)₅CH=CH₂)₃ (**26c**)

P(N(CH₃)₂)₃ (4.467 g, 27.37 mmol) and HO(CH₂)₅CH=CH₂ (10.00 g, 87.57 mmol) were reacted in a procedure analogous to that used for **26a**. A similar workup (distillation at 160 °C, 3.0 × 10⁻² mbar) gave **26c** as colorless oil (9.160 g, 24.74 mmol, 90%).

NMR (CDCl₃, δ/ppm): ¹H, 5.81–5.74 (m, 3H, C*H*=), 5.00–4.89 (m, 6H, =C*H₂*), 3.79–3.73 (m, 6H, OC*H₂*), 2.05–2.00 (m, 6H, C*H₂*CH=), 1.63–1.56 and 1.40–1.33 (2 m, 6H and 12H, OCH₂ (C*H₂*)₃); ¹³C{¹H}, 139.2 (s, *C*H=), 114.8 (s, =*C*H₂), 62.5 (d, ²J_{CP} = 11.0 Hz, O*C*H₂), 34.1 (s, *C*H₂CH=), 31.0 (d, ³J_{CP} = 4.8 Hz, OCH₂*C*H₂), 29.0 (s, *C*H₂), 25.7 (s, *C*H₂); ³¹P{¹H}, 140.4 (s).

6.5. P(O(CH₂)₆CH=CH₂)₃ (**26d**)

P(N(CH₃)₂)₃ (3.978 g, 24.37 mmol) and HO(CH₂)₆CH=CH₂ (10.00 g, 78.00 mmol) were reacted in a procedure analogous to that used for **26a**. A similar workup (distillation at 180 °C, 3.0 × 10⁻² mbar) gave **26d** as colorless oil (8.541 g, 20.71 mmol, 85%).

NMR (CDCl₃, δ/ppm): ¹H, 5.83–5.73 (m, 3H, C*H*=), 5.00–4.90 (m, 6H, =C*H₂*), 3.80–3.74 (m, 6H, OC*H₂*), 2.04–2.00 (m, 6H, C*H₂*CH=), 1.61–1.53 and 1.40–1.27 (2 m, 6H and 18H, OCH₂(C*H₂*)₄); ¹³C{¹H}, 139.5 (s, *C*H=), 114.7 (s, =*C*H₂), 62.7 (d, ²J_{CP} = 10.9 Hz, O*C*H₂), 34.1 (s, *C*H₂CH=), 31.5 (d, ³J_{CP} = 4.9 Hz, OCH₂*C*H₂), 29.3 (s, *C*H₂), 29.2 (s, *C*H₂), 26.1 (s, *C*H₂); ³¹P{¹H}, 140.4 (s).

6.6. $P(O(CH_2)_8CH=CH_2)_3$ (*26e*)

$P(N(CH_3)_2)_3$ (3.264 g, 20.00 mmol) and $HO(CH_2)_8CH=CH_2$ (10.003 g, 64.05 mmol) were reacted in a procedure analogous to that used for **26a**. The mixture was warmed under vacuum (120 °C, 1.0×10^{-2} mbar) and **26e** remained as a colorless oil that was >98% pure by ^{31}P NMR (9.616 g, 19.4 mmol, 97%).

NMR (CDCl$_3$, δ/ppm): ^{1}H, 5.83–5.73 (m, 3H, C*H*=), 4.99–4.89 (m, 6H, =C*H$_2$*), 3.78–3.73 (m, 6H, OC*H$_2$*), 2.04–1.98 (m, 6H, C*H$_2$*CH=), 1.65–1.55 and 1.35–1.27 (2 m, 6H and 30H, OCH$_2$ (C*H$_2$*)$_6$); ^{13}C{^{1}H}, 139.6 (s, *C*H=), 114.5 (s, =*C*H$_2$), 62.6 (d, $^2J_{CP}$ = 11.0 Hz, O*C*H$_2$), 34.2 (s, *C*H$_2$CH=), 31.6 (d, $^3J_{CP}$ = 4.9 Hz, OCH$_2$*C*H$_2$), 29.8 (s, *C*H$_2$), 29.7 (s, *C*H$_2$), 29.5 (s, *C*H$_2$), 29.3 (s, *C*H$_2$), 26.2 (s, *C*H$_2$); ^{31}P{^{1}H}, 140.5 (s).

6.7. $P(O(CH_2)_9CH=CH_2)_3$ (*26f*)

$P(N(CH_3)_2)_3$ (3.744 g, 22.94 mmol) and $HO(CH_2)_9CH=CH_2$ (12.50 g, 73.40 mmol) were reacted in a procedure analogous to that used for **26e**. The mixture was warmed under vacuum (120 °C, 1.0×10^{-2} mbar) and **26f** (11.87 g, 22.02 mmol, 96%) remained as a colorless oil that was 83% pure by ^{31}P NMR and gave satisfactory results in preparative reactions.

NMR (CDCl$_3$, δ/ppm): ^{1}H, 5.85–5.67 (m, 3H, C*H*=), 4.99–4.89 (m, 6H, =C*H$_2$*), 3.79–3.61 (m, 6H, OC*H$_2$*), 2.02–2.00 (m, 6H, C*H$_2$*CH=), 1.79–1.26 (m, 42H, OCH$_2$(C*H$_2$*)$_7$); ^{13}C{^{1}H}, 139.6 (s, *C*H=), 114.5 (s, =*C*H$_2$), 62.7 (d, $^2J_{CP}$ = 11.0 Hz, O*C*H$_2$), 34.2 (s, *C*H$_2$CH=), 31.6 (d, $^3J_{CP}$ = 4.9 Hz, PO*C*H$_2$CH$_2$), 29.9 (s, *C*H$_2$), 29.8 (s, *C*H$_2$), 29.7 (s, *C*H$_2$), 29.5 (s, *C*H$_2$), 29.3 (s, *C*H$_2$), 26.3 (s, *C*H$_2$); ^{31}P{^{1}H}, 140.4 (s, 83%). 9.0 (s, 17 %).

6.8. *trans*-$Fe(CO)_3(P(O(CH_2)_3 CH=CH_2)_3)_2$ (*27a*)

A Schlenk flask was charged with Fe (BDA)(CO)$_3$ [18] (0.800 g, 2.80 mmol), toluene (60 mL), and **26a** (2.162 g, 7.550 mmol). The solution was stirred for two weeks and periodically monitored by ^{31}P NMR. The solvent was removed by oil pump vacuum. Pentane (5 mL) was added, and the mixture was filtered through a short pad of neutral alumina using pentane and then pentane/CH$_2$Cl$_2$ (67:33 v/v). The solvent was removed from the filtrate by oil pump vacuum to give **27a** as a yellow oil (0.339 g, 0.476 mmol, 17%) [29].

NMR (C$_6$D$_6$, δ/ppm): ^{1}H, 5.67–5.65 (m, 6H, C*H*=CH$_2$), 4.98–4.89 (m, 12H, =C*H$_2$*), 4.12–4.00 (m, 12H, OC*H$_2$*), 2.05–2.04 (m, 12H, *C*H$_2$), 1.60–1.49 (m, 12H, *C*H$_2$); ^{13}C{^{1}H}, 212.8 (t, $^2J_{CP}$ = 39.8 Hz, *C*O), 137.9 (s, *C*H=), 115.3 (s, =*C*H$_2$), 65.1 (s, O*C*H$_2$), 30.2 (s, O*C*H$_2$CH$_2$), 29.4 (s, *C*H$_2$); ^{31}P{^{1}H}, 185.7 (s, 90%), 172.0 (s, 10%).

IR (cm^{-1}, oil film): 2953 (w), 2023 (w), 1961 (w), 1895 (s, v_{CO}), 1640 (w), 992 (m). MS [32]: 712 (**27a$^+$**, 3%), 629 ([**27a**–3CO]$^+$, 5%), 342 ([**27a**–3CO–**26a**]$^+$, 100%).

6.9. *trans*-$Fe(CO)_3(P(O(CH_2)_4CH=CH_2)_3)_2$ (*27b*)

Fe(BDA)(CO)$_3$ (0.429 g, 1.50 mmol), toluene (30 mL), and **26b** (1.329 g, 4.047 mmol) were combined in a procedure analogous to that used for **27a**. A similar workup (rinsing with 75:25 v/v pentane/CH$_2$Cl$_2$) gave **27b** as a yellow oil (0.588 g, 0.738 mmol, 49%) [29].

NMR (C$_6$D$_6$, δ/ppm): ^{1}H, 5.69–5.60 (m, 6 H, C*H*=), 4.95–4.87 (m, 12H, =C*H$_2$*), 4.01–4.00 (m, 12H, OC*H$_2$*), 1.93–1.88 (m, 12H, C*H$_2$*CH=), 1.88–1.35 (m, 24H, OCH$_2$C*H$_2$*C*H$_2$*); ^{13}C{^{1}H}, 212.9 (t, $^2J_{CP}$ = 39.5 Hz, *C*O), 138.6 (s, *C*H=), 114.8 (s, =*C*H$_2$), 65.6 (s, O*C*H$_2$), 33.6 (s, *C*H$_2$CH=), 30.1 (s, O*C*H$_2$*C*H$_2$), 25.4 (s, *C*H$_2$); ^{31}P{^{1}H}, 185.5 (s).

IR (cm^{-1}, oil film): 3078 (w), 2935 (w), 2860 (w), 1893 (s, v_{CO}), 1642 (w), 1472 (w), 994 (m), 961 (m). MS: 797 (**27b$^+$**, 3%), 712 ([**27b**–3CO]$^+$, 2%), 384 ([**27b**–3CO–**26b**]$^+$, 100%).

6.10. *trans*-$Fe(CO)_3(P(O(CH_2)_8CH=CH_2)_3)_2$ (*27e*)

Fe(BDA)(CO)$_3$ (0.3029 g, 1.059 mmol), toluene (60 mL), and **26e** (1.420 g, 2.859 mmol) were combined in a procedure analogous to that used for **27b**. A similar workup (neutral alumina column, first fractions only) gave **27e** as a green oil (0.767 g, 0.677 mmol, 64%). Anal. Calc. for C$_{63}$H$_{114}$O$_9$P$_2$Fe: C, 66.77; H, 10.14. Found: C, 66.63; H, 10.29%.

NMR (C$_6$D$_6$, δ/ppm): ^{1}H, 5.85–5.74 (m, 6H, C*H*=), 5.06–4.98 (m, 12H, =C*H$_2$*), 4.26–4.24 (m, 12H, OC*H$_2$*), 2.01–1.96 (m, 12H, C*H$_2$*CH=), 1.76–1.66 (m, 12H, OCH$_2$C*H$_2$*), 1.42–1.22 (m, 50H, OCH$_2$CH$_2$(C*H$_2$*)$_5$); ^{13}C{^{1}H}, 213.3 (s [33], *C*O), 139.2 (s, *C*H=), 114.5 (s, =*C*H$_2$), 66.1 (s, O*C*H$_2$), 34.2 (s, *C*H$_2$CH=), 30.8 (s, O*C*H$_2$*C*H$_2$), 29.8 (s, *C*H$_2$), 29.6 (s, *C*H$_2$), 29.4 (s, *C*H$_2$), 29.3 (s, *C*H$_2$), 26.2 (s, *C*H$_2$); ^{31}P{^{1}H}, 185.6 (s).

IR (cm^{-1}, oil film): 2926 (w), 2856 (w), 1895 (s, v_{CO}), 1640 (w), 1463 (w), 992 (m). MS [32]: 1134 (**27e$^+$**, 1%), 1049 ([**27e**–3CO]$^+$, 1%), 552 ([**27e**–3CO–**26e**]$^+$, 100%).

6.11. $Fe(CO)_3(P(O(CH_2)_9CH=CH_2)_3)_2$ (*27f*)

Fe(BDA)(CO)$_3$ (1.004 g, 3.509 mmol), toluene (50 mL), and **26f** (5.105 g, 9.475 mmol) were combined in a procedure analogous to that used for **27b**. After 8 d, the solvent was removed by oil pump vacuum. Pentane (5 mL) was added, and the mixture was filtered through a short pad of neutral alumina using pentane/CH$_2$Cl$_2$ (75:25 v/v). Two fractions were collected, and the second was similarly filtered. The first fractions from each filtration were combined, and the solvent removed by oil pump vacuum to give **27f** as a green oil (1.117 g, 0.918 mmol, 26%) [29].

NMR (CDCl$_3$, δ/ppm): ^{1}H, 5.84–5.74 (m, 6H, C*H*=), 5.00–4.89 (m, 12H, =C*H$_2$*), 4.02–3.94 (m, 12H, OC*H$_2$*), 2.32–2.01 (m, 12H, C*H$_2$*CH=), 1.69–1.62, 1.35–1.26 (2 m, 12H and 72H, OCH$_2$(C*H$_2$*)$_7$); ^{13}C{^{1}H}, 212.2 (s [33], *C*O), 139.2 (s, *C*H=), 114.1 (s, =*C*H$_2$), 65.6 (s, O*C*H$_2$), 33.8 (s, *C*H$_2$CH=), 30.4 (s, O*C*H$_2$CH$_2$), 29.5 (s, *C*H$_2$),

29.4 (s, CH_2), 29.3 (s, CH_2), 29.1 (s, CH_2), 28.9 (s, CH_2), 25.8 (s, CH_2); ^{31}P{^{1}H}, 185.1 (s).

IR (cm^{-1}, oil film): 2926 (w), 2856 (w), 1895 (s, v_{CO}), 1642 (w), 1463 (w), 992 (m). MS [32]: 1218 (**27f**$^+$, <2%), 1133 ([**27f**–3CO]$^+$, <2%), 384 ([**27f**–3CO–**26f**]$^+$, 100%).

6.12. trans-$\overline{Fe(CO)_3(P(O(CH_2)_4CH=CH(CH_2)_4O)_3P)}$ (28b)

A two-necked flask was charged with **27b** (0.450 g, 0.565 mmol), Grubbs' catalyst (0.0302 g, 0.0367 mmol, 6.5 mol%), and CH$_2$Cl$_2$ (100 mL; the resulting solution is 0.0057 M in **27b**), and fitted with a condenser. The solution was refluxed. After 19 h, a second charge of Grubbs' catalyst was added (0.0302 g, 0.0367 mmol, 6.5 mol%). After another 20 h, the solvent was removed by oil pump vacuum, and CH$_2$Cl$_2$ (3 mL) was added. The mixture was filtered through a short pad of neutral alumina using CH$_2$Cl$_2$. The solvent was removed from the filtrate by oil pump vacuum to give crude **28b** (0.210 g, 0.298 mmol, 52%) as a yellow oil.

NMR (C$_6$D$_6$, δ/ppm): ^{1}H, 5.66–5.10 (m, 6H, CH=), 4.27–4.15 (m, 12H, OCH_2), 2.12–1.93 (m, 12H, CH_2), 2.42–1.35 (m, 36H, CH_2); ^{31}P{^{1}H}, 186.8–182.4 (10 signals).

MS [32]: 712 (**28b**$^+$, 20%), 626 ([**28b**–3CO]$^+$, 100%).

6.13. trans-$\overline{Fe(CO)_3(P(O(CH_2)_8CH=CH(CH_2)_8O)_3P)}$ (28e)

A two-necked flask was charged with **27e** (0.499 g, 0.441 mmol), Grubbs' catalyst (0.024 g, 0.029 mmol, 6.5 mol%), and CH$_2$Cl$_2$ (65 mL; the resulting solution is 0.0059 M in **27e**), and fitted with a condenser. The solution was refluxed. After 24 h, a second charge of Grubbs' catalyst was added (0.024 g, 0.029 mmol, 6.5 mol%). After 3 d, a workup identical to that used for **27b** gave crude **27e** (0.209 g, 0.199 mmol, 45%) as a viscous light yellow oil.

NMR (C$_6$D$_6$, δ/ppm): ^{1}H, 5.52–5.36 (m, 6H, CH=), 4.32–4.10 (m, 12H, OCH_2), 2.28–1.06 (m, 84H, CH_2); ^{31}P{^{1}H}, 185.6 (s, 10%), 185.5 (s, 33%), 185.4 (s, 57%).

MS [32]: 1049 (**27e**, 1%), 964 (**27e**–3CO, 100%).

6.14. trans-$\overline{Fe(CO)_3(P(O(CH_2)_{10}O)_3P)}$ (29b)

A Fischer-Porter bottle was charged with **28b** (0.259 g, 0.363 mmol), ClRh(PPh$_3$)$_3$ (0.050 g, 0.054 mmol, 15 mol%), toluene (15 mL), and H$_2$ (5 bar). The red solution was stirred at 70 °C. After 72 h, the solvent was removed by oil pump vacuum. Then CH$_2$Cl$_2$ (3 mL) was added. The mixture was filtered through a short pad of neutral alumina using CH$_2$Cl$_2$. The solvent was removed by oil pump vacuum to give a yellow oil (0.184 g, 0.256 mmol). The residue was chromatographed on a neutral alumina column (2.0 × 20 cm, 85:15 v/v hexanes/CH$_2$Cl$_2$). The solvent was removed from the product frac-

tion by oil pump vacuum to give **29b** (0.010 g, 0.014 mmol, 4%; 82% NMR purity) as a thick yellow oil.

NMR (C$_6$D$_6$, δ/ppm): ^{1}H, 4.18–4.13 (m, 12H, OCH_2), 1.95–1.18 (m, 48H, CH_2); ^{13}C{^{1}H} (CO signal not detected), 65.6 (s, OCH_2), 29.4 (s, CH_2), 28.4 (s, CH_2), 27.9 (s, CH_2), 25.3 (s, CH_2); ^{31}P{^{1}H}, 184.4 (s, 82%), 184.6 (s, 11%), 185.3 (s, 7%).

IR (cm^{-1}, oil film): 2937 (w), 2860 (w), 1895 (s, v_{CO}), 1011 (m). MS [32]: 718 (**29b**$^+$, 23%), 634 ([**29b**–3CO]$^+$, 100%).

6.15. trans-$\overline{Fe(CO)_3(P(O(CH_2)_{18}O)_3P)}$ (29e)

A Fischer-Porter bottle was charged with **28e** (0.240 g, 0.229 mmol), ClRh(PPh$_3$)$_3$ (0.0318 g, 0.0343 mmol, 15 mol%), toluene (15 mL), and H$_2$ (5 bar). The red solution was stirred at 70 °C. After 72 h, the solvent was removed by oil pump vacuum. Then CH$_2$Cl$_2$ (3 mL) was added. The mixture was filtered through a short pad of neutral alumina using CH$_2$Cl$_2$. The solvent was removed by oil pump vacuum to give **29e** (0.223 g, 0.211 mmol, 92%; 83% NMR purity) as a viscous light yellow oil.

NMR (C$_6$D$_6$, δ/ppm): ^{1}H, 4.26–4.10 (m, 12H, OCH_2), 1.78–1.17 (m, 96H, CH_2); ^{13}C{^{1}H}, 203.7 (s [33], CO), 65.3 (m, OCH_2), 30.0 (s, CH_2), 29.1 (s, CH_2), 28.8 (s, CH_2), 28.6 (s, CH_2), 28.2 (s, CH_2), 27.8 (s, CH_2), 26.1 (s, CH_2), 25.9 (s, CH_2); ^{31}P{^{1}H}, 185.5 (s, 17%), 185.8 (s, 83%).

IR (cm^{-1}, oil film): 2926 (w), 2853 (w), 2358 (w), 1895 (s, v_{CO}). MS [32]: 1054 (**29e**$^+$, 10%), 970 ([**29e**–3CO]$^+$, 100%).

References

[1] Early communications: (a) J.M. Martín-Alvarez, F. Hampel, A.M. Arif, J.A. Gladysz, Organometallics 18 (1999) 955;
(b) E.B. Bauer, J. Ruwwe, J.M. Martín-Alvarez, T.B. Peters, J.C. Bohling, F.A. Hampel, S. Szafert, T. Lis, J.A. Gladysz, Chem. Commun. (2000) 2261.
[2] E.B. Bauer, J.A. Gladysz, in: R.H. Grubbs (Ed.), Handbook of Metathesis, vol. 2, Wiley/VCH, New York, 2003, p. 403.
[3] (a) T.-A.V. Khuong, J.E. Nuñez, C.E. Godinez, M.A. Garcia-Garibay, Acc. Chem. Res. 39 (2006) 413;
(b) M.A. Garcia-Garibay, Proc. Nat. Acad. Sci. 31 (2005) 10771.
[4] K. Skopek, M.C. Hershberger, J.A. Gladysz, Coord. Chem. Rev. 251 (2007) 1723.
[5] Representative full papers from the Garcia-Garibay group: (a) Z. Dominguez, H. Dang, M.J. Strouse, M.A. Garcia-Garibay, J. Am. Chem. Soc. 124 (2002) 7719;
(b) Z. Dominguez, T.-A. Khuong, H. Dang, C.N. Sanrame, J.E. Nuñez, M.A. Garcia-Garibay, J. Am. Chem. Soc. 125 (2003) 8827;
(c) C.E. Godinez, G. Zepeda, C.J. Mortko, H. Dang, M.A. Garcia-Garibay, J. Org. Chem. 69 (2004) 1652;
(d) T.-A.V. Khuong, H. Dang, P.D. Jarowski, E.F. Maverick, M.A. Garcia-Garibay, J. Am. Chem. Soc. 129 (2007) 839;

(e) P.D. Jarowski, K.N. Houk, M.A. Garcia-Garibay, J. Am. Chem. Soc. 129 (2007) 3110.

[6] (a) M.J. Frampton, H.L. Anderson, Angew. Chem., Int. Ed. 46 (2007) 1028;
(b) M.J. Frampton, H.L. Anderson, Angew. Chem. 119 (2007) 1046.

[7] (a) J. Stahl, W. Mohr, L. de Quadras, T.B. Peters, J.C. Bohling, J.M. Martín-Alvarez, G.R. Owen, F. Hampel, J.A. Gladysz, J. Am. Chem. Soc. 129 (2007) 8282;
(b) L. de Quadras, E.B. Bauer, W. Mohr, J.C. Bohling, T.B. Peters, J.M. Martín-Alvarez, F. Hampel, J.A. Gladysz, J. Am. Chem. Soc. 129 (2007) 8296;
(c) L. de Quadras, E.B. Bauer, J. Stahl, F. Zhuravlev, F. Hampel, J.A. Gladysz, New. J. Chem. 31 (2007) 1594;
(d) G.R. Owen, J. Stahl, F. Hampel, J.A. Gladysz, Chem. Eur. J., (2008) 14, in press, doi:10.1002/chem.200701268.

[8] (a) E.B. Bauer, F. Hampel, J.A. Gladysz, Organometallics 22 (2003) 5567;
(b) N. Lewanzik, T. Oeser, J. Blümel, J.A. Gladysz, J. Mol. Catal. A 254 (2006) 20.

[9] T. Shima, E.B. Bauer, F. Hampel, J.A. Gladysz, Dalton Trans. (2004) 1012.

[10] T. Shima, E.B. Bauer, unpublished results, Universität Erlangen-Nürnberg.

[11] G.S. Kottas, L.I. Clarke, D. Horinek, J. Michl, Chem. Rev. 105 (2005) 1281.

[12] T.C. Bedard, J.S. Moore, J. Am. Chem. Soc. 117 (1995) 10662.

[13] (a) T. Shima, F. Hampel, J.A. Gladysz, Angew. Chem., Int. Ed. 43 (2004) 5537;
(b) T. Shima, F. Hampel, J.A. Gladysz, Angew. Chem. 116 (2004) 5653.

[14] A.J. Nawara, T. Shima, F. Hampel, J.A. Gladysz, J. Am. Chem. Soc. 128 (2006) 4962.

[15] L. Wang, T. Shima, F. Hampel, J.A. Gladysz, Chem. Commun. (2006) 4075.

[16] G.D. Hess, F. Hampel, J.A. Gladysz, Organometallics 26 (2007) 5129.

[17] (a) L. Wang, F. Hampel, J.A. Gladysz, Angew. Chem., Int. Ed. 45 (2006) 4372;

(b) L. Wang, F. Hampel, J.A. Gladysz, Angew. Chem. 118 (2006) 4479.

[18] C.R. Graham, G. Scholes, M. Brookhart, J. Am. Chem. Soc. (1977) 1180.

[19] L. Wang, unpublished results, Universität Erlangen-Nürnberg.

[20] K. Skopek, Doctoral Dissertation, Universität Erlangen-Nürnberg, 2008.

[21] A.J. Nawara-Hultzsch, Doctoral Dissertation, Universität Erlangen-Nürnberg, 2008.

[22] G.D. Hess, T. Fiedler, D. Skaper, J.E. Nuñez, unpublished results, Universität Erlangen-Nürnberg.

[23] A.G. Davies, M.J. Parrott, B.P. Roberts, J. Chem. Soc., Chem. Commun. (1974) 27.

[24] S. Bakkas, M. Julliard, M. Chanon, Tetrahedron 43 (1987) 501.

[25] T. König, W.D. Habicher, U. Hähner, J. Pionteck, C. Rüger, K. Schwetlick, J. Prakt. Chem. 334 (1992) 333.

[26] R.L. Keiter, J.W. Benson, E.A. Keiter, T.A. Harris, M.W. Hayner, L.L. Mosimann, E.E. Karch, C.A. Boecker, D.M. Olson, J. VanderVeen, D.E. Brandt, A.L. Rheingold, G.P.A. Yap, Organometallics 16 (1997) 2246, and Refs. [6b,30] therein.

[27] H. Inoue, T. Takei, G. Heckmann, E. Fluck, Z. Naturforsch. 46b (1991) 682.

[28] (a) H.L. Conder, M.Y. Darensbourg, J. Organomet. Chem. 67 (1974) 93;
(b) P.D. Ginderow, Acta Cryst. B30 (1974) 2798;
(c) M. Barrow, N.L. Cromhout, D. Cunningham, A.R. Manning, P. McArdle, J. Renze, J. Organomet. Chem. 563 (1998) 201.

[29] Isolated **27a** is ca. 90% pure (^{31}P NMR), and **27b,e,f** are >98% pure (no other detectable ^{31}P NMR signals). However, **27b,f** did not give satisfactory microanalyses [20].

[30] J. Bravo, J. Castro, S. García-Fontán, E.M. Lamas, P. Rodríguez-Seoane, Z. Anorg. Allg. Chem. 629 (2003) 297.

[31] K. Skopek, F. Hampel, J.A. Gladysz, Inorg. Chem., submitted for publication.

[32] FAB (3-nitrobenzyl alcohol matrix); *m/z* for the most intense peak of the isotope envelope.

[33] Due to the peak width and signal/noise ratio, the phosphorus coupling could not be discerned.