A Monometallic Rh(III) Tetraphosphine Complex: Reductive Activation of CH_2Cl_2 and Selective Meso to Racemic Tetraphosphine Ligand Isomerization

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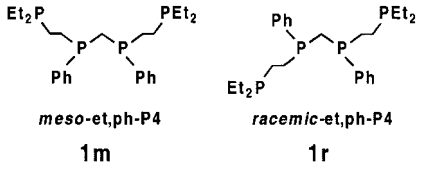
The first Rh complex with an η^4-coordinated *rac*-et,ph-P4 ligand [et,ph-P4 = $(Et_2PCH_2CH_2)(Ph)PCH_2P(Ph)(CH_2CH_2PEt_2)$] has been synthesized by reacting $[Rh(nbd)_2]BF_4$ with *meso*- or *rac*-et,ph-P4 in dichloromethane. The reaction occurs fairly rapidly at room temperature to form [*rac*-$RhCl_2(\eta^4$-et,ph-P4)]$^+$ in high yields, regardless of whether one starts with mixed or even pure *meso*-et,ph-P4 ligand. This unusual and highly selective metal assisted isomerization of the *meso*-et,ph-P4 ligand to its *rac*-et,ph-P4 disastereomer will be discussed.

Introduction

The design of polydentate phosphine ligands to impose specific coordination geometries upon one or more metal centers has been an active area of research for over forty years.[1] The simple diphenylphosphinoethane (dppe) and diphenylphosphinomethane (dppm)[2] ligands, for example, were designed to chelate and bridge metal centers, respectively. Yet the dppe ligand can also bridge two metal centers,[3] just as chelated dppm complexes have long been known.[4] Designing a polydentate ligand to impose a specific coordination geometry upon one or more transition metal atoms can be quite a challenge. Many times, when one least expects it, unexpected metal coordination geometries will be found.

The tetraphosphine ligands, *meso*-, and *rac*-$(Et_2PCH_2CH_2)(Ph)PCH_2P(Ph)(CH_2CH_2PEt_2)$, (et,ph-P4, **1m**, **1r**) are electron-rich, powerful binucleating ligands designed to chelate and bridge two transition metal centers.



The resulting bimetallic complexes can either have closed-mode geometries with M−M bonds[5] or open-mode structures where the metals are rotated apart from one another with M···M separations of 5−7 Å.[6,7] As with bimetallic complexes based on a closely related binucleating hexaphosphine ligand,[8] there is considerable conformational flexibility in the open-mode bimetallic et,ph-P4 complexes. This is quite unlike most ligand-bridged dinuclear complexes, which usually have two bridging ligands that impose a considerably more rigid framework geometry. The conformational flexibility may be quite important in encouraging bimetallic cooperativity between two metal centers.

Rac-et,ph-P4, **1r**, reacts in high yield with 2 equiv of $[Rh(nbd)_2]BF_4$ (nbd = norbornadiene) to produce [*rac*-$Rh_2(nbd)_2$(et,ph-P4)]$(BF_4)_2$, which is a precursor for an active and highly regioselective bimetallic hydroformylation catalyst.[9] In situ spectroscopic studies have determined that [*rac*-$Rh_2(nbd)_2$(et,ph-P4)]$^{2+}$ reacts with H_2/CO to rapidly generate [*rac*-$Rh_2H_2(CO)_2(\mu$-$CO)_2$(et,ph-P4)]$^{2+}$ (along with other dinuclear carbonyl and hydridocarbonyl dicationic rhodium complexes), which we have proposed to be the active hydroformylation catalyst.[10] The *meso*-et,ph-P4 ligand, on the other hand, forms a considerably less active dinuclear hydroformylation catalyst which has lower regioselectivity and higher side reactions.[9]

Quite unlike other phosphine-based monometallic hydroformylation catalysts, where an excess of the phosphine ligand is required to maintain the stability, activity, and selectivity of the catalyst,[11] [*rac*-$Rh_2H_2(CO)_2(\mu$-$CO)_2$(et,ph-P4)]$^{2+}$ is deacti-

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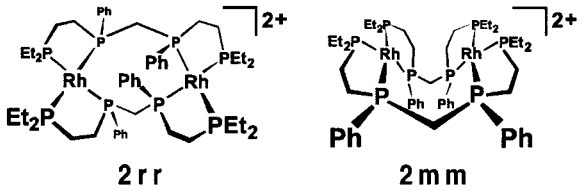
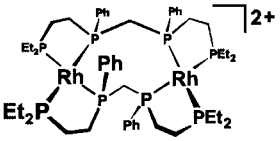
vated by excess et,ph-P4 ligand. Given the mainly alkylated, strongly coordinating nature of the et,ph-P4 ligand, this is not especially surprising. Our studies into the nature of the complexes formed when 2 equiv of et,ph-P4 ligand are reacted with 2 equiv of $[Rh(nbd)_2](BF_4)$ revealed the formation of the double-ligand dinuclear complexes *meso,meso*- (**2mm**), *meso,rac*- (**2mr**), and [*rac,rac*-Rh_2(et,ph-P4)$_2$]$^{2+}$ (**2rr**) in low yields.[12]



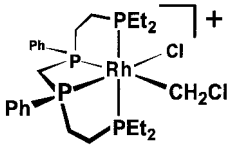
2rr **2mm**



2mr

The best isolated yield, for example, was only 20% for the [*rac,rac*-Rh_2(et,ph-P4)$_2$]$^{2+}$ complex,[12a] while the mixed *meso,rac* (**2mr)** complex was only made in trace amounts. The ^{31}P-{^{1}H} NMR spectra of these reaction solutions clearly indicated the presence of a simple set of ^{31}P resonances (dt) at 56 and 9 ppm that stood out from the complex second-order resonances for the dirhodium double-P4 ligand complexes. This indicated a simpler, symmetrical rhodium et,ph-P4 complex that, quite surprisingly, turned out to be the monometallic cationic Rh(III) complex [*rac*-$RhCl_2(\eta^4$-et,ph-P4)]$^+$, **3**.

This paper describes the reaction of the uncharacterized Rh(I) precursor complex with CH_2Cl_2, which leads to the formation of the monometallic Rh(III) product. Crystal structures of three different solvated forms of **3** and the chloromethyl complex [*rac*-$Rh(CH_2Cl)Cl(\eta^4$-et,ph-P4)]$^+$, **4**, which cocrystallized with **3** in one of the reactions, have been determined.



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The possible mechanism of how this monometallic complex is formed and the very unusual and potentially significant metal-assisted selective isomerization of the *meso*- to *rac*-et,ph-P4 ligand is discussed.

Experimental Section

General. Unless otherwise specified, all reactions and handling of reactants and products were performed in an inert atmosphere (nitrogen) using a glovebox or Schlenk line. Solvents were dried and degassed before use; some were used as obtained from the supplier, and these were generally anhydrous. $Rh_2Cl_2(CO)_4$ was obtained from Strem Chemicals. The $Rh(acac)(CO)_2$ used to prepare the $[Rh(nbd)_2]BF_4$ was donated by Celanese. NMR spectra were recorded on Bruker Avance-250 or ARX-300 spectrometers and performed at room temperature (25 °C) in 5 or 10 mm tubes, unless otherwise stated. ^{31}P{^{1}H} NMR are referenced to H_3PO_4. Not much useful information is present in the ^{1}H NMR due to the complicated overlapping bands of the et,ph-P4 ligand, and as a result the ^{1}H NMR data is generally not reported for the complexes prepared. Elemental analyses were performed by Oneida Research Services, Inc., Whitesboro, New York. *Rac*- and *meso*-et,ph-P4 were synthesized as previously reported.[7]

[*rac*-Rh(η^4-et,ph-P4)Cl_2]BF_4•toluene, 3a. A 100 mL Schlenk flask containing a stir bar was charged with 0.215 g (0.55 mmols) of $Rh_2Cl_2(CO)_4$ and 20 mL of anhydrous toluene. A second 50 mL Schlenk flask containing a stir bar was charged with 0.547 g (1.18 mmols) of mixed et,ph-P4 ligand (1:1 *rac*:*meso*) and 50 mL of toluene, while a third 25 mL Schlenk flask was charged with 0.223 g (1.14 mmols) of $AgBF_4$ and 10 mL of toluene. The three flasks were closed with rubber septa, brought out of the glovebox, and connected to a Schlenk line. After purging the tubing connecting the flasks to the Schlenk line and allowing the reactants to equilibrate to 0 °C (ice bath), the et,ph-P4 ligand solution was slowly added to the flask containing the $Rh_2Cl_2(CO)_4$. Slow addition of $AgBF_4$ to the mixture followed. The reaction flask was vented frequently to release evolved carbon monoxide. After allowing the mixture to stir over the weekend under nitrogen, the ^{31}P-{^{1}H} NMR showed a complex set of sharp resonances on top of a broad band between 42 and 70 ppm, a broad, ill-defined band between 28 and 42 ppm, and a small, sharp doublet at 10 ppm. The flask was taken into the glovebox and the mixture was filtered, yielding a small amount of light brown solid and an orange−red solution. The orange−red solution was placed on a rotary evaporator to remove the toluene solvent. The orange−red residue left after removing the solvent was redissolved in a minimum volume of CH_2Cl_2/toluene and left in the box in vials to slowly evaporate, giving a small amount of crystalline product (approximate yield 10%). ^{31}P{^{1}H} NMR (CH_2Cl_2): δ 10.1 ppm ($P_{internal}$), J_{Rh-P} = 93.7 Hz, J_{P-P} = 24.3 Hz; 57.5 ppm ($P_{external}$), J_{Rh-P} = 80.2 Hz, J_{Rh-P} = 23.8 Hz. Solubility: very soluble in acetone, nitromethane, acetonitrile, and CH_2Cl_2; soluble in MeOH; slightly soluble in ethanol, benzene, and toluene. The toluene solvent present in the crystals was identified from crystallography and ^{1}H NMR.

[*rac*-$RhCl_2$(η^4-et,ph-P4)]BF_4•MeOH, 3b. A 100 mL flask was charged with $[Rh(nbd)_2]BF_4$ (0.233 g, 0.62 mmol)[13,14] and 25 mL toluene in the glovebox. Similarly, a second 100 mL Schlenk flask was charged with *meso*-et,ph-P4 (0.294 g, 0.63 mmol) and 10 mL toluene. After adding the ligand to the rhodium solution, the reaction flask was heated to approximately 75 °C for 3 h and allowed to cool to room temperature. ^{31}P{^{1}H} NMR, once again, showed a complex set of sharp resonances on top of a broad band between 53 and 70 ppm, a small, ill-defined band between 40 and 50 ppm, and a small broad band at −20 ppm. The pale yellow/orange liquid was transferred to a clean flask, and the solvent was removed under vacuum to give an orange paste. The transfer and reaction flasks were taken into the glovebox, and the residue from each dissolved in CH_2Cl_2/hexane and CH_2Cl_2 (reaction and transfer flasks, respectively). Crystals were obtained from MeOH by slow evaporation (approximate yield 10%). Anal. Calcd. (found) % for $C_{26}H_{44}P_4Cl_2BF_4Rh$ (3MeOH, 0.5 BF_4, 0.5 Cl^-): C, 42.25 (43.34); H, 6.65 (5.56); P, 15.56 (15.23).

[*rac*-$RhCl_2$(η^4-et,ph-P4)]BF_4•2CH_2Cl_2, 3c. A 100 mL flask was charged with $[Rh(nbd)BF_4$ (0.354 g, 0.95 mmol), *rac*-et,ph-P4 (0.497 g, 0.96 mmol), and 40 mL CH_2Cl_2 in the glovebox. The mixture was refluxed for 3 h, after which the solvent was evaporated under N_2, and the residue was allowed to cool to room temperature. The orange/brown amorphous solids were collected in a vial, redissolved in a CH_2Cl_2/MeOH mixture, and placed in a glovebox to crystallize. Yield: 0.61 g (89%) of product.

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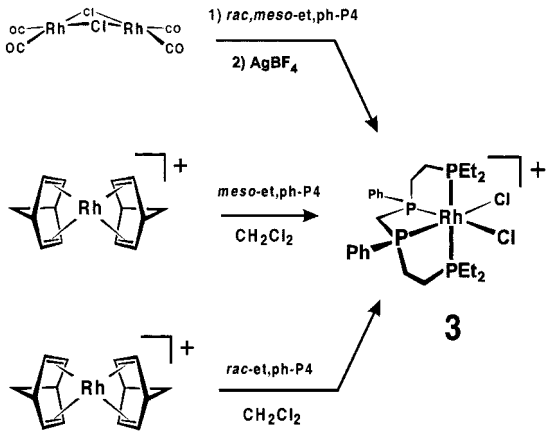
Table 1. Crystal Data

complex	**3a**	**3b**	**3c**
formula	$RhC_{32}H_{48}BF_4P_4Cl_2$	$RhC_{26}H_{44}OBF_4P_4Cl_2$	$RhC_{27}H_{42}BF_4P_4Cl_4$
fw, g mol^{-1}	817.25	757.15	863.49
space group	$P2_1$	$P2_1/n$	$P2_12_12_1$
a, Å	10.885(5)	10.712(1)	10.709(2)
b, Å	14.577(6)	14.467(2)	14.263(3)
c, Å	12.064(6)	21.619(1)	25.065(5)
α, deg	90	90	90
β, deg	92.72(3)	98.21(1)	90
γ, deg	90	90	90
V, Å^3	1912(3)	3315.9(6)	3828.7(13)
Z	2	4	4
λ, Å	1.54184	0.71073	0.71073
μ, cm^{-1}	69.8	9.0	10.5
temp., K	297	100	100
ρ_{calc}, g cm^{-3}	1.42	1.52	1.50
$R(F_o)^a$	0.083	0.030	0.036
$R_w(F_o^2)^b$	0.074	0.038	0.089

^{a} $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w(F_o^2) = (\sum w(F_o^2 - F_c^2)/\sum wF_o^2)^{1/2}$.

Scheme 1



X-ray. Crystallographic data was collected on a Enraf-Nonius CAD4 diffractometer at 24 °C or 100 K using Cu Kα or Mo Kα with a graphite crystal monochromator and the $\theta/2\theta$ scan data collection technique. Structure solutions were performed on a PC using the SHEL-XTL software.[15] Crystal and data collection information is given in Table 1.

Results

Synthesis of [*rac*-RhCl$_2$(η^4-et,ph-P4)]$^+$, 3. This complex was prepared via the several different routes summarized in Scheme 1. The highest yields (80−90%) by far occur when CH_2Cl_2 is used as a solvent for the reaction. Regardless of whether pure *rac*-, *meso*-, or mixed *rac*,*meso*-et,ph-P4 ligand is used, we only observe the formation of the *rac*-et,ph-P4 coordinated rhodium complex **3**. For example, the reaction performed with a 1:1 mixture of *rac*- and *meso*-et,ph-P4 ligand in CH_2Cl_2 produced only the [*rac*-RhCl$_2$(η^4-et,ph-P4)]$^+$ complex, with an isolated yield of 85%. The $^{31}P\{^1H\}$ NMR of **3** shows a simple symmetrical set of doublets of triplets at 10.1 ($P_{internal}$) and 57.5 ppm ($P_{external}$). The large upfield shift of the internal phosphine is typical of four-membered bis(phosphino)−methane rhodium chelate rings. In contrast, five-membered chelate rings show downfield shifts of ∼30 ppm from nonchelate ring phosphines.[16]

The initial reaction of 1 equiv of Rh(I) precursor with either *rac*-, *meso*-, or mixed et,ph-P4 ligand in the absence of chlorinated solvents produces an uncharacterized mixture of products, as indicated by the broad ^{31}P NMR resonance in the 42−70 ppm region. The double-ligand bimetallic complexes $[Rh_2(et,ph\text{-}P4)_2]^{2+}$, **2**, are part of this mixture, but we have not been able to specifically identify ratios of these and other complexes being formed due to the complexity of the NMR. This is in marked contrast to the reaction with 2 equiv of [Rh(nbd)$_2$](BF$_4$) with et,ph-P4, which gives a virtually quantitative yield of the bimetallic complex $[Rh_2(nbd)_2(et,ph\text{-}P4)](BF_4)_2$.[9]

Structural Characterization of [*rac*-RhCl$_2$(η^4-et,ph-P4)]$^+$, 3, and [*rac*-RhCl(CH$_2$Cl)(η^4-et,ph-P4)]$^+$, 4. Single-crystal X-ray structures were performed on the various solvated forms of **3** isolated (toluene, **3a**; MeOH, **3b**; and CH_2Cl_2, **3c**). A disorder present in the structure of the CH_2Cl_2 solvated complex, **3c**, was identified as the cocrystalized chloromethyl substituted complex [*rac*-RhCl(CH_2Cl)(η^4-et,ph-P4)]$^+$, **4**. Table 2 contains selected bond distances and angles for all three solvated structures plus the chloromethyl complex, **4**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **3** and **4**

	3a	**3b**	**3c/4**
Rh−CL1	2.422(5)	2.405(2)	2.417(1)
Rh−CL2	2.424(6)	2.432(2)	2.428(1)
Rh−P1	2.325(6)	2.360(3)	2.353(1)
Rh−P2	2.256(6)	2.251(2)	2.267(1)
Rh−P3	2.250(6)	2.251(2)	2.254(1)
Rh−P4	2.349(6)	2.359(2)	2.354(1)
Rh−C26	−	−	2.165(18)
P2−C3	1.85(2)	1.828(8)	1.840(4)
P3−C3	1.83(2)	1.858(8)	1.830(4)
C26−CL3	−	−	1.773(18)
P2−C3−P3	94(1)	95.1(1)	94.9(2)
CL1−Rh−Cl2	94.7(2)	94.23(2)	93.58(4)
CL1−Rh−P1	91.7(2)	91.20(2)	86.38(3)
CL1−Rh−P2	95.7(2)	95.98(2)	95.80(4)
CL1−Rh−P3	165.4(2)	165.61(3)	165.00(3)
CL1−Rh−P4	87.4(2)	86.96(2)	87.32(4)
CL2−Rh−P1	85.3(2)	88.42(2)	86.38(4)
CL2−Rh−P2	166.3(2)	167.43(3)	167.42(4)
CL2−Rh−P3	97.6(2)	97.43(2)	98.70(4)
CL2−Rh−P4	92.7(2)	92.02(2)	92.24(4)
P1−Rh−P2	85.4(2)	84.07(2)	84.52(4)
P1−Rh−P3	97.1(2)	97.51(2)	96.88(4)
P1−Rh−P4	177.8(2)	178.13(2)	178.60(4)
P2−Rh−P3	73.6(2)	73.68(2)	73.46(4)
P2−Rh−P4	96.7(2)	95.81(2)	96.45(4)
P3−Rh−P4	84.1(2)	84.24(2)	83.95(4)

ORTEP plots of **3b** and the overlapped cocrystallized complexes **3c** and **4** are shown in Figure 1. The structures of all the complexes are quite similar, with a distorted octahedral geometry about the rhodium center. The primary deviation from octahedral arises from the presence of the four-membered bis(phosphino)methane chelate ring (P2−Rh−P3), which compresses this angle down to 73.5° (average). The trans Cl−Rh−Cl angle opens up somewhat to an average value of 94°. The five-membered P−Rh−P chelate ring angles also fall into a rather narrow range of 83.95(4)−85.4(2)°. The Rh−P and Rh−Cl distances are quite consistent between the structures and quite typical for this type of Rh(III) complex. The internal Rh−P2,3 distances are 0.1 Å shorter than the external Rh−P1,4 distances (2.25 versus 2.35 Å). This is tied into the steric and electronic effects of the internal phosphines, being part of two chelate rings and not as electron rich as the terminal phosphines. The smaller spatial extent of the internal phosphorus lone pair can lead to somewhat shorter Rh−P distances. We have observed these effects in other transition metal et,ph-P4 structures.[5−7,9,12]

The other notable distortion concerns the chloride ligands being distorted up and down from the central bis(phosphino)-

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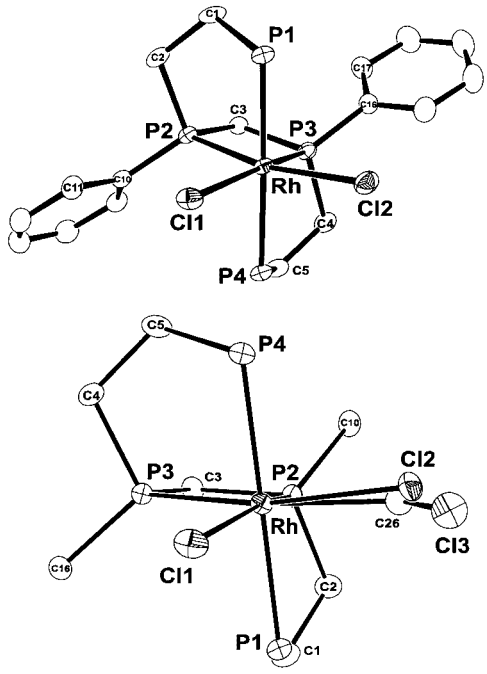
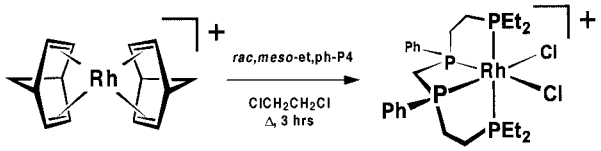


Figure 1. ORTEP plots for **3a** (top) and the overlapping disordered complexes **3c** and **4** (bottom). Hydrogens, counteranions, and solvent molecules are not shown for clarity on both structures. Ethyl groups are also omitted on **3a** (top).

methane P2−Rh−P3 plane. This is illustrated in the ORTEP plot of **3c** (Figure 1 bottom) along with the skewing of the trans P1 and P4 phosphine groups. The twist (dihedral) angle between the planes defined by P2−Rh−P3 and Cl−Rh−Cl are 14.1, 13.0, and 14.2°, for **3a**, **3b**, and **3c**, respectively. Molecular modeling annealing dynamics runs using SYBYL, starting with an ideal octahedral starting geometry for **3**, also demonstrate the same distortion of the two chloride ligands in and out of the plane defined by the Rh and two phosphorus atoms of the central bis(phosphino)methane portion of the et,ph-P4 ligand. This up−down distortion is caused by the chiral twist of the coordinated *rac*-et,ph-P4 ligand around the Rh center coupled with the steric interactions between the chloride ligands and the terminal PEt_2 groups.

Shown in Figure 1 is [*rac*-Rh(Cl)(CH_2Cl)(η^4-et,ph-P4)]$^+$, **4**, which cocrystallized with **3c**. There was a clear disorder in the vicinity of the Cl2 atom of **3c**, and during the refinement, a peak of electron density at about 2.16 Å from the Rh suggested the presence of a carbon or oxygen atom. This best refined as a $-CH_2Cl$ group. Refinements using −OMe gave higher *R* values for the structure, leading us to favor the chloromethyl assignment. The refinement indicates that 87% of the sample is **3c**, while 13% is the chloromethyl complex **4**. Marder et al.[17] have reported the structure of the chloromethyl complex *trans*-[RhCl(dppe)$_2$(CH_2Cl)](Cl)·CH_2Cl_2, which was used as a crystallographic model for refining **4**. We do not have spectroscopic or other data to confirm the presence of **4**, but, as discussed later, the chloromethyl complex is a very likely minor side product in the formation of [*rac*-$RhCl_2$(η^4-et,ph-P4)]$^+$ from the reaction of the Rh(I)−P4 precursor with CH_2Cl_2.

Reaction with 1,2-Dichloroethane. Using $ClCH_2CH_2Cl$ as a solvent for the reaction of [Rh(nbd)$_2$](BF_4) with 1 equiv of et,ph-P4 at 83 °C for 3 h produces [*rac*-$RhCl_2$(η^4-et,ph-P4)]$^+$, **3**, in a similar fashion as found for the reaction in CH_2Cl_2.

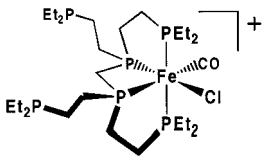


The product from this reaction was characterized by $^{31}P\{^1H\}$ NMR and X-ray crystallography. However, the single-crystal structure is not presented here because it is essentially identical to the three structures already discussed. The $^{31}P\{^1H\}$ NMR spectrum of the filtrate from this reaction showed a larger mixture of products compared to the reaction using CH_2Cl_2. The isolated yield for this reaction was around 30%, which is considerably lower than when CH_2Cl_2 is used as the solvent. Given the higher reactivity of 1,2-dichloroethane relative to CH_2Cl_2, the presence of additional side reactions is not especially surprising.

Discussion

The monometallic [*rac*-$RhCl_2$(η^4-et,ph-P4)]$^+$ complex, **3**, was initially obtained by accident when CH_2Cl_2 was used as a crystallization solvent. Additional experiments led to the use of CH_2Cl_2 as the reaction solvent, leading to the high yield synthesis of [*rac*-$RhCl_2$(η^4-et,ph-P4)]$^+$. We have also synthesized **3** via the activation of 1,2-dichloroethane, however, product yields are highest when CH_2Cl_2 is used as the solvent. The synthesis of a monometallic Rh(III) complex with an η^4-coordinated et,ph-P4 ligand was both unexpected and surprising, as this is the first η^4-et,ph-P4 coordinated transition metal complex that we have characterized in over 10 years of work with this ligand.

Several monometallic Ni−P4 complexes have been characterized in our laboratory:[18] (*meso*-Ni(NCS)(η^3-et,ph-P4)$^+$, *trans,-rac*-Ni(CN)$_2$($\eta^{2.5}$-et,ph-P4), [*rac*-Ni(NCS)(η^3-et,ph-P3,P_{int}=S)]$^+$, and [*rac*-Ni(NCS)(η^3-et,ph-P3,P_{int}=O)]$^+$. All of these have η^3- or lower coordination numbers, leading us to believe that the full η^4-et,ph-P4 monometallic coordination mode was not favored. But the stronger Rh−P bonds, relative to Ni−P, coupled with the stable octahedral coordination geometry around the Rh(III) center helps drive the coordination of the P4 ligand all the way to η^4. Perhaps the closest related complex is the η^4-hexaphosphine coordinated complex [FeCl(CO)(η^4-eHTP)]$^+$ that was synthesized from the reaction of 1−2 equiv of $FeCl_2$ with the hexaphosphine ligand, eHTP, ($Et_2CH_2CH_2P$)$_2$$PCH_2P$-($CH_2CH_2PEt_2$)$_2$, **5**.[19]



5

The eHTP ligand is the direct precursor to et,ph-P4 and was also designed to bridge and chelate two metal centers in close proximity, but it's higher coordination ability and larger steric profile severely limited any catalytic reactions of the bimetallic complexes prepared. **5** shows the same type of chiral twist

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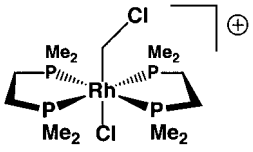
present in **3**, with a 13.0° dihedral angle of the Cl−Fe−CO plane relative to the P_{int}−Fe−P_{int} plane.

Brown and Canning reported similar mono- and bimetallic rhodium complexes based on the tetraphos ligand, ($Ph_2PCH_2CH_2$)(Ph)PCH_2CH_2P(Ph)($CH_2CH_2PPh_2$), in 1984.[20] Tetraphos was originally prepared by King and Kapoor and has a central ethylene group that makes it easier to chelate a single metal center.[21] This is in contrast to our et,ph-P4 ligand that has a central methylene group and mainly alkylated phosphines, which was designed to be a stronger bridging, binucleating ligand. Brown found that dirhodium complexes based on tetraphos, $[Rh_2(COD)_2(tetraphos)]^{2+}$, readily fragment on exposure to H_2 to produce the monometallic complexes [Rh(η^4-tetraphos)]$^+$ and [RhH_2(η^4-tetraphos)]$^+$.

Suzuki et al. reported the synthesis of cis- and *trans*-$[RhCl_2(dmpp)_2]^+$ and cis- and *trans*-$[RhCl_2(dmpe)_2]^+$ by reacting *trans*-$[RhCl_2(py)_4]Cl\cdot 5H_2O$ with dmpp ($Me_2PCH_2CH_2CH_2PMe_2$) and dmpe ($Me_2PCH_2CH_2PMe_2$) in acetonitrile.[22] The Rh−P bond lengths reported for these dmpe and dmpp complexes are similar to those observed for **3**. The Rh−Cl bond lengths, however, are slightly longer for the trans isomers (∼0.06 Å) than those for **3,** which are cisoidal. Chatt and Butter[23] prepared a series of cis and trans isomers of dmpe by reacting *trans*-$[Rh(dmpe)_2]Cl$ with Cl_2, chloroform, or carbon tetrachloride. Their work relates to **3** from the standpoint that their products are made by oxidative addition of halogens or halocarbons to $[Rh(dmpe)_2]^+$.

The synthesis of [$RhCl_2$(η^4-rac-et,ph-P4)]$^+$ in high yield in the presence of CH_2Cl_2, especially when that is the only source of chlorine atoms, demonstrates that this monometallic complex is formed via the activation of CH_2Cl_2. The activation of dihalomethanes by late transition metal complexes has been studied as a method of generating the useful metal−halomethane unit, M−CH_2X.[24,25,26] Occasionally, double activation of the dihalomethane results in the synthesis of bridging methylene (μ-CH_2) binuclear complexes. Marder et al.,[17] for example, reported the synthesis of *trans*-$[RhCl(CH_2Cl)(dppe)_2]^+$, **6**, from the reaction of $[Rh(dppe)_2(CH_2X)]$ with CH_2Cl_2.



6

Suzuki and co-workers reported the oxidative addition of CH_2Cl_2 to Rh(I) to produce the cationic complexes *trans*-$[RhCl(CH_2Cl)(P{-}N)_2]^+$, where P−N = $H_2NCH_2CH_2PR_2$ (R = Me or Ph).[27] The majority of dihalomethane activation reactions include only a handful of examples with CH_2Cl_2, which is usually difficult to activate. Most researchers have concentrated on reactions of the considerably more reactive CH_2I_2, CH_2Br_2, and CH_2ICl substrates.[24b,25b,28] Werner et al.[24] conducted elegant studies on the $CpRhL_2$ half-sandwich complexes and their reactions with CH_2X_2 (X = Br, I, CN) substrates. Their work demonstrated halide−methylene migrations (e.g., Rh(L)(CH_2X) to Rh(X)(CH_2L), where L = tertiary phosphine) and the attack by external nucleophiles (e.g., methoxide, pyridine) on the Rh−CH_2X moiety. The products observed were all of the type $CpRhX(CH_2X)L$ formed from the oxidative addition of CH_2X_2 to the Rh(I) center.

The reactivity of the uncharacterized monometallic Rh(I)-η^x-et,ph-P4 precursor(s) with CH_2Cl_2 and $ClCH_2CH_2Cl$ does, therefore, have direct analogies with literature systems. But the high-yield production of the Rh(III)−dichloride product **3**, instead of the chloromethyl complex, **4**, indicates that the mechanism may be different from other rhodium systems that produce $[RhCl(CH_2Cl)(P4)]^+$ products. We believe that it is likely that the reaction with CH_2Cl_2 involves electron transfer from a reactive monometallic Rh(I)-η^x-et,ph-P4 precursor to release chloride anions and free radical CH_2Cl-coupling processes (vide infra). One driving force for this is the formation of the rather stable η^4-chelated *rac*-P4 ligated octahedral Rh(III) structure. It is also likely that the initial coordination of et,ph-P4 to the Rh(I) starting material generates an unusually high energy structure that favors initial electron transfer to substrates such as halocarbons.

***Meso*- to *Rac*-et,ph-P4 Isomerization.** The observation that we are selectively isomerizing the *meso*-et,ph-P4 ligand to the racemic form was completely unexpected and potentially very significant. The separation of the *meso*- and *rac*-et,ph-P4 diastereomers via $Ni(NCS)_2$ chemistry has proven to be complex, frustratingly messy, and often in low yield.[18] We have recently cleaned up this separation chemistry significantly through the use of $NiCl_2\cdot 6H_2O$.[29] Because only the racemic form of the ligand is useful in our bimetallic hydroformylation catalytic studies,[9] the possibility that one could use this isomerization chemistry to selectively convert *mixed*-et,ph-P4 to pure *rac*-et,ph-P4 via **3** is exciting.

One critical aspect of this isomerization involves the overall stereochemistry of the P4 ligand coordination to a single metal center. Unlike tetraphos, the et,ph-P4 ligand cannot easily coordinate around a square planar metal center to support an η^4-coordinated configuration due to the increased strain caused by the fused four- and five-membered chelate rings. All the monometallic et,ph-P4 complexes we have prepared previous to this involve nickel and have reduced η^3 or trans-spanning $\eta^{2.5}$ type P4 ligand coordination. The square planar monometallic Ni complex [*meso*-Ni(NCS)(η^3-et,ph-P4)]$^+$, **7m**, is easily and cleanly prepared from the reaction of 1 equiv of $Ni(NCS)_2$ with *meso*-et,ph-P4 and has been spectroscopically and crystallographically characterized.[18]

The reaction of 1 equiv of the *rac*-et,ph-P4 ligand with 1 equiv of $Ni(NCS)_2$, on the other hand, does not produce anything that we can assign as [*rac*-Ni(NCS)(η^3-et,ph-P4)]$^+$, **7r**. Instead, in MeOH or THF solvent, we only observe the symmetric bimetallic complex *rac*-$Ni_2(NCS)_4$(et,ph-P4), free *rac*-et,ph-P4 ligand, and relatively small amounts of variable intensity, complicated ^{31}P resonances that depend on reaction time and

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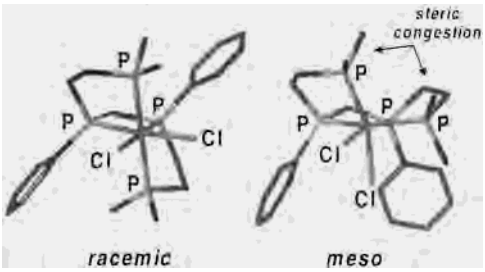
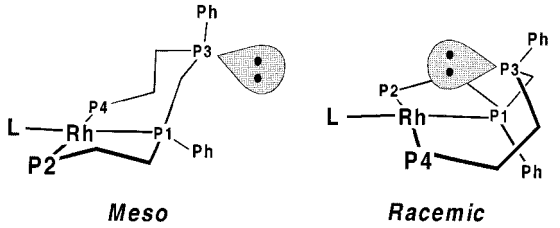


Figure 2. Stick figure views from the molecular modeling study on the model racemic and meso octahedral complexes $[RhCl_2(\eta^4\text{-me,ph-P4})]^+$. The hypothetical meso complex (on the right) was calculated to be +13 kcal/mol (no electrostatics) higher in energy than the racemic complex.

Scheme 2



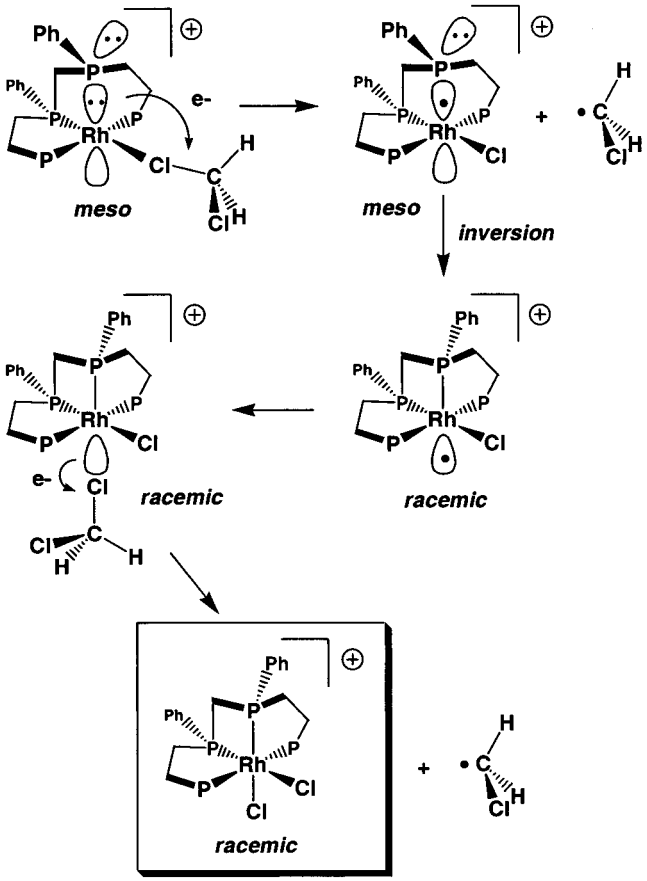
exact conditions used.[18,30] These probably correspond to low symmetry oligomeric nickel−P4 complexes, but have not been identified. The key factor in the difference in reactivity between the *meso*- and *rac*-et,ph-P4 ligands toward single metal centers appears to be the ability of the *racemic*-P4 ligand to use the one nominally free internal phosphorus lone pair to interact with the square planar metal via the empty axial coordination site, thereby activating the metal for further reactions. The *meso*-P4 ligand has the same internal phosphorus lone pair oriented away from the metal. This is illustrated in Scheme 2 for the proposed, unobserved, square planar Rh(I)-et,ph-P4 precursor complexes.

The *racemic*-P4 ligand's ability to easily donate this extra lone pair of electrons to the metal boosts the e^- density, thereby activating the Rh(I) center as a nucleophile for oxidative addition or electron-transfer reactions with CH_2Cl_2. SYBYL molecular modeling studies on the proposed η^3-coordinated monometallic Rh(I) complexes with *rac*- and *meso*-me,ph-P4 (methyl groups replacing the ethyl groups for simplicity) ligands confirm the coordination geometry shown in Scheme 2 with essentially equivalent steric energies. We have not seen any strong NMR spectroscopic evidence for the formation of these two complexes, although the small, low intensity resonances that are occasionally seen in the $^{31}P\{^1H\}$ NMR (54, 36, 30, and −20 ppm) of reaction mixtures containing chloride anions could indicate the formation of the meso monometallic $RhCl(\eta^3\text{-et,ph-P4})$ complex, which, in analogy to the nickel systems, should be more stable than the racemic complex.

A molecular modeling study on the *rac*- and unobserved *meso*-monometallic Rh(III) octahedral complexes $[RhCl_2(\eta^4\text{-me,ph-P4})]^+$, **3r** and **3m**, has also been performed. Unlike the proposed η^3-coordinated Rh(I) complexes discussed above, there is a large steric energy difference between the η^4-coordinated racemic and meso structures. Stick figure diagrams for these from the modeling study are shown in Figure 2.

The $[meso\text{-}RhCl_2(\eta^4\text{-me,ph-P4})]^+$ complex was calculated to be 13 kcal/mol higher in energy (steric factors only) than the racemic diastereomer. The main energy-raising feature is the steric hindrance of the two terminal (external) PMe_2−phosphine groups that are oriented cis to one another in the meso structure (Figure 2). This causes a fairly serious distortion of the structure relative to the modeled *rac*-me,ph-P4 rhodium complex, where these two external phosphines are oriented trans to one another. This is precisely what Brown observed in his monometallic rhodium complexes of tetraphos.[20] The *rac*-tetraphos ligand adopts the same type of coordination geometry seen for the *rac*-et,ph-P4 ligand in **3**, while *meso*-tetraphos has a stronger preference for η^4-equatorial, square-planarlike monometallic coordination. The *meso*-et,ph-P4 ligand cannot easily adopt this coordination mode due to the extra ring strain induced by the presence of the four-membered central bis(phosphino)methane chelate ring.

Scheme 3



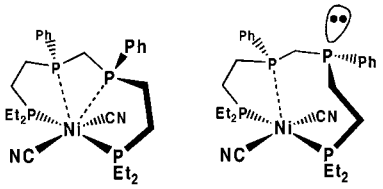
Proposed Mechanism for *Meso*- to *Racemic*-P4 Isomerization. All the data we have collected indicates that we are completely isomerizing the *meso*-et,ph-P4 ligand to form $[rac\text{-}RhCl_2(\eta^4\text{-et,ph-P4})]^+$, **3**. Our hypothesis is that the initially formed monometallic Rh(I) *rac*- and *meso*-$[Rh(\eta^3\text{-et,ph-P4})]^+$ complexes react with and reduce CH_2Cl_2 to ultimately form the oxidized Rh(III) complex $[rac\text{-}RhCl_2(\eta^4\text{-et,ph-P4})]^+$, **3**, chloride anions, and carbon radicals. This is shown in Scheme 3 for a complex with a *meso*-et,ph-P4 ligand. The reaction of 1 equiv of $[Rh(nbd)_2]^+$ and *meso*-et,ph-P4 generates the 14e$^-$ complex, $[meso\text{-}Rh(\eta^3\text{-et,ph-P4})]^+$. Despite being cationic, the Rh center is electron rich enough to perform an electron transfer to CH_2Cl_2 to generate a chloride anion that coordinates to form the 15e$^-$ Rh(II) complex, $[meso\text{-}RhCl(\eta^3\text{-et,ph-P4})]^+$.

The presence of an empty p_z and half-filled d_{z^2} radical orbital on the Rh center, which are both directed at the backside of the uncoordinated meso-internal phosphorus atom, can activate it for an orbital inversion to form the racemic η^4-coordinated 17e$^-$

(30) Aubry, D. A.; Alburquerque, P. R.; Fronczek, F. R.; Stanley, G. G., manuscript in preparation.

complex. The molecular modeling study shows that the Rh center certainly comes close enough to the uncoordinated phosphorus atom to promote the inversion of the phosphorus lone pair. Also helping to drive this inversion is the formation of a strong Rh−P bond and avoidance of the bad steric interactions that exist in the η^4-meso monometallic et,ph-P4 Rh(III) complex (the *meso*-η^4-complex is 13 kcal/mol higher in energy than the racemic based on the molecular modeling study). The involvement of a Rh(II) radical orbital in the phosphorus inversion seems quite reasonable from an electronic viewpoint. The isomerization at this point allows coordination of another strongly donating phosphine to the rhodium, increasing the electron count and promoting the halide and electron-transfer reaction to generate the final Rh(III) product, **3**. This selective metal assisted stereochemical isomerization is highly unusual and is the first reported example for a phosphine ligand. The lack of such examples for the similar tetraphos ligand, which also exists as meso and racemic diastereomers, is most likely tied into the considerably larger energy difference between the monometallic η^4-coordination geometries for the *meso*- and *rac*-et,ph-P4 ligands and their stronger metal coordination abilities. The possibility of this type of metal-activated isomerization should be kept in mind when designing other polydentate ligands with chiral centers.

We have observed partial *meso*- to *rac*-et,ph-P4 ligand isomerization via the *trans*-Ni(CN)$_2$(η^2-et,ph-P4) complex **8m**, which is an intermediate during the cyanolysis of *meso*-Ni_2Cl_4(et,ph-P4).[6,29]



8r **8m**

Even though one starts with pure *meso*-Ni_2Cl_4(et,ph-P4), the cyanolysis almost always produces some *rac*-et,ph-P4 ligand. We have attempted to push this all the way to the racemic ligand by using a minimal amount of cyanide to maximize the amount and length of time that **8m** exists in solution. But the maximum amount of **8r** that we can produce from **8m** is about 60%. The considerably weaker Ni−P bonding in the axial site of this d^8 complex, combined with the higher resistance of the Ni(II) center toward oxidation, does not provide enough driving force to completely favor the isomerization to the racemic diastereomer, as seen with the rhodium chemistry. The inability to identify stable monometallic Rh(I)−et,ph-P4 complexes clearly indicates that these complexes are far more reactive than the Ni(II) systems.

The nickel system is rather unlikely to proceed through a free radical isomerization mechanism due to the stability of the Ni(II) oxidation state. Furthermore, there is no evidence that the nickel chemistry involves any change in oxidation state. This might seem to argue against the proposed free radical mechanism for the rhodium complex. The previous work in preparing metal−CH_2X complexes from the reaction with CH_2X_2, however, demonstrates that the mechanism is most consistent with a relatively simple and classic $2e^-$ oxidative addition reaction.[17,24,25,26] The only evidence we have of a [*rac*-Rh(Cl)(CH_2-Cl)(η^4-et,ph-P4)]$^+$ complex being formed is the 13% disordered complex present in the one crystal structure discussed previously. There are no examples that we could find of simple reactions of CH_2Cl_2 with Group 8 transition metal complexes that form metal dichloride complexes in high yields, such as we see here. We do know that the rhodium is being oxidized from Rh(I) to Rh(III) and that we are not getting the expected Cl−Rh−CH_2Cl complex, except as a minor side product. This certainly indicates that one may need to consider another mechanism to account for the formation of **3**. The proposed free radical mechanism is certainly speculative, and additional studies to determine whether this is occurring need to be performed.

This *meso*- to *rac*-et,ph-P4 isomerization chemistry could become a very important reaction for converting the mixed-et,-ph-P4 ligand into the currently considerably more valuable pure racemic ligand. To effectively make use of this isomerization chemistry, however, additional research will have to be performed to see if [*rac*-$RhCl_2$(η^4-et,ph-P4)]$^+$, **3**, can be converted into a usable bimetallic catalyst precursor or if a clean way of releasing and isolating the *rac*-et,ph-P4 ligand can be found. Preliminary studies, however, indicate that **3** is remarkably stable. Attempts to react **3** with a variety of hydride reagents or H_2 to form [*rac*-RhH_2(η^4-et,ph-P4)]$^+$, which we believe is a fragmentation side product in our bimetallic hydroformylation catalysis, have so far failed.

Acknowledgment. We would like to thank the National Science Foundation for financial support (CHE-92-01051 and CHE-97-00526).

Supporting Information Available: Crystal data collection table, atomic coordinates, thermal parameters, bond lengths and angles for **3a**, **3b**, and **3c/4**, and the CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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