Cite this: *Dalton Trans.*, 2016, **45**, 7131

Gyroscope like molecules consisting of trigonal or square planar osmium rotators within three-spoked dibridgehead diphosphine staters: syntheses, substitution reactions, structures, and dynamic properties†

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Reactions of $(\text{NH}_4)_2\text{OsX}_6$ ($\text{X} = \text{Cl}, \text{Br}$) with CO and the phosphines $\text{P}((\text{CH}_2)_m\text{CH}=\text{CH}_2)_3$ ($m = 6$, **a**; 7 , **b**; 8 , **c**) give *cis,cis,trans*- $\text{Os}(\text{CO})_2(\text{X})_2(\text{P}((\text{CH}_2)_m\text{CH}=\text{CH}_2)_3)_2$ (46–73%). These are treated with Grubbs' catalyst (7 mol%, 0.0010 M, $\text{C}_6\text{H}_5\text{Cl}$). Subsequent hydrogenations (PtO_2) yield the gyroscope like complexes *cis,cis,trans*- $\text{Os}(\text{CO})_2(\text{X})_2(\text{P}((\text{CH}_2)_n)_3)_2$ ($n = 2m + 2$; $\text{X} = \text{Cl}$, **6a–c**; Br , **7a–c**; 5–31%) and the isomers *cis,cis,trans*- $\text{Os}(\text{CO})_2(\text{X})_2(\text{P}(\text{CH}_2)_{n-1}\text{CH}_2)((\text{CH}_2)_n)(\text{P}(\text{CH}_2)_{n-1}\text{CH}_2)$ ($\text{X} = \text{Cl}$, **6'a–c**; Br , **7'a–c**; 12–51%) derived from a combination of interligand and intraligand metatheses. Reductions of **6a,c**, **6'b**, and **7'b** with C_8K under CO atmospheres afford *trans*- $\text{Os}(\text{CO})_3(\text{P}((\text{CH}_2)_n)_3)$ (**9a,c**, 79–82%) and *trans*- $\text{Os}(\text{CO})_3(\text{P}(\text{CH}_2)_{15}\text{CH}_2)((\text{CH}_2)_{16})(\text{P}(\text{CH}_2)_{15}\text{CH}_2)$ (**9'b**, 53–84%). Reaction of **9a** and $\text{CF}_3\text{SO}_3\text{H}$ yields the cationic hydride complex *mer,trans*- $[\text{Os}(\text{H})(\text{CO})_3(\text{P}((\text{CH}_2)_{14})_3)]^+ \text{CF}_3\text{SO}_3^-$ (**9a-H**⁺ CF_3SO_3^- ; quantitative by NMR). Preparative reactions of **9a,c** or **9'b** and $[\text{H}(\text{OEt}_2)_2]^+ \text{BARf}^-$ ($\text{BARf}^- = \text{B}(3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2)_4^-$) afford **9a,c-H**⁺ BARf^- (80%) or **9'b-H**⁺ BARf^- (68%). Reactions of **6a**, **6'b**, and **7a** with MeLi or PhLi give *cis,cis,trans*- $\text{Os}(\text{CO})_2(\text{Me})_2(\text{P}((\text{CH}_2)_{14})_3)_2$ (**11a**, 98%), *cis,cis,trans*- $\text{Os}(\text{CO})_2(\text{Me})_2(\text{P}(\text{CH}_2)_{15}\text{CH}_2)((\text{CH}_2)_{16})(\text{P}(\text{CH}_2)_{15}\text{CH}_2)$ (98%), and *cis,cis,trans*- $\text{Os}(\text{CO})_2(\text{Ph})_2(\text{P}((\text{CH}_2)_{14})_3)_2$ (**12a**, 58%). NMR data for **6a–c**, **7a–c**, **9a,c**, **9a-H**⁺ X^- , and **11a** indicate that rotation of the OsL_2 moieties is fast on the NMR time scale at room temperature. In contrast, the phenyl groups in **12a** act as “brakes” and two sets of ^{13}C NMR signals are observed for the methylene chains (2 : 1). The crystal structures of **6a–c**, **7b,c**, **7'a**, **9a**, **9a-H**⁺ BARf^- , **11a**, and **12a** are analyzed with respect to OsL_2 rotation in solution and the solid state.

Received 22nd February 2016,

Accepted 15th March 2016

DOI: 10.1039/c6dt00692b

www.rsc.org/dalton

Introduction

Macroscopic gyroscopes have played key roles in numerous technologies over the last century, but consumer consciousness was elevated when Steve Jobs rolled out the iPhone against a backdrop of a classical toy gyroscope, and touted an interface to an accelerometer to provide the six axis motion sensing that is essential to so many applications.¹ Accordingly, there are many

objectives driving the miniaturization of gyroscopes, and all of the underlying physics remains in force at the molecular level.² Although the term “gyroscope” has been applied rather loosely to molecules,³ only a few investigators have been actively trying to engineer working devices.^{4–6} A common denominator among these efforts has been the construction of cage like housings, often termed “stators”, which shield the rotating moieties or “rotators” from their surroundings.

As shown in Scheme 1, we have discovered that three fold intramolecular and interligand ring closing alkene metatheses of *trans* bis(phosphine) complexes of the type **I** can be effected in surprisingly high yields.^{7–12} This methodology has been used to access square planar, trigonal bipyramidal, and octahedral complexes, as detailed in earlier reports. Since mixtures of *Z/E* C=C isomers are commonly obtained, hydrogenations are subsequently effected, giving homogeneous samples featuring cage like *trans* spanning dibridgehead diphosphines that encapsulate the remaining ligands (**II**). Analogous routes

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†Electronic supplementary information (ESI) available: Experimental procedures, representative spectra, tables of characterization data. CCDC 1446694–1446703. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt00692b

Scheme 1 General syntheses of gyroscope like complexes with different coordination geometries.

have been used to prepare conceptually related *trans* bis(pyridine) complexes in which the *ortho* or *meta* carbon atoms are tethered by two connecting bridges.¹³

Many properties of **II** can be correlated to the coordination geometry. Earlier, we briefly communicated syntheses, structures, and substitution reactions of some octahedral rhenium(i) complexes with rotators of the formula $\text{Re}(\text{CO})_3(\text{X})$ (**V**; $\text{X} = \text{Cl}, \text{Br}$).¹¹ In this full paper, no part of which has been previously disclosed, we describe related efforts with octahedral osmium(ii) and trigonal bipyramidal osmium(0) complexes. The effectiveness of the three-fold interligand ring closing metathesis is studied as a function of macrocycle size. The feasibility of addition, substitution, and reduction reactions within the diposphine cages is then demonstrated. The sizes of the ligands are varied to probe rotational dynamics within the cage. A number of crystal structures are determined that provide insight, and define constraints on rotation in the solid state. Additional related results have been detailed elsewhere.¹⁴

Results

Ring closing metatheses of octahedral osmium(ii) complexes

Treatment of the readily available hexabromoosmate(iv) salt $(\text{NH}_4)_2\text{OsBr}_6$ ^{15a} with CO and then PPh_3 has been shown to give the osmium(ii) bis(phosphine) complex *cis,cis,trans*- $\text{Os}(\text{CO})_2(\text{Br})_2(\text{PPh}_3)_2$,¹⁶ in which the phosphine ligands are *trans*.¹⁷ Accordingly, the hexachloride and hexabromide complexes $(\text{NH}_4)_2\text{OsX}_6$ ¹⁵ were suspended in 2-methoxyethanol and heated under CO (10 bar) to give light yellow solutions. Subsequent additions of the alkene containing phosphines $\text{P}((\text{CH}_2)_m\text{CH}=\text{CH}_2)_3$ ($m = 6$, **1a**; 7 , **1b**; 8 , **1c**)¹⁸ gave, as depicted in Scheme 2, the bis(phosphine) complexes *cis,cis,trans*- $\text{Os}(\text{CO})_2(\text{X})_2(\text{P}((\text{CH}_2)_m\text{CH}=\text{CH}_2)_3)_2$ ($\text{X} = \text{Cl}$, **2a-c**; $\text{X} = \text{Br}$, **3a-c**) as yellow oils in 46–73% yields after chromatographic workups.¹⁹

All new complexes were characterized by NMR (^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$) and IR spectroscopy, mass spectrometry, and microanalysis, as summarized in the ESI.† The most diagnostic NMR and IR data are provided in Table 1. The $\text{PCH}_2\text{CH}_2\text{CH}_2$ ^1H NMR signals were assigned using $^1\text{H}, ^1\text{H}$ COSY 2D NMR spectra. The $\text{PCH}_2\text{CH}_2\text{CH}_2$ ^{13}C NMR signals could in turn be assigned by $^1\text{H}, ^{13}\text{C}\{^1\text{H}\}$ gHMQC spectra, per the example in Fig. 1. The PCH_2 and $\text{PCH}_2\text{CH}_2\text{CH}_2$ signals were phosphorus coupled virtual triplets ($^1J_{\text{CP}} = 15.5\text{--}15.9$ Hz and $^3J_{\text{CP}} = 6.3\text{--}6.4$ Hz, respectively),²⁰ whereas the PCH_2CH_2 signals were singlets (y axis, Fig. 1). The CO ligands gave triplets due to coupling to two equivalent phosphorus atoms ($^2J_{\text{CP}} = 7.2\text{--}7.5$ Hz). Representative ^1H NMR spectra are provided in the ESI (see Fig. s1† and the x axis, Fig. 1).

The IR spectra of **2a-c** and **3a-c** showed two ν_{CO} bands at $2019\text{--}2023$ cm^{-1} and $1945\text{--}1949$ cm^{-1} (Table 1), consistent with *cis* CO ligands and comparable to literature values for related complexes.^{16,21} If the CO ligands were *trans*, only a single IR band would be expected. As shown in Scheme 2, the reference compound *cis,cis,trans*- $\text{Os}(\text{CO})_2(\text{Br})_2(\text{P}(\text{n-C}_8\text{H}_{17})_3)_2$ (**8a**) was isolated in 85% yield following the hydrogenation of the dibromide complex **3a**. As given in Table 1, the ν_{CO} values, ^{13}C NMR chemical shifts and J_{CP} values, and ^{31}P NMR chemical shift were very close to those of **2a-c** and **3a-c**.

As shown in Scheme 2, dilute chlorobenzene solutions of **2a-c** and **3a-c** (0.0010 M) were treated with Grubbs' first generation catalyst (7.0–7.5 mol%). To help remove the ethene byproduct, the mixtures were aspirated with a slow stream of nitrogen. Aliquots were analyzed by ^1H NMR, and representative spectra are shown in the ESI (Fig. s2†). In all cases, the two $\text{CH}=\text{CH}_2$ multiplets were replaced by new $\text{CH}=\text{CH}$ signals with intermediate chemical shifts (mixtures of *E/Z* isomers). The patterns for **2b** and **3b** differed from those of **2a,c** and **3a,c**, reflecting differing product distributions as described below.

After the starting materials could no longer be detected, the mixtures were aspirated with air and filtered through Al_2O_3 to remove ruthenium residues. Incomplete catalyst oxidation or removal seemed to increase the amount of insoluble polymeric material upon concentration. The crude metathesis products, denoted **4a-c** and **5a-c**, were isolated as light brown sticky oils. The major components of those mixtures were, as inferred from purified derivatives below and shown in Scheme 2, either the gyroscope like complexes *cis,cis,trans*- $\text{Os}(\text{CO})_2(\text{X})_2(\text{P}((\text{CH}_2)_m\text{CH}=\text{CH}(\text{CH}_2)_m)_3)_2$ (**4a,c** and **5a,c**) or isomeric species *cis,cis,trans*- $\text{Os}(\text{CO})_2(\text{X})_2(\text{P}(\text{CH}_2)_m\text{CH}=\text{CH}(\text{CH}_2)_{m-1}\text{CH}_2)((\text{CH}_2)_m\text{CH}=\text{CH}(\text{CH}_2)_m)(\text{P}(\text{CH}_2)_m\text{CH}=\text{CH}(\text{CH}_2)_{m-1}\text{CH}_2)$ (**4'b** and **5'b**). The former are derived by interligand metatheses, and the latter by combinations of intraligand and interligand metatheses. These mixtures were characterized by ^1H and ^{31}P NMR (Experimental section) and no attempts were made to separate the various products. For **4a-c** and **5a-c**, four C=C isomers are possible (*EEE*, *EEZ*, *EZZ*, *ZZZ*), and for **4'a-c** and **5'a-c**, six C=C isomers are possible (*ZEE*, *ZEZ*, *ZZZ*, *EEE*, *EEZ*, *EZZ*; the first letter designates the interligand linkage). Hence, as many as ten ^{31}P NMR signals may be present.

Scheme 2 Syntheses and three fold ring closing alkene metatheses of osmium complexes **2a–c** and **3a–c**.

Fig. 1 Partial ^1H , $^{13}\text{C}\{^1\text{H}\}$ gHMQC NMR spectrum (500 MHz) of **3a** illustrating signal assignments and virtual triplets for complexes of the formula $\text{cis,cis,trans-Os}(\text{CO})_2(\text{X})_2(\text{P}((\text{CH}_2)_m\text{CH}=\text{CH}_2)_3)_2$.

THF solutions of **4a–c** and **5a–c** were then stirred under H_2 (balloon pressure) in the presence of PtO_2 (10–17 mol%). Aliquots were assayed by ^1H NMR until the

$\text{CH}=\text{CH}$ signals were no longer detected. Chromatographic workups afforded two series of isomeric products as shown in Scheme 2. The gyroscope like complexes $\text{cis,cis,trans-Os}(\text{CO})_2(\text{X})_2(\text{P}((\text{CH}_2)_n)_3)_2$ (X = Cl, **6a–c**; Br, **7a–c**) were obtained in 5–31% overall yields from **2a–c** or **3a–c**. The new index n , indicating the number of consecutive methylene groups, corresponds to $2m + 2$. The isomeric complexes $\text{cis,cis,trans-Os}(\text{CO})_2(\text{X})_2(\text{P}(\text{CH}_2)_{n-1}\text{CH}_2)((\text{CH}_2)_n(\text{P}(\text{CH}_2)_{n-1}\text{CH}_2))$ (X = Cl, **6'a–c**; Br, **7'a–c**) were obtained in 12–51% yields. These are comprised of two phosphacycles (from intraligand metatheses; ring size $n + 1$) and one diphosphaosmacycle (from interligand metathesis; ring size $n + 3$).

Key characterization data for **6a–c**, **7a–c**, **6'a–c**, and **7'a–c** are summarized in Tables 1 and S1.† The ^1H and ^{13}C NMR spectra of the gyroscope like complexes **6a–c** and **7a–c** were relatively simple, with $\text{PCH}_2\text{CH}_2\text{CH}_2$ and CO chemical shifts and coupling constants similar to those of the acyclic precursors **2a–c** and **3a–c** (Table 1), and a total of $n/2$ methylene ^{13}C signals. Representative ^1H and ^{13}C NMR spectra are provided in the ESI (Fig. S3 and S4†).

Table 1 Selected NMR data for osmium complexes

Complex	$^{13}\text{C}\{^1\text{H}\}$ (δ/ppm) ^a					$^{31}\text{P}\{^1\text{H}\}$ (δ/ppm)	^1H (δ/ppm) ^a OsH [$^2J_{\text{PH}}$, Hz]	IR (cm^{-1}) ν_{CO} ^b
	PCH ₂ [$^1J_{\text{CP}}$, Hz]	PCH ₂ CH ₂	PCH ₂ CH ₂ CH ₂ [$^3J_{\text{CP}}$, Hz]	CO [$^2J_{\text{CP}}$, Hz]	CH ₃ or i-Ph [$^2J_{\text{CP}}$, Hz]			
2a ^c	23.5 [15.6] ^d	23.3 ^d	31.1 [6.4]	176.6 [7.2]	—	−16.3	—	2019 (s), 1945 (s)
2b ^c	23.6 [15.5] ^d	23.4 ^d	31.2 [6.4]	176.6 [7.3]	—	−15.6	—	2019 (s), 1945 (s)
2c ^c	23.7 [15.5] ^d	23.5 ^d	31.4 [6.4]	176.6 [7.4]	—	−16.3	—	2019 (s), 1945 (s)
3a ^c	24.3 [15.9]	23.3	30.8 [6.3]	174.0 [7.5]	—	−25.3	—	2023 (s), 1949 (s)
3b ^c	24.3 [15.9]	23.9	31.3 [6.4]	175.2 [7.4]	—	−25.9	—	2023 (s), 1949 (s)
3c ^c	25.0 [15.9]	23.9	31.3 [6.4]	175.2 [7.3]	—	−25.3	—	2023 (s), 1949 (s)
6a ^c	24.8 [15.7]	22.5	30.0 [6.7]	176.6 [7.5]	—	−14.2	—	2019 (s), 1945 (s)
6b ^c	23.4 [15.6]	22.4	30.1 [6.5]	176.5 [7.5]	—	−13.8	—	2016 (s), 1941 (s)
6c ^c	23.4 [15.7]	22.8	30.5 [6.4]	176.4 [7.5]	—	−16.3	—	2016 (s), 1946 (s)
7a ^c	26.3 [16.0]	22.8	29.8 [6.6]	175.2 [7.2]	—	−23.2	—	2019 (s), 1949 (s)
7b ^c	24.9 [15.9]	22.9	30.1 [6.3]	175.1 [7.4]	—	−24.9	—	2019 (s), 1947 (s)
7c ^c	24.6 [16.0]	23.1	30.4 [6.4]	175.1 [7.6]	—	−25.8	—	2020 (s), 1946 (s)
6'a ^c	25.5 [15.9] ^e	23.4 ^e	30.5 [6.8] ^e	176.5 [7.4]	—	−14.4	—	2017 (s), 1944 (s)
6'b ^c	22.6 [15.3] ^e	21.8 ^e	29.0 [6.0] ^e	—	—	—	—	—
	25.4 [15.7] ^e	23.5 ^e	30.7 [6.3] ^e	176.5 [7.4]	—	−14.1	—	2019 (s), 1945 (s)
6'c ^c	22.50 [15.4] ^{e,f}	22.48 ^{e,f}	30.1 [6.0] ^e	—	—	—	—	—
	25.5 [15.9] ^e	23.6 ^e	31.0 [6.7] ^{e,g}	176.5 [7.4]	—	−16.6	—	2024 (s), 1946 (s)
7'a ^c	22.6 [15.6] ^{d,e}	22.8 ^{d,e}	30.8 [6.1] ^{e,g}	—	—	—	—	—
	26.6 [16.3] ^{d,e}	23.6 ^e	30.4 [6.8] ^e	175.1 [7.3]	—	−24.0	—	2019 (s), 1946 (s)
7'b ^c	24.0 [15.7] ^e	22.1 ^e	28.9 [6.0] ^e	—	—	—	—	—
	26.4 [16.2] ^e	23.8 ^e	30.6 [6.5] ^e	175.1 [7.5]	—	−25.4	—	2018 (s), 1946 (s)
7'c ^c	24.1 [15.8] ^e	23.0 ^e	30.1 [6.0] ^e	—	—	—	—	—
	26.3 [16.1] ^e	23.7 ^e	30.7 [6.7] ^{e,h}	175.2 [7.3]	—	−26.1	—	2018 (s), 1947 (s)
8a ^c	24.0 [15.9] ^e	23.1 ^e	30.6 [6.1] ^{e,h}	—	—	—	—	—
	24.3 [16.0]	23.4	31.0 [6.4]	173.9 [7.5]	—	−24.8	—	2019 (s), 1950 (s)
9a ^c	31.2 [17.1]	24.4	30.4 [7.0]	197.5 [12.2]	—	−2.6	—	1864 (s)
9'b ^c	30.55 [16.6] ^{e,h}	24.9 ^e	31.0 [6.0] ^e	198.8 [11.9]	—	−8.9	—	1856 (s)
9c ^c	30.53 [17.4] ^{e,h}	23.8 ^e	29.8 [6.2] ^e	—	—	—	—	—
	30.7 [16.8] ^g	24.5	30.8 [7.0] ^g	198.0 [11.8]	—	−6.8	—	1863 (s)
9a-H ⁺ CF ₃ SO ₃ ^{−i}	30.0 [17.3]	23.8	29.3 [7.3]	176.8 [9.5] ^j	—	−10.2	−8.50 [15.3]	— ^k
9a-H ⁺ BARf ^{−i}	30.0 [16.9]	23.8	29.3 [6.5]	174.9 [5.9] ^j	—	−10.8	−8.53 [15.3]	2114 (w), 2054 (m), 2031 (s)
				174.7 [5.4] ^j				
9'b-H ⁺ BARf ^{−i}	29.0 [17.8] ^e	24.0 ^e	29.9 [7.1] ^e	176.2 [9.4] ^j	—	−16.5	−8.48 [16.3]	2114 (w), 2052 (m), 2027 (s)
				174.5 [5.4] ^j				
9c-H ⁺ BARf ^{−i}	28.5 [17.3] ^e	23.0 ^e	29.3 [5.9] ^e	174.5 [5.4] ^j	—	−15.0	−8.45 [16.3]	2112 (w), 2050 (m), 2025 (s)
				174.6 [5.5] ^j				
10a ^c	30.9 [17.0]	24.7	31.3 [6.7]	198.7 [11.8]	—	−9.1	—	2922 (s), 2853 (m)
11a ^c	26.5 [14.9]	23.1	30.1 [6.3]	184.5 [7.9]	−22.2 [9.1]	−21.0	—	1967 (s), 1886 (s)
11'b ^c	26.5 [15.2] ^e	23.6 ^e	30.9 [6.4] ^e	184.1 [7.6]	−22.5 [9.4]	−25.3	—	1971 (s), 1896 (s)
12a ⁱ	24.0 [14.5] ^e	22.8 ^e	30.3 [5.6] ^e	—	—	—	—	—
	25.3 [16.0] ^j	21.8 ^j	— ⁱ	184 [7.0]	145.7 [12.5]	−27.8	—	1983 (s), 1911 (s)
	— ⁱ	21.3 ^j	—					

^a All signals for which *J* values are given correspond to triplets. ^b Oil or powder film. ^c NMR spectra were recorded in C₆D₆. ^d These two signals overlap, such that one of the outer peaks of the triplet is obscured. The coupling constant is derived from the two peaks of the triplet that are visible. ^e Approximate intensity ratio 1 : 2. ^f These two signals overlap, but the outer peaks of the virtual triplet are visible on each side of a broadened central peak. ^g These two virtual triplets overlap, but at least two peaks of each are distinguishable. ^h These two virtual triplets overlap, but all six peaks are distinguishable. ⁱ NMR spectra were recorded in CDCl₃. ^j Approximate intensity ratio 2 : 1. ^k Not recorded. ^l These three triplets overlap with other signals and the chemical shifts and coupling constants could not be unambiguously assigned.

The PCH₂CH₂CH₂ ¹H and ¹³C NMR signals of 6'a–c and 7'a–c (Table 1) could be assigned using ¹H,¹H COSY and ¹H,¹³C{¹H} gHMQC or gHSQC techniques. The spectra were more complex than those of the gyroscope like compounds 6a–c and 7a–c, in part due to the greater numbers of inequivalent methylene groups, making for *n* ¹³C signals, with the intensities of half roughly twice those of the others (see Fig. s4†). Furthermore, the protons of each methylene group of the phosphacycles are now diastereotopic. In the representative case of 7'b, the PCHH' signals exhibited quite different chemical shifts (2.47 and 2.20 ppm), both

downfield of the PCH₂ signal associated with the diphosphacycle (2.02 ppm). The PCHH'C'HH' protons also exhibited quite different chemical shifts (1.70 and 1.37 ppm), but these overlapped with other methylene signals and could only be assigned *via* 2D techniques (see Fig. s5 and s6†). The ³¹P NMR chemical shifts of 6'a–c and 7'a–c were always slightly downfield of the gyroscope like analogs (Table 1).

The thermal behavior of the new complexes was investigated as summarized in Table s1 (ESI†). The melting points of the gyroscope like complexes 6a–c and 7a–c were significantly

higher than those of the isomers **6'a-c** and **7'a-c** (e.g., 199 °C for **7b** vs. 54 °C for **7'b**). Only three of the latter were solids; the others were sticky oils. The melting points decreased with methylene chain lengths. TGA measurements showed no mass losses below 255 °C. With **6a,b** and **7a**, DSC measurements revealed additional endotherms at temperatures below the melting endotherms, suggestive of phase transitions.

The gyroscope like complex with the shortest methylene chain ((CH₂)₁₄) and the largest ligands (bromide), **7a**, was analyzed by variable temperature ¹³C NMR. Spectra were recorded in 10–20 °C intervals between 20 and –100 °C in CD₂Cl₂ (see Fig. S7†). Seven signals were detected at room temperature, consistent with rapid rotation of the Os(CO)₂(Br)₂ moiety. At lower temperatures no decoalescence – only line broadening and some loss of intensity – was observed. Thus, Os(CO)₂(Br)₂ rotation remains fast on the NMR time scale at low temperatures. Since the CO ¹³C NMR signal exhibits phosphorus coupling, this eliminates the possibility of CO or diphosphine dissociation in the process that renders the methylene chains equivalent.

Trigonal bipyramidal osmium(0) complexes

As represented in Scheme 1, a family of trigonal bipyramidal, Fe(CO)₃ based gyroscope like complexes has been previously reported.⁷ We sought to access analogous osmium(0) species. The first complex of the formula *trans*-Os(CO)₃(PR₃)₂ was described by Collman and Roper.¹⁶ It was prepared by reduction of the osmium(II) complex *cis,cis,trans*-

Os(CO)₂(Br)₂(PPh₃)₂ with zinc under CO (4–5 bar) in DMF at 140 °C. In order to avoid these harsh conditions, two alternative reducing agents were tested. The first, potassium graphite (C₈K),²² was heterogeneous, and had already been used to reduce other osmium(II) complexes;²¹ the second was a strong homogeneous ditungsten(II) reductant, W₂(hpp)₄,²³ where hpp is a bridging anionic donor of the type R'N[–]C(NR₂)[–]NR'.

As shown in Scheme 3, THF suspensions of C₈K (20–30 equiv.) were added to CO saturated solutions of the chloride and bromide substituted gyroscope like complexes **6a** and **7a,c**, as well as **6'b** and **7'b**. The mixtures were aspirated with a slow stream of CO at room temperature. Conversions were monitored by ³¹P NMR or IR spectroscopy (see Fig. S8†). The bromide complexes were reduced significantly faster than the chloride complexes (ca. 1 h vs. overnight). In each case, the product ³¹P NMR signal was downfield from that of the starting material. The IR ν_{CO} bands of the starting materials were replaced by a single absorption at lower frequencies, indicative of enhanced backbonding.

Workups gave the target complexes *trans*-Os(CO)₃(P((CH₂)_n))₂ (**9a,c**) in 79–82% yields, and the phosphacycle containing species *trans*-Os(CO)₃(P((CH₂)₁₅CH₂))₂ (**9'b**) in 53–84% yields, all as white solids. A model complex with two acyclic trialkylphosphine ligands, *cis,cis,trans*-Os(CO)₃(P(*n*-C₈H₁₇))₂ (**10a**), was similarly prepared in 85% yield from **8a** (Scheme 2). The spectroscopic data, summarized in Table 1, exhibited several trends in addition to those noted above. The CO ligand ¹³C NMR signals shifted 22.3–23.7 ppm downfield from those of the osmium(II) complexes to 197.5–198.8 ppm, and the ²J_{CP} values increased

Scheme 3 Syntheses of the osmium(0) complexes **9a,c** and **9'b** and their protonation: (a) C₈K, CO, THF; (b) [H(OEt₂)₂]⁺ BARf[–]/CH₂Cl₂ or CF₃SO₃H/CDCl₃.

(11.8–12.2 vs. 7.2–7.6 Hz). The PCH_2 signals ($^1J_{\text{CP}} = 16.6\text{--}17.4$ Hz) shifted 4.2–6.4 ppm downfield from the osmium(II) complexes, but the other methylene signals were comparable.

The reaction of **6a** and $\text{W}_2(\text{hpp})_4$ (ca. 5 equiv.) was investigated under similar conditions. However, workup gave **9a** in only 23% yield. Hence, this method was not pursued further, and additional details are provided elsewhere.¹⁴ Complex **9a** would also very likely be available *via* metathesis of the trigonal bipyramidal complex $\text{trans-Os}(\text{CO})_3(\text{P}((\text{CH}_2)_m\text{CH}=\text{CH}_2)_3)_2$, but this precursor proved difficult to synthesize in pure form.

Protonation reactions

The next objective was to modify the rotators in the gyroscope like complexes. Osmium tricarbonyl complexes of the type $\text{trans-Os}(\text{CO})_3(\text{PR}_3)_2$ are readily protonated by a variety of strong acids to yield cationic metal hydrides of the formula $\text{mer,trans-[Os(H)(CO)}_3(\text{PR}_3)_2]^+ \text{X}^-$.²⁴ As a test reaction, $\text{CF}_3\text{SO}_3\text{H}$ was added to a solution of **9a** in CDCl_3 in a NMR tube (Scheme 3). A ^1H NMR spectrum showed the quantitative generation of the target complex $\text{mer,trans-[Os(H)(CO)}_3(\text{P}((\text{CH}_2)_{14})_3\text{P})]^+ \text{CF}_3\text{SO}_3^-$ (**9a-H**⁺ CF_3SO_3^-). The hydride signal appeared at -8.50 ppm as a phosphorus coupled triplet ($^2J_{\text{HP}} = 15.3$ Hz). The ^{13}C NMR spectrum showed seven methylene signals and two triplets for the carbonyl groups *cis* and *trans* to the hydride ligand (intensity 2 : 1). Partial ^1H and ^{13}C NMR spectra are illustrated in Fig. S9.† However, attempts to isolate **9a-H**⁺ CF_3SO_3^- as a solid were unsuccessful.

In hopes of obtaining crystalline hydride complexes, BARf^- salts were sought ($\text{BARf}^- = \text{B}(3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2)_4^-$). Thus, CH_2Cl_2 solutions of **9a,c** as well as **9'b** were treated with the proton containing oxonium salt $[\text{H}(\text{OEt}_2)_2]^+ \text{BARf}^-$ (1 equiv.).²⁵ As shown in Scheme 3, workups gave the gyroscope like hydride complexes **9a,c-H**⁺ BARf^- as well as $\text{mer,trans-[Os(H)(CO)}_3(\text{P}(\text{CH}_2)_{15}\text{CH}_2)((\text{CH}_2)_{16})(\text{P}(\text{CH}_2)_{15}\text{CH}_2)]^+ \text{BARf}^-$ (**9'b-H**⁺ BARf^-) in 68–80% yields. The complex **9a-H**⁺ BARf^- was

obtained as a white powder that could be crystallized, and the others as yellow gums.

Characteristic data are presented in Table 1. The hydride ^1H NMR signals were similar to that of **9a-H**⁺ CF_3SO_3^- , and two $\text{CO } ^{13}\text{C}$ NMR signals were observed (2 : 1). The ^{31}P NMR signals were 7.6–8.2 ppm upfield from those of the precursors. As exemplified in Fig. S10,† three IR ν_{CO} bands with a weak/medium/strong intensity pattern were found between 2114 and 2025 cm^{-1} . This is consistent with literature data for other *mer,trans*- $[\text{Os(H)(CO)}_3(\text{PR}_3)_2]^+ \text{X}^-$ species²⁴ and can be derived theoretically.²⁶ The ν_{OSH} bands have been identified for related complexes (ca. 2000 cm^{-1} , m),²⁴ and broad, weaker bands were apparent with our compounds ($1964\text{--}1967\text{ cm}^{-1}$). However, no effort was made to unambiguously assign them by preparing deuterated analogs.

Substitution and other reactions

Replacements of the halide ligands in the osmium(II) complexes were attempted next. As shown in Scheme 4, the gyroscope like dichloride complex **6a** or the phosphacycle containing species **6'b** were treated with MeLi in THF. Workups gave the dimethyl complexes *cis,cis,trans*- $\text{Os}(\text{CO})_2(\text{Me})_2(\text{P}((\text{CH}_2)_{14})_3\text{P})$ (**11a**) or *cis,cis,trans*- $\text{Os}(\text{CO})_2(\text{Me})_2(\text{P}(\text{CH}_2)_{15}\text{CH}_2)((\text{CH}_2)_{16})(\text{P}(\text{CH}_2)_{15}\text{CH}_2)$ (**11'b**) in 98% yields. The structures followed readily from their spectroscopic properties. For example, the ^1H and ^{13}C NMR spectra showed characteristic upfield phosphorus coupled triplets for the methyl groups (0.05 or 0.20 ppm and -21.0 or -25.3 ppm). The ^{31}P NMR signals (-21.0 or -25.3 ppm) were significantly upfield from those of the precursors. The ^{13}C NMR spectrum of **11a** showed seven methylene signals, indicative of rapid $\text{Os}(\text{CO})_2(\text{Me})_2$ rotation. Other NMR data are collected in Table 1. The IR ν_{CO} bands (Table 1) were at lower frequencies than those of the precursors ($48\text{--}59\text{ cm}^{-1}$), consistent with enhanced backbonding.

Scheme 4 Substitutions of halide ligands by carbon nucleophiles.

It was then sought to introduce significantly larger ligands that would preclude rotation of the rotator. In previous studies of gyroscope like complexes, it has proved possible to replace halide ligands by phenyl ligands utilizing Ph_2Zn .^{8,11} Accordingly, **6a**, **7a**, and **6'b** were combined with Ph_2Zn in refluxing THF. After several days, ^{31}P NMR spectra showed no reaction. Similar results were obtained with PhMgBr . However, as shown in Scheme 4, a reaction of **7a** and PhLi in refluxing THF gave the desired diphenyl complex *cis,cis,trans*- $\text{Os}(\text{CO})_2(\text{Ph})_2\text{P}[(\text{CH}_2)_{14}]_3\text{P}$ (**12a**) in 58% yield after working. Most spectroscopic data were similar to those of **11a**.

Fig. 2 shows a portion of the ^{13}C NMR spectrum of **12a**. The three $(\text{CH}_2)_{14}$ chains gave a total of fourteen signals, consisting of two sets of seven with an approximate 2:1 intensity ratio. All of the above gyroscope like complexes with $(\text{CH}_2)_{14}$ chains exhibited only seven signals. X-ray crystallography (below) suggests that the unique methylene chain is located between the two *cis* phenyl ligands, as shown in **VI** (Fig. 2). However, the spectroscopic data do not exclude the alternative conformation **VII**. The virtual triplets associated with the $\text{PCH}_2\text{CH}_2\text{CH}_2$ signals of the all the preceding compounds are also apparent in Fig. 2 (three overlap with other signals).

It has been shown that reactions of iron tricarbonyl complexes *trans*- $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ as well as gyroscope like analogs (**IV**, Scheme 1) with $\text{NO}^+ \text{X}^-$ ($\text{X} = \text{PF}_6^-$, BF_4^-) give the cationic nitrosyl complexes *trans*- $[\text{Fe}(\text{CO})_2(\text{NO})(\text{PR}_3)_2]^+ \text{X}^-$ in high yields.^{7,27} However, many attempts to carry out analogous substitutions with the osmium(0) tricarbonyl complexes described above failed, as detailed elsewhere.¹⁴ Close analogs of the target complexes, *trans*- $[\text{Os}(\text{CO})_2(\text{NO})(\text{PPh}_3)_2]^+ \text{X}^-$ ($\text{X}^- = \text{PF}_6^-$, BPh_4^-) have been reported, but were synthesized from the precursor $\text{Os}(\text{H})(\text{Cl})(\text{CO})(\text{PPh}_3)_3$, which features three monodentate phosphine ligands.²⁸

Fig. 2 Partial $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz) of **12a** illustrating the fourteen CH_2 signals consistent with the idealized limiting conformations **VI** and **VII**; lines associated with virtual triplets are noted with a *.

The redox properties of selected complexes were probed by cyclic voltammetry using standard conditions.²¹ These included two model osmium(0) species with trialkylphosphine ligands, the *trans*- $\text{Os}(\text{CO})_3(\text{P}(n\text{-C}_8\text{H}_{17})_3)_2$ (**10a**) described above and previously reported *trans*- $\text{Os}(\text{CO})_3(\text{PCy}_3)_2$.²¹ Representative traces are shown in Fig. S11.† The latter complex exhibited a partially reversible oxidation with a current ratio (i_a/i_c) of 1.08 ($E_{\text{p,a}}/E_{\text{p,c}}/\Delta E = 101/-139/240$ mV; CH_2Cl_2 , 200 mV s^{-1}). In contrast, **10a** as well as the osmium(0) complexes **9a,c** and **9'b** and osmium(II) complex **7a** gave irreversible oxidations, with no significant cathodic current on the return scans.

Crystallography: molecular structures

Although the identities of the complexes in Schemes 2–4 were viewed as secure based upon spectroscopic data, crystal structures of as many as possible were sought. This was motivated by interest in the conformations of the rotators and diphosphine cages (stators), the separations between rotators and neighboring molecules in the solid state, and the alignment of rotators in the solid state – features relevant to developing functional molecular gyroscopes. Crystals of the complexes depicted in Fig. 3–12 were easily obtained as described in the Experimental section, despite the poor reputation associated with molecules with multiple polymethylene segments.²⁹ X-ray data were acquired and the structures solved as outlined in

Fig. 3 Thermal ellipsoid plots (50% probability) of the dominant conformation of **6a**: side view (left) and view along the P–Os–P axis (right).

Fig. 4 Thermal ellipsoid plots (50% probability) of the two independent molecules in the lattice of **6b**: side views (left) and views along the P–Os–P axis (right).

Fig. 5 Thermal ellipsoid plots (50% probability) of the dominant conformation of **6c**: side view (left) and view along the P–Os–P axis (right).

Fig. 6 Thermal ellipsoid plots (50% probability) of the two independent molecules of in the lattice of **7a**: side views (left) and views along the P–Os–P axis (right).

Fig. 7 Thermal ellipsoid plots (50% probability) of **7b**: side view (left) and view along the P–Os–P axis (right).

Table s2[†] and the Experimental section. Key bond lengths and angles have been summarized in Tables 2 and s3.[†]

The gyroscope like dichloride complex **6a**, which features seventeen membered macrocycles, showed disorder of one chloride and one CO ligand over two positions. This could be refined to a 51 : 49 occupancy ratio. Two views of the dominant

Fig. 8 Thermal ellipsoid plots (50% probability) of **7c**: side view (left) and view along the P–Os–P axis (right).

Fig. 9 Thermal ellipsoid plots (50% probability) of **9a**: side view (left) and view along the P–Os–P axis (right).

Fig. 10 Thermal ellipsoid plots (50% probability) of **9a-H⁺ BAR_f⁻**: side view (top) and view along the P–Os–P axis (bottom).

conformation are given in Fig. 3, one with the P–Os–P axis in the plane of the paper and the other with the axis perpendicular. Analogous perspectives are provided for the other complexes in subsequent figures.

The unit cell of the dichloride complex **6b**, which possesses nineteen membered macrocycles, contained two independent molecules, denoted **6b**(1) and **6b**(2) in the tables. As illustrated in Fig. 4, these differed in the conformations of the methylene

Fig. 11 Thermal ellipsoid plots (50% probability) of **11a**: side view (left) and view along the P–Os–P axis (right). Only one rotamer is depicted (occupancy ratio 50 : 50).

Fig. 12 Thermal ellipsoid plots (50% probability) of **12a**: side view (left) and view along the P–Os–P axis (right).

chains. One (bottom, Fig. 4) exhibited whole molecule disorder, which refined to a 53 : 47 occupancy ratio. The higher homolog **6c**, featuring twentyone membered macrocycles, showed disorder of one chloride and one CO ligand over two positions. This refined to an 80 : 20 occupancy ratio, and the dominant conformation is depicted in Fig. 5.

Fig. 6 illustrates the first crystal structure of a complex derived from mixed intra/interligand metathesis of the precursor **1** (Scheme 1). Two independent molecules of **7'a** were present, distinguished by minor variations in the macrocycle conformations. The crystal structure of the bis(BH₃) adduct of the free diphosphine ligand has been described elsewhere.³⁰ The molecular structures of the gyroscope like dibromide complex **7b** and its longer chain homolog **7c** (nineteen and twentyone membered macrocycles) are given in Fig. 7 and 8. The latter is quite similar to the dichloride analog **6c** in Fig. 5.

The molecular structure of the gyroscope like osmium(0) complex **9a** is depicted in Fig. 9. As with the iron analog (Scheme 1),⁷ a crystallographic C₂ axis passes through the M–C2–O2 linkage. It is also worth noting that the osmium–phosphorus distance (2.3626(6) Å) is 6% longer than the iron–phosphorus distance (2.2056(5) Å), providing additional “vertical” clearance for M(CO)₃ rotation.

The structure of the corresponding cationic hydride complex **9a-H⁺ BAR_f[−]** is given in Fig. 10. The hydride ligand was not located, but the formulation is secure based upon ¹H NMR data; the position in Fig. 10 was modeled. Only one

cationic hydride complex featuring a Os(H)(CO)₃ moiety and *trans* phosphine ligands could be found in the Cambridge Structural Database.³¹ However, the hydride ligand bridges between osmium and rhodium atoms in that molecule.

The molecular structure of the gyroscope like dimethyl complex **11a** is depicted in Fig. 11. One methyl and one CO ligand were disordered over two positions (50 : 50 occupancy ratio), analogous to the situation with the dichloride complex **6a** (Fig. 3). These structures also exhibited very similar macrocycle conformations. The structure of the analogous diphenyl complex **12a** is shown in Fig. 12. The phenyl rings are tilted relative to each other, with the least square planes defining an angle of 42°. No other structurally characterized osmium complexes with two *cis* phenyl ligands could be located. However, crystal structures have been reported for several square planar platinum complexes with *cis* phenyl or 4-fluorophenyl ligands, and the corresponding angles fall in the range of 50.84–63.60°.³²

Crystallography: rotator/stator/lattice analyses

As noted above, additional features of the preceding crystal structures are of interest. These include the radii of the rotators of the gyroscope like complexes. For the carbonyl halide complexes, the osmium–oxygen (OSCO) distances (2.926–3.126 Å) are greater than the osmium–halide distances (OsCl 2.346–2.452 Å; OsBr 2.5805–2.5835 Å). When the van der Waals radius of oxygen is added (1.52 Å),³³ an effective rotator radius is obtained; these values (4.503–4.673 Å) are compiled in Table 2. Although the van der Waals radii of chlorine and bromine are greater (1.75 Å, 1.85 Å), the carbonyl ligands remain “radius determining”. The same holds for the tricarbonyl hydride complex **9a-H⁺ BAR_f[−]** and the dimethyl complex **11a**. With the diphenyl complex **12a**, the phenyl ligands are radius determining. When the distance from osmium to the *para* hydrogen atom is added to the van der Waals radius of a hydrogen atom (1.20 Å), a value of 7.218 Å is obtained.

Similarly, measures of the void space between the rotator and (CH₂)_n chains of the stator are desirable. For this purpose, the distances from each osmium atom to the two carbon atoms closest to the plane of the rotator can be calculated. These are often the “innermost” CH₂ groups, and are abbreviated C_{dis} for “distal”. However, exceptions exist, as easily visualized from the structures of **6c** and **7c** in Fig. 5 and 8. In any case, the van der Waals radius of an sp³ hybridized carbon atom is then subtracted from these distances. As illustrated in Fig. 13 (left), these six values constitute a type of “horizontal clearance” for the rotator, and are compiled for each complex in Table 2. Although the data can be analyzed in different ways, we usually focus on the shortest distance of the six (see Discussion section). The dihedral angles diagrammed in Fig. 13 (right) are useful in analyzing “vertical clearance” for the rotator (Discussion section).

Intermolecular relationships are also important. For example, the closest contact between each osmium atom and a non-hydrogen atom of a neighboring molecule was identified. For every neutral complex, this involved a methylene carbon

Table 2 Intramolecular and intermolecular distances involving rotator and stator atoms in gyroscope like complexes [Å], and angles defined by gyroscope axes [°]

	6a ^a	6b(1) ^b	6b(2) ^b	6c ^a	7b	7c	9a	9a-H ⁺ BAr _F [−]	11a ^c	12a
Os–P	2.4048(5)	2.408(2)	2.404(3)	2.3989(7)	2.4137(15)	2.3983(11)	2.3526(5)	2.391(2)	2.3703(11)	2.400(5)
P to P	2.4094(5)	2.4087(19)	2.406(3)	2.3981(7)	2.4188(15)	2.4041(12)	2.3526(5)	2.3928(19)	2.3735(11)	2.403(5)
C–O	4.803	4.815	4.806	4.792	4.832	4.798	4.705	4.764	4.734	4.798
	1.134(3)	1.016(8)	1.038(4)	1.122(3)	1.105(9)	1.053(5)	1.159(2)	1.112(10)	1.150(4)	1.136(19)
	1.159(11)	1.135(7)	1.104(4)	1.132(4)	1.116(9)	1.119(5)	1.159(2)	1.125(9)	1.219(7)	1.156(19)
							1.165(4)	1.152(10)	1.220(7)	
<u>Os–CO</u>	1.878(3)	1.8827(4)	1.882(4)	1.882(3)	1.875(8)	1.875(4)	1.891(3)	1.952(10)	1.906(3)	1.90(2)
	1.967(12)	1.9096(4)	1.902(4)	1.887(3)	1.879(8)	1.920(5)	1.913(2)	1.954(9)	1.934(7)	1.92(2)
							1.913(2)	1.980(10)	1.934(7)	
<u>Os–CO</u>	3.012	2.926	2.928	3.004	2.984	2.973	3.056	3.076	3.055	3.054
	3.126	3.018	2.983	3.019	2.991	2.994	3.072	3.092	3.151	3.056
							3.072	3.102	3.153	
Os–CO _{rotor} ^d	4.646	4.538	4.503	4.539	4.511	4.514	4.592	4.622	4.673	4.576
Os–X ^{e,f}	2.346(3)	2.438(2)	2.450(3)	2.4270(9)	2.5805(7)	2.5816(9)	—	1.6002	2.179(7)	5.987
	2.4469(6)	2.451(2)	2.452(3)	2.4414(7)	2.5835(7)	2.5826(7)			2.179(7)	6.018
									2.213(3)	
Os–X _{rotor} ^{e,f}	4.197	4.201	4.202	4.1914	4.434	4.433	—	2.8002	3.913	7.218
	6.945/7.236	8.025/8.080	6.534/7.028	6.174/6.329	5.938/6.861	5.934/6.120	6.602/7.424	6.865/7.494	6.978/7.252	6.402/6.655
Os to C _{dis} ^g	6.964/7.247	5.863/6.030	7.204/7.526	5.980/6.216	6.746/7.363	6.454/7.205	7.833/7.833	7.483/7.871	6.627/6.662	6.530/7.189
	6.610/6.612	6.280/6.543	6.935/7.307	5.861/5.910	6.728/7.546	5.739/5.850	6.602/7.424	6.795/7.316	6.956/7.238	6.620/7.453
Shortest/longest	4.910/5.547	4.163/6.380	4.834/5.826	4.161/4.629	4.238/5.846	4.039/5.505	4.902/6.133	5.095/6.171	4.841/5.552	4.702/5.753
Os/C _{dis} –vdW ^h										
Os to C _{inter} ⁱ	5.137	5.127	5.745	5.071	4.511	5.401	6.086	4.295 ⁱ	5.161	5.234
Os/C _{inter} –vdW ^j	3.437	3.427	4.045	3.371	2.811	3.701	4.386	2.795	3.461	3.534
Sets of parallel	2	4	1	2	1	1	2	2	2	2
P–Os–P axes ^k										
∠[P–M–P + P–M–P] ^k	33.25	13.85	33.82 (2×)	—	89.98	—	—	52.99	32.34	53.58
		66.17	80.01 (2×)							
∠[ML _n] ^{k,l}	31.42 (2×)	14.95	32.49	—	89.75	—	—	58.07	30.89	56.71
		67.60 (2×)	80.00 (2×)							

^a Values for the dominant Os(CO)₂(Cl)₂ rotamer (6a,c). ^b Values for the two independent molecules of 6b in the unit cell. ^c One CO and one methyl ligand are disordered (50 : 50 occupancy ratio). Therefore the values are given for each conformation. ^d The longest of the Os–CO (osmium–oxygen) distances plus the van der Waals radius of oxygen (1.52 Å). ^e X = Cl, Br, H, CH₃, or H_{para}. ^f The longest of the Os–X distances (X = Cl, Br, H, CH₃, or H_{para}) plus the corresponding van der Waals radius (Cl, 1.75 Å; Br, 1.85 Å; H 1.20 Å, C, 1.70 Å). ^g Distances (non-bonded) from osmium to the two carbon atoms of each macrocycle that are closest to the plane of the rotator (C_{dis}); see Fig. 13. ^h The shortest/longest of the previous six distances, minus the van der Waals radius of carbon (1.70 Å). ⁱ Distance from osmium to the nearest non-hydrogen atom of a neighboring molecule. This is always a carbon atom, except for 9a-H⁺ BAr_F[−], where it is a fluorine atom (nearest carbon 6.781 Å). ^j The previous entry minus the van der Waals radius of carbon (1.70 Å) or fluorine (1.50 Å). ^k Planes used for angle calculations between sets of molecules with parallel P–M–P axes; see also the text and Fig. 13. ^l All ligating atoms of the rotator and osmium; four-five atoms total.

Fig. 13 Spatial relationships involving the osmium rotators and methylene carbon atoms connecting the *trans* phosphorus atoms.

atom. In the case of **9a**-H⁺ BAR_F[−], a fluorine atom of the anion proved closest. Although there is no requirement that these atoms lie in the plane of the rotator, only moderate deviations would normally be expected. These distances, minus the van der Waals radius of the carbon or fluorine atom, are summarized in Table 2. A value greater than the radius of the rotator would indicate that rotation should not be intramolecularly impeded in the crystal lattice. Only in the case of **9a** was this limit approached (4.592 Å radius *vs.* 4.386 Å intermolecular contact).

In all of the crystal lattices, sets of molecules with parallel P–Os–P axes were apparent. In **6c**, **7c**, and **9a**, there was only one such set; *i.e.*, all axes were parallel. This feature is illustrated for **9a** in Fig. 14 (left).

A greater number of complexes – **6a**, **7b**, **9a**-H⁺ BAR_F[−], **11a**, and **12a** – exhibited two distinct sets of molecules with parallel axes. One motif is illustrated with **7b** in Fig. 14 (middle). The angles between these axes were quantified in two ways. First, a plane was defined by taking two axes from one

set (P–Os–P + P–Os–P; six atoms total). An analogous plane was defined using the other set. The resulting angles are listed in Table 2. Another calculation was carried out using the rotator planes (all ligating atoms and osmium), and gave similar values. Most of the angles ranged from 57° to 31°, but **7b** was unique in having nearly orthogonal axes (89.8–90.0°).

As noted above, **6b** exhibited two independent molecules in the unit cell. For each, two sets with parallel axes were present, making for multiple angles as listed in Table 2. The unit cell is depicted in Fig. 14 (right), representing the upper limit of complexity, and is not analyzed further.

Finally, it should be emphasized that the osmium tricarbonyl complex **9a** crystallizes analogously to the corresponding iron tricarbonyl complex,⁷ with an identical space group (*C*2/*c*) and *Z* value (4), and similar unit cell volumes (4693.71(16) *vs.* 4633.5(3) Å³). The slight volume increase reflects the longer metal–ligand bonds per examples given above. All special properties of **9a** noted above are also manifested in the iron

Fig. 14 Packing diagrams of **9a**, **7b**, and **6b** (disordered atoms are depicted in their dominant conformation; the dibridgehead diphosphine ligands are omitted in the bottom representations).

analog (e.g., radius of rotator (4.449 Å) only slightly greater than closest intermolecular contact (4.339 Å)).

Discussion

Scope of syntheses

The reaction sequence in Scheme 2 establishes that octahedral $\text{Os}(\text{CO})_2(\text{X})_2$ based gyroscope like complexes can be accessed *via* three fold intramolecular ring closing metatheses involving *trans* phosphine ligands of the formula $\text{P}((\text{CH}_2)_m\text{CH}=\text{CH}_2)_3$ with $m \geq 6$. The overall yields of **6a–c** and **7a–c** are modest (31–5%), but given the obvious possibilities for oligomeric or polymeric byproducts, it is perhaps surprising that they are obtained at all. As noted above, this study was in part prompted by analogous syntheses of related adducts with $\text{Re}(\text{CO})_3(\text{X})$ rotators ($\text{X} = \text{Cl}, \text{Br}$).¹¹ Here, yields with $m = 6$ ($n = 14$) were 61% for the chloride complex and 37% for the bromide complex. This reproducible trend has been viewed as a ligand size effect, but the yields for the osmium dichloride and osmium dibromide complexes in Scheme 2 are quite close.

Scheme 2 also establishes the viability of a topologically distinct metathesis mode involving both intraligand and interligand ethene elimination and leading to **6'a–c** and **7'a–c**. When both types of products are considered, the overall yields of monoosmium complexes range from 56% to 35%. Regardless, the yields of gyroscope like complexes remain lower than those commonly obtained from square planar and trigonal bipyramidal precursors (Scheme 1).^{7–10} Fig. 15 provides Newman type

projections of the conformational energy minima of each type of educt (**VIII–X**). It is easily appreciated that the trigonal bipyramidal complexes (**IX**) are optimally preorganized for three fold interligand metatheses. On the other hand, torsional relationships in the octahedral complexes (**X**) interfere with the formation of *trans* spanning linkages. Products analogous to **6'a–c** and **7'a–c** have never been detected in any metathesis of a trigonal bipyramidal precursor, and are less common with square planar precursors (**VIII**).^{8b,34}

Another trend in Scheme 2 involves precursors with even numbers of methylene groups in each phosphine substituent (**2a,c**, **3a,c**) *versus* those with odd numbers of methylene groups (**2b**, **3b**). The former affords *ca.* 2 : 1 ratios of products derived from interligand *vs.* mixed intra/interligand metathesis modes. However, the latter gives *ca.* 1 : 10 ratios. Although the data are suggestive of a broader relationship, a wider range of precursors is needed to confirm generality. Even/odd patterns involving the properties of polymethylene compounds have considerable empirical precedent.^{35,36}

We generally view metathesis reactions of **I** (Scheme 1) to be largely under kinetic control. In an effort to better appreciate the factors that may be at play in Scheme 2, the metathesis of **2b** was repeated, and the crude tris(alkenes) (**4*b** or **4b/4'b**) divided into two portions. One was hydrogenated, and the other was treated with Grubbs' second generation catalyst, and then hydrogenated. The first sample gave a 1 : 6 ratio of **6b/6b'**, and the latter a *ca.* 1 : 16 ratio. Hence, at least for this macrocycle size, the mixed intra/interligand metathesis mode is thermodynamically preferred. In this context, protocols for increasing selectivities for non-oligomeric products in ring closing metathesis have been reported,³⁷ and may well prove applicable to our substrates.

Substitution reactions within the diphosphine cages of gyroscope like complexes, such as those presented in Scheme 4 with MeLi and PhLi , now have abundant precedent.^{8–11} Mechanistic questions remain extant, but in a preparative sense the same general reagents may be applied as with analogous bis(phosphine) complexes. The protonation reactions in Scheme 3 also have precedent with bis(phosphine) complexes as well as gyroscope like iron tricarbonyl complexes. What is surprising is the efficacy of a heterogeneous reductant, potassium graphite (C_8K), for converting the osmium(II) dicarbonyl dihalide complexes to osmium(0) tricarbonyl complexes. Apparently, the diphosphine cage does not interfere with a transformation that presumably requires a biphasic outer sphere electron transfer.

Dynamic properties

When CD_2Cl_2 solutions of the trigonal bipyramidal $\text{Fe}(\text{CO})_2(\text{NO})^+$ analog of **9a** are cooled, some of the methylene ^{13}C NMR signals associated with the two inequivalent $(\text{CH}_2)_{14}$ chains decoalesce. This, coupled with line shape analyses, provides a barrier to $\text{Fe}(\text{CO})_2(\text{NO})^+$ rotation ($\Delta H^\ddagger = 9.5 \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = -6.5 \text{ eu}$).⁷ With the octahedral complexes **6a** and **7a**, the barriers to $\text{Os}(\text{CO})_2(\text{X})_2$ rotation appear lower, as suggested by the absence of any well defined decoalescence

Fig. 15 Top: dominant conformations of square planar, trigonal bipyramidal, and octahedral precursors to gyroscope like complexes. Middle and bottom: energy minima and maxima associated with rotators in square planar, trigonal bipyramidal, and octahedral gyroscope like complexes.

upon cooling ($-100\text{ }^{\circ}\text{C}$, Fig. s7†). Newman type projections help provide insight regarding this trend.

In the ground state conformations of trigonal bipyramidal complexes (**IV**, Scheme 1), the ligands on the rotator are approximately staggered with respect to the phosphorus alkyl substituents, as shown in **XII** in Fig. 15. On the other hand, the transition state for ML_3 rotation requires triply eclipsing interactions, with all three ligands simultaneously passing through the three macrocycles (**XV**). This should maximize the $\Delta G^\ddagger$ value. In contrast, the transition state for ML_4 rotation in an octahedral complex involves only a single ligand passing through a macrocycle, as shown in **XVI** (although two other ligands are on the threshold of interacting with the two other macrocycles). Furthermore, in the ground state conformations of octahedral complexes (**XIII**), there are significant interactions between two ligands and two macrocycles. This translates into a “ground state destabilization” that has no counterpart in the trigonal bipyramidal complexes. The net result is intrinsically lower rotational barriers.³⁸

Another way of viewing this phenomenon is that there are twelve energy maxima (and twelve minima) as a rotator in an octahedral complex is stepped through 360° , but only three in the case of a trigonal bipyramidal complex. As has been long appreciated in conformational analyses of organic molecules, it would be very unusual for the maxima/minima for a “twelve fold barrier” to exhibit a greater amplitude than for a “three fold barrier” (with substituents of comparable sizes).³⁸ To complete the picture, square planar complexes have a “six fold barrier” as reflected by the minima and maxima **XI** and **XIV**. Accordingly, experiments have established that $\text{Rh}(\text{CO})(\text{I})$ has a much lower barrier to rotation than $\text{Rh}(\text{CO})_2(\text{I})$.^{10a}

Our NMR data also indicate very rapid rotation of the osmium rotators in the dimethyl complex **11a** and the cationic hydride complexes **9a**- H^+ X^- . However, for the diphenyl complex **12a**, rotation becomes slow on the NMR time scale, and as illustrated in Fig. 2 two sets of ^{13}C signals for the two macrocycles are observed. However, for none of the complexes in this paper were both the fast and slow exchange regimes accessible, and therefore the exact barriers remain unquantified. It was also a disappointment that trigonal bipyramidal complexes with $\text{Os}(\text{CO})_2(\text{NO})^+$ rotators could not be accessed, since given the results with the iron analog, there would have been a good chance of observing both regimes.

Crystal structures

As analyzed in more detail elsewhere,¹⁴ there is nothing exceptional about the bond lengths and angles in the structurally characterized complexes.³⁹ Thus, the features most relevant to the dynamic properties treated in the previous section are considered. First, the conformation of the $\text{Os}(\text{CO})_3$ rotator in the trigonal bipyramidal complex **9a** (Fig. 9, right) closely corresponds to the anticipated energy minimum **XII** in Fig. 15. Second, the conformations of the $\text{Os}(\text{CO})_2(\text{X})_2$ rotators in the octahedral complexes **6b,c** and **12a** (Fig. 4, 5, and 12; right or upper right) closely correspond to the anticipated energy minimum **XIII** (Fig. 15). However, the rotator conformations in

the other octahedral complexes more closely resemble the anticipated energy maximum **XVI**, with one ligand positioned within a macrocycle (Fig. 3, 7, 8, 10, 11; right). This is interpreted as evidence for the much closer maxima/minima energy spacing in the octahedral complexes.

As noted above, the $\text{Os}(\text{CO})_2(\text{L})_2$ moieties in the octahedral complexes **6a**, **7a**, **11a**, and **9a**- H^+ BAr_f^- , all of which feature seventeen membered macrocycles, undergo rapid rotation on the NMR time scale at room temperature. Per the results section, computing the radii of the rotators is straight forward. As summarized in Table 2, the carbonyl ligands are “radius determining” in every case (4.622–4.673 Å for the three of these four complexes that have been structurally characterized). Estimating an “interior void space” or “horizontal clearance” for the stator is less exact. As diagrammed in Fig. 13, we focus upon the two carbon atoms of each macrocycle that are closest to the plane of the rotator (C_{dis}), and subtract the van der Waals radius of a carbon atom from the shortest of the six osmium- C_{dis} distances (4.841–5.095 for the three complexes). These are all comfortably longer than the radii of the rotators, a feature nicely illustrated by the space filling representations of **6a** and **9a** in Fig. 16. However, other analyses can be considered. For example, given that the macrocycles will exhibit facile conformational equilibria in solution, an average osmium- C_{dis} value might be applied. Nonetheless, for the purpose of designing target molecules, we favor the most conservative (space restrictive) approach.

The radius of the phenyl substituted $\text{Os}(\text{CO})_2(\text{Ph})_2$ rotator in **12a** (7.318 Å) greatly exceeds the horizontal clearances in the complexes with seventeen membered macrocycles (4.702 Å–5.095 Å; five complexes). Importantly, the complexes in Table 2 that contain nineteen and twentyone membered macrocycles do *not* exhibit additional clearance (**6b**(1), 4.163 Å; **6b**(2), 4.834 Å; **6c**, 4.161 Å; **7b**, 4.238 Å; **7c**, 4.039 Å). In other words, larger macrocycles do not necessarily translate into more laterally spacious interior domains, at least in the “snapshots” afforded by crystal structures. For **6c** and **7c**, it is easy to see (Fig. 5 and 7) that the “extra length” is applied more in a vertical than horizontal dimension. However, other methylene carbon atoms in **6c** and **7c** extend to nearly the same radius as the phenyl substituted rotator (7.159–7.193 Å). Accordingly, the $\text{Pt}(\text{Ph})_2$ rotators in analogous square planar complexes

Fig. 16 Space filling representations of the crystal structures of **6a** and **9a** illustrating the “horizontal clearance” between the rotator and the distal carbon atoms of the macrocycles.

undergo rapid rotation through twentyone membered macrocycles, but are blocked by seventeen membered macrocycles.^{8b}

In an earlier study involving large numbers of crystal structures of square planar gyroscope like platinum and palladium complexes, the *gauche/anti* torsional sequences in the macrocycles were mapped, but little was found in the way of “conserved motifs” or common features.^{8b} The situation is similar for the structurally characterized osmium complexes in Fig. 3–12, and therefore these data are archived in the ESI (Table S3†). However, with a single exception, all of the P–CH₂–CH₂–CH₂ segments exhibit *anti* conformations, with torsion angles ranging from $\pm 153.53^\circ$ to $\pm 179.50^\circ$.

In connection with the P–CH₂–CH₂–CH₂ segments, another consideration briefly mentioned above concerns the vertical or “top/bottom” clearance associated with the stators. In other words, to what extent does a rotator substituent passing through the macrocycle interact with the phosphorus bound methylene groups H₂C–P–M–P–CH₂? This is best appreciated by referring to the representations in Fig. 17, which show typical dichloride (**6a**) and dibromide (**7b**) complexes with key atoms at van der Waals radii. Moderate interactions are evident, some of which will increase as the rotators rotate. Those within the dibromide complex are greater.

In terms of metrics, the H₂C–P–P–CH₂ torsion angles within each macrocycle (Fig. 13, right) average 25.17° for the octahedral complexes (for trigonal bipyramidal **9a**, 38.13°). The corresponding carbon–carbon distances range from 5.947 Å to 6.656 Å. When the van der Waals radii of two carbon atoms are subtracted (3.40 Å), effective clearances of 2.547 Å to 3.256 Å are obtained. In all cases, these values are smaller than the ligand with the largest *diameter* (van der Waals diameter of Br, 3.70 Å; Cl, 3.50 Å; C, 3.40 Å; said differently, in this dimension that “fatness” of the rotator trumps the radius). Thus, the attendant steric interactions must con-

tribute to the rotational barriers. This furthermore suggests, in accord with intuitive expectations, that the rotation of the rotator is correlated to conformational changes in the macrocycles that expand these distances.

Anything that can increase the dimensions imposed by the stator should attenuate the “friction” associated with rotation of the rotator, and the lower barriers should give more effective molecular gyroscopes. Obviously, interactions are reduced upon going from iron to osmium based stators and rotators, and as is currently under study with iron analogs, from phosphorus to arsenic or antimony containing stators.⁴⁰ Another strategy would involve replacing the ligating phosphorus atoms with alkynyl groups.

As briefly noted in the results section and reflected by the data in Table 2, there is only one adduct in which the osmium rotator may be able to rotate in the solid state without being significantly impeded by a neighboring molecule, namely trigonal bipyramidal **9a** (4.592 Å rotator radius *vs.* 4.386 Å closest contact). Interestingly, this is found quite often in the crystal structures of neutral trigonal bipyramidal gyroscope like complexes.⁴¹ Therefore, with this class of compounds it may be possible to realize molecular gyroscopes both in solution and the solid state. The latter would represent, in the Garcia-Garibay formalism, “amphidynamic crystals”.⁴

Summary and prospective

Scheme 1 has been successfully extended to syntheses of gyroscope like complexes with Os(CO)₂(X)₂ rotators (X = Cl, Br) and stators comprised of *trans* spanning P(CH₂)_nP linkages (*n* = 14, 16, 18). However, they are accompanied by isomers derived from a mixed intra/interligand metathesis mode, which dominate in the case of *n* = 16. The chloride or bromide ligands in these octahedral systems undergo both substitution and reduction, with the latter affording (under CO atmospheres) trigonal bipyramidal gyroscope like complexes with Os(CO)₃ rotators. These can be protonated by acids HX to give octahedral cationic hydride complexes.

The rotators of all of these complexes except a Os(CO)₂(Ph)₂ species undergo rapid rotation on the NMR time scale in solution at room temperature or below. For the octahedral complexes, this ease has been attributed to a combination of ground state strain and fewer eclipsing interactions in the transition state. Many of the gyroscope like complexes can be crystallized, but except for the Os(CO)₃ species (*n* = 14), rotations of the rotators are blocked by intermolecular contacts in the solid state.

These data are part of a larger body of work directed at enhancing the void space within the cage like stators, such that rotational barriers are minimized. In all of these molecules, rotation is Brownian – *i.e.*, both clockwise and counter-clockwise. However, unidirectional rotation is required for gyroscopic properties. Towards this end, any dipole moment associated with a rotator can be used to orient the rotator in a static electric field, or drive rotation in a rotating electric field.^{2,42} All of the compounds described above except **9a** feature dipolar rotators, but for various reasons most are less

Fig. 17 Crystal structures of the octahedral dichloride and dibromide complexes **6a** and **7b** illustrating the “vertical clearance” between ligands on the rotators (chloride or bromide, CO) and the P(CH₂)₃ moieties of the stators (these atoms shown at van der Waals radii).

than ideal (e.g., with salts, interactions with counter ions lead to increased barriers). However, many attractive derivatives or homologs are easily identified, and these will be synthesized and investigated in future reports from this laboratory.

Experimental section

The full Experimental section is provided in the ESI.[†] The portion presented below is restricted to one representative procedure for each type of transformation. Homologous or isomeric compounds were synthesized analogously. Full spectroscopic data are presented in the ESI.[†]

cis,cis,trans-Os(CO)₂(Cl)₂(P((CH₂)₆CH=CH₂)₃)₂ (2a)

A Fischer-Porter bottle was charged with (NH₄)₂OsCl₆ (0.507 g, 1.16 mmol) and 2-methoxyethanol (40 mL). The red suspension was stirred at 110 °C under CO (10 bar) until it turned pale yellow (5–7 d). Then **1a** (1.55 g, 4.25 mmol) was added with stirring and the solution kept at 80 °C for 24 h. The solvent was removed by oil pump vacuum and the resulting red-brown oil chromatographed (SiO₂ column, 3.5 cm × 30 cm, 2 : 1 v/v hexanes/CH₂Cl₂). The solvent was removed from the product containing fractions by oil pump vacuum to give **2a** (0.883 g, 0.844 mmol, 73%) as a pale yellow oil. Anal. calcd (%) for C₅₀H₉₀Cl₂O₂P₂Os (1046.33): C 57.39, H 8.67; found C 56.97, H 8.74.

cis,cis,trans-Os(CO)₂(Br)₂(P((CH₂)₆CH=CH₂)₃)₂ (3a)

A Fischer-Porter bottle was charged with (NH₄)₂OsBr₆ (0.500 g, 0.709 mmol) and 2-methoxyethanol (40 mL). The deep red solution was stirred at 80 °C under CO (10 bar) until it turned pale yellow (3–5 d). Then **1a** (0.950 g, 2.61 mmol) was added with stirring and the solution kept at 80 °C for 24 h. The solvent was removed by oil pump vacuum and the resulting red-brown oil chromatographed (SiO₂ column, 3.5 cm × 30 cm, 5 : 2 v/v hexanes/CH₂Cl₂). The solvent was removed from the product containing fractions by oil pump vacuum to give **3a** (0.441 g, 0.388 mmol, 55%) as a pale yellow oil. Anal. calcd (%) for C₅₀H₉₀Br₂O₂P₂Os (1135.23): C 52.90, H 7.99; found C 53.22, H 8.26.

Alkene metathesis of 2a

A Schlenk flask was charged with **2a** (0.714 g, 0.683 mmol) and chlorobenzene (700 mL; the resulting solution was 0.0010 M). Then solid Grubbs' catalyst (0.039 g, 0.048 mmol, 7.0 mol%) was added with stirring. The solution was aspirated with N₂, and periodically monitored by ¹H NMR. After the reaction was complete (ca. 24 h), the solution was aspirated with air (30 min) to decompose the remaining catalyst. The solution was filtered through Al₂O₃ (3 cm × 5 cm), which was washed with CH₂Cl₂. The solvents were removed from the filtrate to give crude **4a** (0.571 g, 0.594 mmol, 87%) as a light brown sticky oil.

cis,cis,trans-Os(CO)₂(Cl)₂(P((CH₂)₁₄)₃)₂ (6a) and *cis,cis,trans*-Os(CO)₂(Cl)₂(P(CH₂)₁₃CH₂)((CH₂)₁₄)(P(CH₂)₁₃CH₂) (6'a)

A Schlenk flask was charged with **4a** (0.571 g, 0.594 mmol; the entire quantity prepared above), THF (30 mL), and PtO₂ (0.023 g, 0.102 mmol), connected to a gas balloon, and partially evacuated. Then H₂ (1 bar) was introduced, and the suspension was stirred. After 3 d, the solvent was removed by oil pump vacuum. The black residue was filtered through Al₂O₃ with CH₂Cl₂. The solvent was removed from the filtrate and the residue was chromatographed (SiO₂ column, 3.5 cm × 30 cm, 3 : 2 v/v hexanes/CH₂Cl₂). The solvents were removed from the product containing fractions by oil pump vacuum to give **6a** (0.186 g, 0.192 mmol, 28% from **2a**) as a white solid and **6'a** (0.084 g, 0.087 mmol, 13% from **2a**) as a colorless sticky oil that solidified after one week.

6a: Dec. pt. (capillary) 260 °C.⁴³ DSC (*T_i*/*T_e*/*T_p*/*T_c*/*T_f*):⁴⁴ 32.3/39.6/41.1/42.7/56.1 °C (endotherm); 74.0/84.5/85.8/87.6/109.2 °C (endotherm); 165.6/181.5/183.1/184.8/199.0 °C (endotherm), 244.5/248.0/253.4/258.2/273.3 °C (endotherm). TGA: onset of mass loss, 295.0 °C. Anal. calcd (%) for C₄₄H₈₄Cl₂O₂P₂Os (968.22): C 54.58, H 8.74; found C 55.01, H 8.90.

6'a: mp (capillary) 67 °C. Anal. calcd (%) for C₄₄H₈₄Cl₂O₂P₂Os (968.22): C 54.58, H 8.74; found C 54.58, H 8.70.

trans-Os(CO)₃(P((CH₂)₁₄)₃) (9a)

A Schlenk flask was charged with **2a** (0.100 g, 0.107 mmol) or **3a** (0.100 g, 0.098 mmol) and THF (10 mL). The solution was aspirated with CO (15 min). Then a suspension of C₈K (0.331 g, 2.45 mmol or 0.361 g, 2.68 mmol) in THF (10 mL) was slowly added. The reaction was monitored by ³¹P NMR. After the educt had been consumed, graphite powder and unreacted C₈K were removed by cannula filtration. The filtrate was concentrated to 5 mL by oil pump vacuum, and MeOH (20 mL) was added. The colorless precipitate was isolated by filtration and washed with MeOH. The filter was rinsed with CH₂Cl₂ to dissolve the product and remove insoluble solids. The solvent was removed from the filtrate and the residue dried by oil pump vacuum to give **9a** (0.086 g, 0.093 mmol, 87%, or 0.074 g, 0.080 mmol, 82%) as a white solid, mp 248 °C, dec (gradual darkening, >180 °C; capillary). DSC (*T_i*/*T_e*/*T_p*/*T_c*/*T_f*):⁴⁴ 94.7/95.3/118.1/127.8/127.8 °C (endotherm, minor); 127.9/144.9/148.3/150.5/155.8 °C (endotherm). TGA: onset of mass loss, 230.6 °C. Anal. calcd (%) for C₄₅H₈₄O₃P₂Os (925.32): C 58.41, H 9.15; found C 58.38, H 8.80.

mer,trans-[Os(H)(CO)₃(P((CH₂)₁₄)₃)]⁺ CF₃SO₃[−] (9a-H⁺CF₃SO₃[−])

A 5 mm NMR tube was charged with **9a** (0.010 g, 0.011 mmol), CDCl₃ (0.5 mL), and CF₃SO₃H (0.002 mL, 0.02 mmol). NMR spectra showed the quantitative generation of **9a-H⁺CF₃SO₃[−]**.

mer,trans-[Os(H)(CO)₃(P((CH₂)₁₄)₃)]⁺ BARf[−] (9a-H⁺BARf[−])

A Schlenk flask was charged with **9a** (0.047 g, 0.051 mmol), CH₂Cl₂ (10 mL), and [H(OEt₂)₂]⁺ BARf[−] (0.052 g, 0.051 mmol)

with stirring. After 24 h, the solvent was removed by oil pump vacuum. The residue was washed with hexanes and dried by oil pump vacuum to give **9a**-H⁺ BAr_f⁻ (0.073 g, 0.041 mmol, 80%) as a colorless powder, mp 181 °C (capillary). TGA:⁴⁴ onset of mass loss, 190.9 °C. Anal. calcd (%) for C₇₇H₉₇-BF₂₄O₃P₂Os (1789.54): C 51.68, H 5.46; found C 51.96, H 5.63.

cis,cis,trans-Os(CO)₂(Me)₂(P((CH₂)₁₄)₃P) (**11a**)

A Schlenk flask was charged with **6a** (0.100 g, 0.104 mmol) and THF (10 mL) and cooled to 0 °C. Then MeLi (1.6 M in Et₂O, 1.35 mL, 2.16 mmol) was added with stirring. After 24 h, a few drops of water were added. The solvent was removed by oil pump vacuum and the residue filtered through Al₂O₃ using CH₂Cl₂. The solvent was removed from the filtrate by oil pump vacuum to give **11a** (0.095 g, 0.102 mmol, 98%) as a colorless powder, mp 247 °C (capillary). DSC (T_i/T_e/T_p/T_c/T_f):⁴⁴ 36.6/39.0/47.0/49.8/53.5 °C (endotherm); 53.5/54.3/56.6/58.8/60.7 °C (endotherm, minor); 61.0/61.8/68.5/74.7/77.3 °C (endotherm, minor); 79.8/85.0/91.1/95.7/97.5 °C (endotherm, minor); 201.9/210.5/213.8/215.6/220.9 °C (endotherm, minor). TGA: onset of mass loss, 230.3 °C. Anal. calcd (%) for C₄₆H₉₀O₂P₂Os (927.38): C 59.58, H 9.78; found C 59.87, H 9.52.

cis,cis,trans-Os(CO)₂(Ph)₂(P((CH₂)₁₄)₃P) (**12a**)

A Schlenk flask was charged with **7a** (0.205 g, 0.194 mmol) and THF (20 mL) and cooled to 0 °C. Then PhLi (2.0 M in Bu₂O, 1.00 mL, 2.16 mmol) was added with stirring. The cold bath was removed. After 2 h, the solution was refluxed. After 1 h, a few drops of water were added. The solvents were removed by oil pump vacuum and the residue chromatographed (SiO₂ column, 2.5 cm × 30 cm, 3 : 1 v/v hexanes/CH₂Cl₂). The solvents were removed from the product-containing fractions by oil pump vacuum to give **12a** (0.118 g, 0.112 mmol, 58%) as a colorless oil that solidified after one week, mp 162–164 °C (capillary). Anal. calcd (%) for C₅₆H₉₄O₂P₂Os (1051.52): C 63.96, H 9.01; found C 63.70, H 8.96.

Acknowledgements

We thank the US National Science Foundation (CHE-0719267, CHE-1153085), the Deutsche Forschungsgemeinschaft (DFG, GL 300/9-1), and Johnson Matthey PMC (precious metal loans) for support.

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