1456 *Organometallics* **2001,** *20,* 1456−1461

Synthesis and Characterization of Chair and Boat Forms of *fac*-Re(CO)$_3$(P$_3$)(X) [P$_3$ = η^2-CH$_3$C(CH$_2$PPh$_2$)$_3$, X = Br, Cl]

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Received November 28, 2000

The syntheses of complexes having the general formula *fac*-Re(CO)$_3$(η^2-triphos)X (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane; **1** and **2**, X = Br; **5** and **6**, X = Cl) from reactions of Re(CO)$_5$X and triphos are described. The X-ray structure of **1** shows that the six-membered metallacyclic ring (ReP$_2$C$_3$) adopts a chair conformation like the known complex **5**, while structural data for **2** and **6** indicate boat forms for the metallacyclic rings. This represents the first identification of boat forms of these complexes. The pendant phosphines in compounds **1** and **2** can be oxidized, yielding compounds **3** and **4**, respectively. The X-ray structure of **4** retains the boat form of its precursor and the properties of **3** are different, suggesting that the ring conformation was retained here also. Thermolysis reactions of **5** and **6** were conducted to probe for differences in the ease of decarbonylation and conversion to the known η^3-coordinated complex, **7**. The boat complex **6** is converted more readily to **7**; there is no evidence for any thermal conversion of **6** to **5**.

Introduction

Transition metal complexes with the tripodal polyphosphine ligand CH$_3$C(CH$_2$PPh$_2$)$_3$ (1,1,1-tris(diphenylphosphinomethyl)ethane: triphos) have received attention in recent years due to their high catalytic activity in a wide range of reactions such as hydrogenation and hydroformylation of olefins.[1] Triphos, with electronic properties resembling the cyclopentadienyl anion, is able to form stable complexes with metals in a variety of oxidation states by occupying three facial sites at the metal centers.[2] Complexes with the Re(CO)$_2$(η^3-triphos) fragment were reported several years ago[3] and demonstrated interesting reactivities.[4] While triphos could form complexes in η^3-fashion, dissociation of one phosphine, known as "arm-off" dissociation, has been implicated in some catalytic reactions.[5] In several instances, the formation of species with η^2-coordination of the triphos has been implicated from ^{31}P NMR spectral data or oxidation of the pendant phosphine.[6−8] In some cases, this species was observed to exhibit two forms.[7−9] Since we are interested in catalysts and catalytic intermediates in CO$_2$ reduction processes,[10] we sought synthetic methods for new rhenium(I) complexes with bidentate triphos ligands. We found that chair and boat isomers of the six-membered metallacyclic ring (ReP$_2$C$_3$) formed by η^2-coordination of triphos to rhenium were present in products with the general formula *fac*-Re(CO)$_3$(η^2-triphos)X (X = Br, Cl); see Chart 1 (phenyl groups have been omitted for clarity). This is the first identification of boat isomers in this series. Herein we report the synthesis and characterization of all four complexes and the phosphine oxide derivatives of two of them.

Results and Discussion

1. Synthesis and Spectral Properties of Complexes 1−6. Reaction of Re(CO)$_5$Br with triphos for 7 h in refluxing methanol produced a white precipitate, which was collected from the cooled mixture. Examination of the NMR spectra of the product indicated the presence of two compounds, which could be separated

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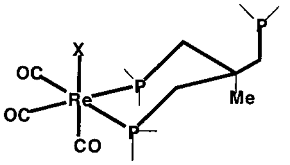
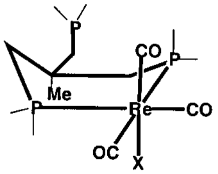
10.1021/om001018l CCC: $20.00

Chart 1



1: X = Br; **5**: X = Cl



2: X = Br; **6**: X = Cl

readily because of differences in their solubility in acetone. The insoluble complex **1** shows ^{1}H resonances at δ 3.54 (d), 2.42 (dd), 2.35 (s) for the CH$_2$ groups and a single resonance at δ 0.32 for the CH$_3$ group; the ^{13}C NMR spectrum showed a triplet at δ 192.40 and a slightly overlapped doublet of triplets at δ 189.41 for the carbonyl groups in addition to resonances for the triphos ligand (see Experimental Section). Complex **2** displays resonances at δ 3.41 (dd), 2.66 (dd), 1.83 (s) for the CH$_2$ groups and a resonance at δ 1.03 for the CH$_3$ group in CD$_2$Cl$_2$; the ^{13}C NMR spectrum showed a triplet at δ 190.89 and an overlapped doublet of triplets at δ 189.91 in addition to resonances for the triphos ligand (see Experimental Section). Integration of CH$_3$ groups in the ^{1}H NMR spectrum of the crude mixture indicated that it was composed of 54% **1** and 46% **2**. The IR spectrum of **1** showed strong bands for the carbonyl ligands at 2028, 1952, and 1891 cm^{-1}, and the spectrum of **2** showed strong bands at 2030, 1949, and 1909 cm^{-1}; these patterns are consistent with facial arrangements of the carbonyl ligands in each compound.[11] Elemental analyses were in agreement with the formulation of both compounds as Re(CO)$_3$(triphos)Br, suggesting η^2-coordination of the triphos ligand. The two isomers showed very similar ^{31}P NMR spectra; each consisted of two singlets (δ −14.71 and −27.69 for **1** and δ −14.26 and −28.89 for **2**) with relative ratios of 2:1, respectively. The high-field resonances in the ^{31}P spectra of both compounds are close to that of free triphos (δ −25.86 ppm in CD$_2$Cl$_2$) and are assigned to the noncoordinated phosphorus atom. This assignment is also supported by their COSY (^{1}H−^{1}H correlation) and HSQC (^{1}H−^{13}C correlation) spectra. The COSY spectrum of **2** (in CD$_2$Cl$_2$) shows correlation of the proton resonances at δ 2.66 and 3.41, identifying these as the diastereotopic protons of the methylene carbons bound to the coordinated phosphorus ligands. The HSQC spectrum of **2** shows correlation of both of these proton resonances with the carbon resonance at δ 34.96, while the proton resonance at δ 1.83 is correlated with the carbon resonance at δ 45.53 (CH$_2$ adjacent to the uncoordinated phosphorus) and the proton resonance at δ 1.03 (methyl protons) correlates with the carbon resonance at δ 34.32. The COSY spectrum of **1** was obtained initially in CD$_2$Cl$_2$ and suggests that the proton resonances at δ 3.54 and 2.42 are correlated. The spectrum was also obtained in toluene-*d*$_8$, which allowed better separation of the close resonances at δ 2.35 and 2.42; in toluene, these are at δ 2.19 and 2.29 and the correlation is clear. The HSQC spectrum of **1** (in CD$_2$Cl$_2$) showed that both resonances at δ 2.42 and 3.54 correlate with the carbon resonance at δ 34.71, while the methylene protons adjacent to the uncoordinated phosphorus, at δ 2.35, are correlated with the carbon resonance at δ 51.86 and the methyl protons at δ 0.32 are correlated with the carbon resonance at δ 30.24.

The chair and boat isomers are stable in the solid form and in solution at room temperature. Also, these complexes are stable toward oxygen even in solution. However, when **1** or **2** was dissolved in ether, traces of the corresponding phosphine oxide complexes (**3** and **4**) were detected. It appears that peroxide impurities in the solvent may be responsible for the oxidation. Treating **1** and **2** with *tert*-butyl hydroperoxide afforded near quantitative conversions into **3** and **4**, respectively. The ^{31}P NMR spectrum of **3** and **4** showed that the resonances for the phosphine oxides shifted greatly (to δ 25.36 and 24.54 for **3** and **4**, respectively), while those for the coordinated phosphines were changed only slightly. The ^{13}C NMR chemical shifts of **3** and **4** exhibit little variation as compared with those in **1** and **2**. The ^{1}H NMR spectra for **3** and **4** are very similar to those of **1** and **2**, except for the methylene resonances adjacent to the pendant phosphorus ligands, which shift downfield slightly and change from broad singlets to doublets.

The synthesis and structure of *fac,chair*-Re(CO)$_3$(η^2-triphos)Cl (**5**) has been reported previously.[12] The complex was prepared in low yield by photolysis of a solution of Re$_2$(CO)$_{10}$ and triphos in dichloromethane.[12a] The ^{31}P NMR spectrum was reported to consist of two singlets at δ −11.26 and −11.43 in a ratio of 2:1, which the authors assigned to **5**. In view of the ^{31}P NMR spectral properties of the bromo derivatives, it seemed unlikely to us that either single chloro complex would exhibit these resonances. We carried out the synthesis of Re(CO)$_3$(η^2-triphos)Cl by refluxing Re(CO)$_5$Cl with triphos in MeOH overnight; a white precipitate formed during this time. As expected, the ^{1}H NMR spectrum of the crude mixture was very similar to that of the bromo complexes, even in the composition, revealing a 54% to 46% ratio of two compounds. The two isomers were separated by trituration with ether; the minor isomer is soluble, while the major isomer is almost insoluble. Compounds **5** and **6** exhibit IR and ^{1}H, ^{13}C, and ^{31}P NMR spectra that are very similar to the corresponding bromo derivatives **1** and **2** (see Experimental Section) and appeared to have η^2-coordinated triphos ligands. The boat form of the metallacyclic ring in **6** was confirmed for this isomer by X-ray crystallography (see discussion below). The ^{31}P NMR spectrum of **5** showed resonances at δ −10.49 and −27.39 in a ratio of 2:1. The ^{31}P NMR spectrum of **6** showed resonances at δ −10.32 and −28.39 in a ratio of 2:1. Thus, the ^{31}P NMR spectral data reported previously appear to represent the lower field resonances of a mixture containing both **5** and **6**.

The phosphine oxide derivative of **6** was reported previously as a minor product from the reaction that produced **5**;[12b] the compound was structurally characterized, although its origin was not detailed. However, this supports our conclusion that the previous synthesis of **5** probably also produced **6**.

A few generalizations can be made about the spectral properties of these compounds. The IR spectra of all of

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Table 1. Crystal Data and Structure Refinement Parameters for Complexes 1, 2, 4, and 6

	1	**2**	**4**	**6**
empirical formula	$C_{44}H_{39}BrO_3P_3Re$	$C_{44}H_{39}BrO_3P_3Re{\cdot}0.7CH_2Cl_2$	$C_{44}H_{39}BrO_4P_3Re{\cdot}C_6H_{14}$	$C_{44}H_{39}ClO_3P_3Re{\cdot}1.4CH_2Cl_2$
fw	974.77	1034.22	1062.83	1046.39
temp, K	293(2)			
wavelength, Å	0.71073			
cryst syst	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a, Å	9.837(2)	11.090(2)	11.088(5)	14.630(4)
b, Å	9.867(2)	14.560(3)	14.868(6)	15.309(4)
c, Å	21.297(7)	14.690(3)	15.044(6)	21.382(7)
α, deg	77.66(3)	103.27(3)	74.82(3)	90
β, deg	83.09(3)	91.48(3)	73.21(4)	99.78(3)
γ, deg	83.11(3)	105.09(3)	89.95(3)	90
V, Å^3	1995.2(7)	2219.8(8)	2284(2)	4719.3(16)
Z	2	2	2	4
D_{calcd}, g/cm^3	1.623	1.547	1.545	1.473
abs coeff, mm^{-1}	4.206	3.867	3.683	2.928
θ range, deg	2.10−24.97	2.08−26.48	2.04−24.97	2.06−23.00
no. reflns measd	7241	9685	8473	10349
no. unique (R_{int})	7032 (0.0258)	9173 (0.0162)	8011 (0.0345)	6212 (0.0251)
R1, wR2^a ($I > 2\sigma I$)	0.0297, 0.0692	0.0292, 0.0758	0.0449, 0.1236	0.0352, 0.0806
GOF	1.023	1.051	1.149	1.068
max diff peak, e/Å^3	1.257	1.103	1.322	0.807

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 1

Bond Distances			
Re−C(1)	1.949(5)	Re−Br	2.6414(9)
Re−C(2)	1.894(5)	Re−P(1)	2.4624(14)
Re−C(3)	1.944(5)	Re−P(2)	2.4931(14)
Bond Angles			
C(1)−Re−P(1)	89.13(14)	Br−Re−C(1)	86.85(16)
C(2)−Re−P(1)	96.37(15)	Br−Re−C(2)	174.78(14)
C(3)−Re−P(1)	171.27(15)	Br−Re−C(3)	84.98(15)
C(1)−Re−P(2)	170.82(15)	Br−Re−P(1)	86.38(4)
C(2)−Re−P(2)	100.24(14)	Br−Re−P(2)	84.26(4)
C(3)−Re−P(2)	92.27(15)	P(1)−Re−P(2)	88.03(4)
C(1)−Re−C(2)	88.8(2)		
C(1)−Re−C(3)	89.2(2)		
C(2)−Re−C(3)	92.2(2)		

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for 2.

Bond Distances			
Re−C(1)	1.943(4)	Re−Br	2.6489(8)
Re−C(2)	1.902(4)	Re−P(1)	2.4639(12)
Re−C(3)	1.949(5)	Re−P(2)	2.4634(11)
Bond Angles			
C(1)−Re−P(1)	94.13(13)	Br−Re−C(1)	85.82(13)
C(2)−Re−P(1)	92.29(14)	Br−Re−C(2)	173.77(12)
C(3)−Re−P(1)	175.75(12)	Br−Re−C(3)	86.84(13)
C(1)−Re−P(2)	173.12(13)	Br−Re−P(1)	91.97(4)
C(2)−Re−P(2)	97.53(13)	Br−Re−P(2)	87.35(4)
C(3)−Re−P(2)	90.61(13)	P(1)−Re−P(2)	85.26(4)
C(1)−Re−C(2)	89.34(18)		
C(1)−Re−C(3)	89.86(18)		
C(2)−Re−C(3)	89.23(18)		

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for 4

Bond Distances			
Re−C(1)	1.945(7)	Re−P(1)	2.4674(18)
Re−C(2)	1.896(8)	Re−P(2)	2.4655(18)
Re−C(3)	1.956(8)	P(3)−O(4)	1.474(7)
Re−Br	2.6523(9)		
Bond Angles			
C(1)−Re−P(1)	95.9(2)	Br−Re−C(1)	86.5(2)
C(2)−Re−P(1)	91.6(2)	Br−Re−C(2)	174.6(2)
C(3)−Re−P(1)	175.2(2)	Br−Re−C(3)	88.2(2)
C(1)−Re−P(2)	173.6(3)	Br−Re−P(1)	91.35(5)
C(2)−Re−P(2)	97.6(3)	Br−Re−P(2)	87.15(5)
C(3)−Re−P(2)	89.9(2)	P(1)−Re−P(2)	85.27(6)
C(1)−Re−C(2)	88.6(4)		
C(1)−Re−C(3)	88.9(3)		
C(2)−Re−C(3)	89.3(3)		

the chair complexes (**1**, **3**, and **5**) show two strong carbonyl bands above 1900 cm^{-1} and one strong band slightly below this frequency. All boat complexes (**2**, **4**, and **6**) show three strong bands above 1900 cm^{-1}. In the ^{1}H NMR spectra, the methyl resonances of the triphos ligand appear at less than 1 ppm in all chair complexes, while those of the boat complexes appear at more than 1 ppm.

Solid-State Structures of Compounds 1, 2, 4, and 6. The structures of the compounds were determined by X-ray crystallography. Data collection parameters are given in Table 1. Selected bond distances and angles of these complexes are listed in Tables 2−5. The Re atom in all four complexes is octahedrally coordinated to three carbonyl ligands (in a facial arrangement), two phosphorus atoms of triphos, and a halide atom. There are two unusual characteristics for these complexes: (a) the conformations of the metallacyclic rings (ReP_2C_3) formed by η^2-coordination of the triphos to rhenium and (b) the orientation of the pendant phosphine group with respect to the halide atom.

The ORTEP view of **1** is shown in Figure 1. The bond distances of Re−CO, 1.894(5), 1.944(5), and 1.949(5) Å, Re−P, 2.4624(14) and 2.4931(14) Å, and Re−Br, 2.6414(9) Å, are unexceptional when compared with other structurally characterized rhenium complexes with diphosphine ligands, *fac*-Re(CO)$_3$(P$_2$)X (X = Br or Cl).[13] The equatorial Re−CO bonds are slightly longer than the axial Re−CO, consistent with the phosphines' greater trans influence. The six-membered ring formed by Re, P(1), C(4), C(5), C(6), and P(2) exhibits a chair

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Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for 6

Bond Distances

Re−C(1)	1.942(8)	Re−Cl	2.511(2)
Re−C(2)	1.892(9)	Re−P(1)	2.482(2)
Re−C(3)	1.940(9)	Re−P(2)	2.4545(18)

Bond Angles

C(1)−Re−P(1)	91.7(3)	Cl−Re−C(1)	90.6(3)
C(2)−Re−P(1)	99.3(3)	Cl−Re−C(2)	177.1(2)
C(3)−Re−P(1)	170.6(3)	Cl−Re−C(3)	88.7(3)
C(1)−Re−P(2)	175.7(3)	Cl−Re−P(1)	82.08(6)
C(2)−Re−P(2)	90.0(2)	Cl−Re−P(2)	92.65(6)
C(3)−Re−P(2)	93.0(2)	P(1)−Re−P(2)	86.02(6)
C(1)−Re−C(2)	86.8(4)		
C(1)−Re−C(3)	89.9(3)		
C(2)−Re−C(3)	90.0(4)		

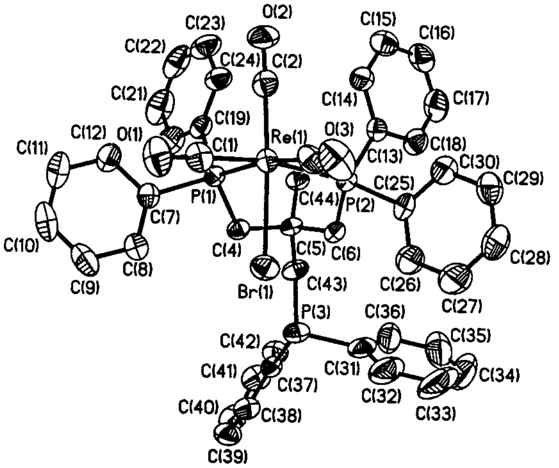

Figure 1. ORTEP drawing of **1** with thermal ellipsoids shown at the 50% probability level.

conformation with P(1), C(4), C(6), and P(2) at the base (mean deviation 0.0135 Å); deviations of Re and C(5) from the least-squares plane defined by P(1), C(4), C(6), and P(2) are −1.063 and +0.708 Å, respectively. The P(1)−Re(1)−P(2) angle, 88.03(4)°, is significantly larger than those in the Re(CO)$_2$(η^3-triphos) fragment[3] (average value 85.1°) but closer to those of Re(CO)$_3$(dppp)X (X = O, C; dppp = 1, 3-bis(diphenylphosphino)propane) with an average of 88.5°,[14] which exhibit the chair conformation exclusively. The pendant phosphine group adopts a position syn to Br and below the six-membered metallacyclic ring. This arrangement avoids steric crowding between the phenyl groups of the pendant phosphine and those of the coordinated P(1) and P(2). There are a number of bond angles that are distorted with respect to octahedral geometry: C(2)−Re−P(1) and C(2)−Re−P(2) are both greater than 90°, resulting in Br−Re−P(1) and Br−Re−P(2) angles that are compressed well below 90°. Also, C(2)−Re−Br is compressed to less than 175°, and C(1)−Re−P(2) is compressed even lower.

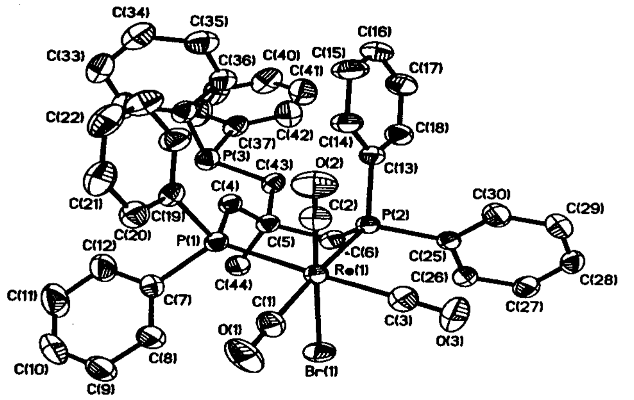

Figure 2. ORTEP drawing of **2** with thermal ellipsoids shown at the 50% probability level.

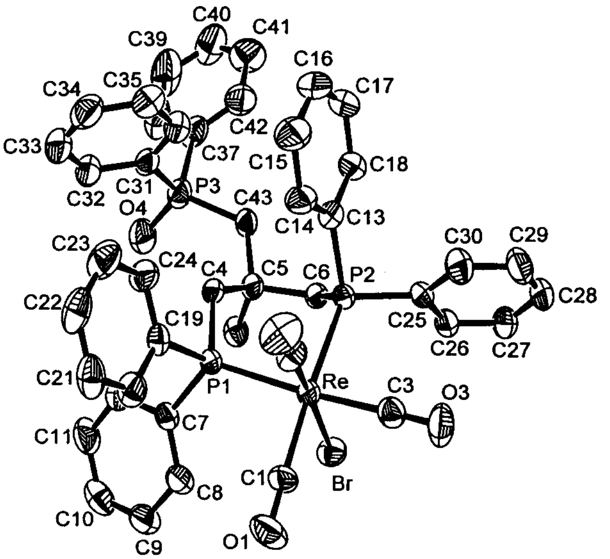

Figure 3. ORTEP drawing of **4** with thermal ellipsoids shown at the 50% probability level.

The ORTEP view of **2** is shown in Figure 2. The bond distances of Re−CO, 1.902(4), 1.943(4), and 1.949(5) Å, Re−P, 2.4634(11) and 2.4639(12) Å, and Re−Br, 2.6489(8) Å, are close to those of **1**. The six-membered metallacyclic ring formed by Re(1), P(1), C(4), C(5), C(6), and P(2) clearly exhibits a boat conformation in the solid state. Re(1), P(1), C(5), and C(6) form the base of the boat (mean deviation 0.0002 Å), while P(2) and C(4) are out of this plane; deviations of P(2) and C(4) from the base are +0.977 and +0.619 Å, respectively. The P(1)−Re(1)−P(2) angle, 85.26(4)°, is significantly smaller than that in **1** but close to that typical of the Re(CO)$_2$(η^3-triphos) fragment (see discussion above). The pendant phosphine group adopts an anti position with respect to Br and syn to C(2)−O(2). Again, the shortest Re−C(carbonyl) bond is the one trans to Br. The C(2)−Re−P(2) bond angle is enlarged, resulting in slight compression of the Br−Re−P(2) angle, but greater compression of the C(1)−Re−P(2) and C(1)−Re−Br angles. The pendant phosphorus is anti to the Br, and the P(3)−C(43)−C(5) angle is 116.9(3)°.

The ORTEP view of **4** is shown in Figure 3 and clearly shows that the pendant phosphorus has been oxidized. The Re−CO bond distances, 1.945(7), 1.896(8), and 1.956(8) Å, and those of Re−P, 2.4674(18) and 2.4655(18) Å, and Re−Br, 2.6523(9) Å, are similar to those in **2**. Again, Re, P(1), C(5), and C(6) form the base of the boat with P(2) and C(4) out of this plane by 0.9727 and 0.6336 Å, respectively. As in **1** and **2**, the shortest Re−C(carbonyl) bond distance is the one trans to the halogen atom. Oddly, the shortest Re−C(carbonyl) bond

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[14] (a) Williams, M. T.; McEachin, C.; Becker, T. M.; Ho, D. M.; Mandal, S. K. *J. Organomet. Chem.* **2000**, *599*, 308. (b) Brown, D. A.; Mandal, S. K.; Ho, D. M.; Becker, T. M.; Orchin, M. *J. Organomet. Chem.* **1999**, *592*, 61. (c) Mandal, S. K.; Ho, D. M.; Orchin, M. *J. Organomet. Chem.* **1992**, *439*, 53.

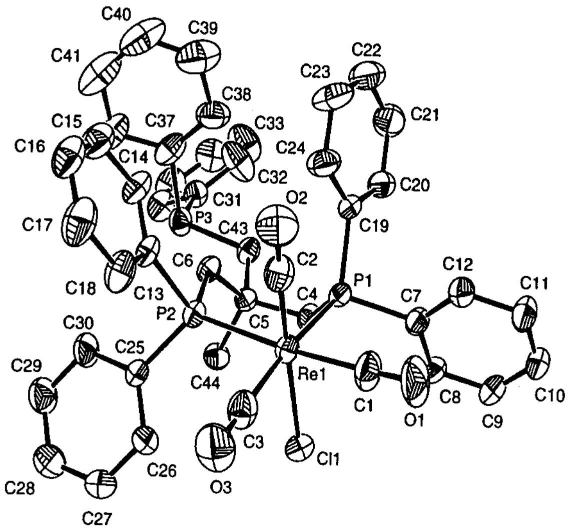

Figure 4. ORTEP drawing of **6** with thermal ellipsoids shown at the 50% probability level.

distance in the chloro derivative reported previously[12b] is *not* the one trans to Cl. There are angle deviations from octahedral geometry present in **4**, too, but these are diminished as compared to the distortions in **2**. The presence of the P(3)−O(4) bond increases the P(3)−C(43)−C(5) angle to 120.3(5)°, apparently due to steric crowding between O(4) and the methyl group at C(5).

The ORTEP view of **6** is shown in Figure 4 and shows a boat form for the metallacyclic ring. The Re−C bond distances, 1.892(9), 1.942(8), and 1.940(9) Å, are similar to those in the bromide with this ring conformation (**2**), and, again, the shortest Re−C bond is the one trans to the halogen. The atoms Re, P(2), C(4), and C(5) are coplanar (deviation is 0.0001 Å), and P(1) and C(6) are out of this plane, 0.9211 and 0.6414 Å, respectively. As in **2**, the pendant phosphorus is anti to the halogen. There are numerous angular distortions around the metal center here, also: C(2)−Re-P(1) is large, resulting in a compressed P(1)−Re−Cl angle and a C(3)−Re−P(1) angle that, at 170.6(3)°, is far less than 180°. Thermolysis reactions of the chair and boat isomers **5** and **6** were conducted to determine how readily these η^2-forms might be decarbonylated and converted to the fully chelated form and to see if there were differences in the ease of conversion of the chair and boat forms. In **5**,[12a] as in the corresponding bromide (**1**), the pendant phosphorus ligand is syn to the halogen atom, whereas, in **6**, the pendant phosphorus is anti to the halogen (and syn to a CO). In accord with expectations based on these differences in geometry, the solid-state thermolysis of **6** proceeds more easily than that of **5**, although both require high temperatures for conversion to the η^3-coordinated compound, **7**, which has been characterized previously.[3] Compound **5** showed no conversion to **7** after 4.5 h at 180 °C, but was fully converted to **7** after 1 h at 245 °C. About one-third of a sample of compound **6** was converted to **7** after 4.5 h at 180 °C. A second sample was heated to 220 °C for 20 min and showed complete conversion to **7**. Solution thermolysis of **6** was attempted in refluxing toluene; after 7 h, approximately half of the sample had converted to **7**. In no case involving the thermolysis of **6** was there any evidence of its conversion to **5**.

Experimental Section

General Materials and Methods. All reactions were carried out under a nitrogen atmosphere. Reagent grade dichloromethane, methanol, acetone, pentane, and hexane were used as received. Ether and THF were refluxed over sodium benzophenone and freshly distilled prior to use. $Re(CO)_5Cl$ and $Re(CO)_5Br$ were prepared according to the literature procedure.[15] The 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) and *tert*-butyl hydroperoxide were used as received from Aldrich. ^1H, ^{13}C, and ^{31}P NMR were recorded on a Varian INOVA-500 and a Bruker AMX-500; the ^1H and ^{13}C chemical shifts (ppm) were referenced to residual protons and carbons, respectively, in the deuterated solvents; the ^{31}P chemical shifts were determined using H_3PO_4 (85%) as the external standard. Infrared spectra were obtained by the DRIFTS[16] technique and were recorded on a ATI Mattson RS-1 FT-IR instrument by means of a Graseby Specac Inc. "Mini-Diff" accessory as KCl dispersions. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN.

Preparation of *fac,chair*-$Re(CO)_3(\eta^2$-triphos)Br (1) and *fac,boat*-$Re(CO)_3(\eta^2$-triphos)Br (2). A suspension of triphos (1.88 g, 3 mmol) with $Re(CO)_5Br$ (1.23 g, 3 mmol) in 100 mL of MeOH was refluxed for 7 h at 85 °C. After cooling, the precipitate was collected, washed with MeOH, then dried to produce a white solid (2.27 g, yield 78%). ^1H NMR analysis showed that the solid was composed of 54% **1** and 46% **2**. The two isomers can be separated easily by trituration with acetone; isomer **2** is soluble in acetone, while isomer **1** is almost insoluble. Further purification was done by recrystallization from $CH_2Cl_2-Et_2O$.

Compound 1. Anal. Calcd for $C_{44}H_{39}BrO_3P_3Re$: C, 54.21; H, 4.03. Found: C, 53.87; H, 4.27. IR ν_{CO}: 2028 (s), 1952 (s), 1891 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.79−7.26 (30H, m), 3.54 (2H, d), 2.42 (2H, dd), 2.35 (s, 2H), 0.32 (3H, s). ^{13}C NMR (CD_2Cl_2): δ 192.40 (t), 189.41 (dt), 139.43−128.15 (m), 51.86 (dt), 40.05 (d); 34.71 (dd), 30.24 (d). ^{31}P NMR (CD_2Cl_2): δ −14.71 (2), −27.69 (1).

Compound 2. Anal. Calcd for $C_{44}H_{39}BrO_3P_3Re$: C, 54.21; H, 4.03. Found: C, 54.31; H, 4.10. IR ν_{CO}: 2030 (s), 1949 (s), 1909 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.63−7.00 (30H, m), 3.41 (2H, dd), 2.66 (2H, dd),1.83 (2H, s), 1.03 (3H, s). ^{13}C NMR (CD_2Cl_2): δ 190.89 (t), 189.91 (dt), 139.56−128.30 (m), 45.53 (d), 39.24 (d); 34.96 (td), 34.32 (m). ^{31}P NMR (CD_2Cl_2): δ −14.26 (2), −28.89 (1).

Preparation of *fac,chair*-$Re(CO)_3(\eta^2$-triphos oxide)Br (3). To 10 mL of THF containing **1** (0.20 g) was added *tert*-butyl hydroperoxide (5.5 M, 80 μL). After standing for 3 h, the solution was concentrated almost to dryness, then MeOH was added to precipitate the product, 0.19 g (94% yield). Anal. Calcd for $C_{44}H_{39}BrO_4P_3Re\cdot H_2O$: C, 52.39; H, 4.10. Found: C, 52.32; H, 3.97. IR ν_{CO}: 2026 (s), 1948 (s) and 1896 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.74−7.34 (30 H, m), 3.54 (2 H, d), 2.67 (2H, dd), 2.47 (2H, d), 0.60 (3H, s). ^{13}C NMR (CD_2Cl_2): δ 191.74 (t), 189.52 (dt), 137.20−128.23 (m), 48.45 (dt), 40.28 (s, br), 34.74 (m), 31.25 (m). ^{31}P NMR (CD_2Cl_2): δ 25.36 (1), −15.02 (2).

Preparation of *fac,boat*-$Re(CO)_3(\eta^2$-triphos oxide)Br (4). To 3 mL of THF containing **2** (0.10 g) was added *tert*-butyl hydroperoxide (5.5 M, 30 μL). The solution was allowed to stand for 3 h, then pentane (30 mL) was added to precipitate **5** (0.10 g, yield 98%), mp 175−177 °C. Anal. Calcd for $C_{44}H_{39}BrO_3P_3Re$: C, 53.34; H, 3.97. Found: C, 52.98; H, 3.95. IR ν_{CO}: 2029 (s), 1962 (s), 1911 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.63−7.26 (30H, m), 3.52 (2H, dd), 2.88 (2H, dd), 1.95 (2H, d),

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[15] Schmidt, S. P.; Trogler, W. C.; Basolo, F. *Inorg. Synth.* **1990**, *28*, 160.

[16] Griffiths, P. W.; de Haseth, J. A. *Fourier Transform Infrared Spectroscopy;* Wiley: New York, 1986; Chapter 5.

1.22 (3H, s). ^{13}C NMR (CD$_2$Cl$_2$): δ 190.97 (t), 189.83 (dt), 136.30−128.33 (m), 43.16 (d), 39.58 (d); 35.23 (td), 34.51 (m). ^{31}P NMR (CD$_2$Cl$_2$): δ 24.54 (1), −14.40 (2).

Preparation of *fac,chair*-Re(CO)$_3$(η^2-triphos)Cl (5) and *fac,boat*-Re(CO)$_3$(η^2-triphos)Cl (6). A suspension of triphos (0.94 g, 1.5 mmol) with Re(CO)$_5$Cl (0.55 g, 1.5 mmol) in 50 mL of MeOH was refluxed overnight. After cooling, the precipitate was collected, washed with MeOH, then dried to produce a white solid (1.23 g, yield 87%). ^{1}H NMR analysis showed that the solid was composed of 54% **5** and 46% **6**. The two isomers can be separated easily by trituration with ether; isomer **6** is soluble in ether, while isomer **5** is almost insoluble. Further purification was done by recrystallization in CH$_2$Cl$_2$−pentane.

Compound 5. Anal. Calcd for C$_{44}$H$_{39}$ClO$_3$P$_3$Re: C, 56.80; H, 4.23. Found: C, 56.57; H, 4.27. IR ν_{CO}: 2026 (s), 1945 (s), 1892 (s) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.81−7.36 (30H, m), 3.44 (2H, d), 2.38 (4H, m), 0.44 (3H, s). ^{13}C NMR (CD$_2$Cl$_2$) δ 192.54 (t), 190.42 (dt), 139.48−128.29 (m), 51.39 (dt), 39.91 (d); 34.23 (dd), 30.41 (d). ^{31}P NMR (CD$_2$Cl$_2$): δ −10.49 (2), −27.39(1).

Compound 6. Anal. Calcd for C$_{44}$H$_{39}$ClO$_3$P$_3$Re: C, 56.80; H, 4.23. Found: C, 56.71; H, 4.35. IR ν_{CO}: 2028 (s), 1945 (s), 1907 (m) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.66−7.02 (30H, m), 3.35 (2H, dd), 2.61 (2H, dd), 1.94 (2H, s), 1.05 (3H, s). ^{13}C NMR (CDCl$_3$): δ 190.68 (t), 190.10 (dt), 138.98−128.14 (m), 46.06 (dt), 38.77 (d); 34.46 (td), 33.67 (m). ^{31}P NMR (CD$_2$Cl$_2$): δ −10.32 (2), −28.39 (1).

Thermolysis of 5. A sample of **5** (0.02 g) was placed in a Schlenk tube and then heated in an oil bath, under nitrogen, for 4.5 h at 180 °C. Spectral analysis of the sample after this time showed only compound **5**. A second sample (0.02 g) was heated, in the same way, to 245 °C for 1 h. NMR analysis of the sample showed that all of **5** had been converted to a new compound whose spectral properties are consistent with those reported for Re(CO)$_2$(η^3-triphos)Cl[3] (**7**): IR (KCl, DRIFTS) ν_{CO} 1946 (s) and 1884 (s) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$) δ 7.58−7.05 (30H, m), 2.50 (6H, m), 1.49 (3H, s). Lit.[3] IR (KBr): 1948 (s) and 1887 (s) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$) δ 2.48 (6H, m), 1.45 (3H, q).

Thermolysis of 6. A sample of **6** (0.02 g) was heated, as described for **5**, for 4.5 h at 180 °C. Spectral analysis of the sample showed that approximately one-third of **6** had been converted to **7**. A second sample was heated, in the same way, at 220 °C for 20 min; spectral analysis then showed that all of **6** had been converted to **7**. In solution in toluene (10 mL), a new sample of **6** (0.20 g) was refluxed for 7 h. After evaporation to dryness, spectral analysis showed that approximately half of **6** had been converted to **7**.

X-ray Crystal Structures of 1, 2, 4, and 6. A colorless block crystal of **1** was obtained by diffusion of ether into a CH$_2$Cl$_2$ solution of the compound. A colorless block crystal of **2** was grown from a CH$_2$Cl$_2$−Et$_2$O solution of compound maintained at 0 °C. A thin colorless needle crystal of **4** was produced by diffusion of hexane into a benzene solution of the compound. A colorless block crystal of **6** was formed by layering a CH$_2$Cl$_2$ solution of the compound with pentane.

All data were collected on an Enraf-Nonius CAD4 diffractometer at 293 K. Crystallographic data are outlined in Table 1. The structures were solved by direct methods[17] and refined[18] using the Bruker SHELXTL (version 5.10[19]) software package. ORTEP diagrams for **4** and **6** were generated from ORTEP-3.[20] Hydrogen atom positions were calculated using a riding model with U(H) = 1.2U_{eq} (attached atom) for the phenyl and methylene H's. For methyl groups, the torsion angle that defines its orientation was allowed to refine, and these hydrogen atoms were assigned U(H) = 1.5U_{eq} (attached carbon atom). Scattering and anomalous dispersion factors were taken from Cromer and Waber.[21]

For structure **1**, the final anisotropic full-matrix least-squares refinement (based on F^2) for 470 variables using 7032 (all) data converged at R1 = 0.0446 and wR2 = 0.0745. For structure **2**, the final anisotropic full-matrix least-squares refinement (based on F^2) for 497 variables using 9173 (all) data converged at R1 = 0.0384 and wR2 = 0.0793. For structure **4**, the final anisotropic full-matrix least-squares refinement (based on F^2) for 567 variables using 8011 (all) data converged at R1 = 0.0577 and wR2 = 0.1292. The hexane solvate present in this structure has numerous sites of disorder, which were adequately modeled as follows. A half-occupancy set of six carbon atoms C(70)−C(75) refined anisotropically were used to model one portion of the disorder in the hexane. C(70), C(81), and C(82) (refined anisotropically at one-half occupancy) in combination with C(83A), C(75), and C(85A) (refined isotropically at one-quarter occupancy) comprise the second set of atoms in the hexane disorder. Similarly, a third set of atoms C(70), C(81), C(82), C(83B), C(74), and C(85B) were employed to model the final site of disorder in the hexane. For structure **6**, the final anisotropic full-matrix least-squares refinement (based on F^2) for 551 variables using 6212 (all) data converged at R1 = 0.0642 and wR2 = 0.0878. There are two fractional (0.7) dichloromethane solvate molecules present in this structure which contain disorder. The first solvent molecule was modeled with Cl(4a) and C(70), both refined anisotropically at 0.70 occupancy with the site of disorder involving the second chlorine atom: Cl(5a) (0.40) and Cl(5b) (0.30). The second solvent molecule was modeled with one carbon atom, C(60) at 0.70 occupancy, one set one chlorine atoms Cl(2a) and Cl(3a) at 0.40 occupancy, and the second set of chlorine atoms at 0.30 occupancy.

Acknowledgment. Support of this work by the United States Department of Energy, Office of Science, Office of Basic Energy Sciences, is gratefully acknowledged.

Supporting Information Available: Tables of crystallographic data, positional and isotropic thermal parameters, anisotropic displacement parameters, H atom positional parameters, bond distances and bond angles for **1**, **2**, **4**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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