Separating the Racemic and Meso Diastereomers of a Binucleating Tetraphosphine Ligand System through the Use of Nickel Chloride

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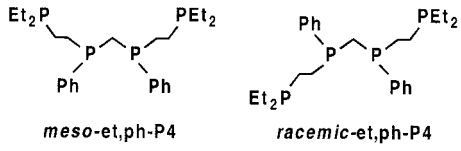
Received January 9, 2001

The reaction of a 1:1 mixture of *rac*- and *meso*-et,ph-P4 (et,ph-P4 = $(Et_2PCH_2CH_2)(Ph)PCH_2P(Ph)CH_2CH_2PEt_2$) with 2 equiv of $NiCl_2 \cdot 6H_2O$ in EtOH produces soluble *rac*-Ni_2Cl_4(et,ph-P4) and precipitates *meso*-Ni_2Cl_4-(et,ph-P4), allowing facile isolation of each bimetallic complex. Subsequent reaction with more than 250 equiv of NaCN in H_2O/MeOH releases the et,ph-P4 ligand and $[Ni(CN)_4]^{2-}$. The *rac*,*trans*- and *meso*,*trans*-$Ni(CN)_2$-($\eta^{2.5}$-et,ph-P4) form as intermediates in the cyanolysis of *rac*- and *meso*-Ni_2Cl_4(et,ph-P4). These have been characterized by X-ray crystallography. The unusual partial isomerization of the *meso*- to *rac*-et,ph-P4 ligand via the monometallic *trans*-$Ni(CN)_2$($\eta^{2.5}$-et,ph-P4) intermediate complex is discussed.

Introduction

The tetraphosphine ligands, *meso*- and *rac*-$(Et_2PCH_2CH_2)$-$(Ph)PCH_2P(Ph)(CH_2CH_2PEt_2)$ (et,ph-P4, **1m** and **1r**), are electron-



meso-et,ph-P4 (1m) *racemic*-et,ph-P4 (1r)

rich, powerful binucleating ligands designed to chelate and bridge two transition metal centers. The resulting bimetallic complexes can have either closed-mode geometries with M−M bonds[1] or open-mode structures in which the metals are rotated apart from one another with M···M separations of 5−7 Å.[2,3] As with open-mode bimetallic complexes based on the previously reported binucleating hexaphosphine ligand,[4] there is considerable conformational flexibility in the open-mode bimetallic et,ph-P4 complexes. This is quite unlike most ligand-bridged dinuclear complexes that usually have two bridging ligands that impose a considerably more rigid framework geometry. We believe that this conformational flexibility may be quite important in encouraging bimetallic cooperativity between two metal centers.

The ligand *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 (90 °C, 90 psig, 1:1 H_2/CO, acetone solvent, 1 mM catalyst, 1.8 M 1-hexene substrate, initial turnover frequency = 640 turnovers/h, 28:1 linear/branched regioselectivity, 8% alkene isomerization, 3% alkene hydrogenation).[5] 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*-$Rh_2H_2(CO)_2(\mu\text{-}CO)_2$(et,ph-P4)]$^{2+}$ (along with other complexes), which we believe is the active hydroformylation catalyst.[6] Compound **1** was originally referred to as eLTTP;[3] however, because of the current syntheses of P4 ligand derivatives to produce better dirhodium hydroformylation catalysts, the nomenclature has been modified to more clearly indicate what substituents are attached to the phosphines as these have a major impact on the catalytic activity of the bimetallic complexes formed.

The racemic bimetallic catalyst precursor [*rac*-$Rh_2(nbd)_2$-(et,ph-P4)]$(BF_4)_2$ is 12 times faster for the hydroformylation of 1-hexene than [*meso*-$Rh_2(nbd)_2$(et,ph-P4)]$^{2+}$, gives higher product regioselectivity (28:1 vs 14:1 l/b), and gives fewer side reactions (12% vs 34%).[5] The higher rate of the racemic bimetallic complex relative to that of the meso is proposed to arise in part from the ability of the racemic bimetallic catalyst to more readily form an edge-sharing bioctahedral hydride/carbonyl-bridged intermediate that allows facile hydride transfers from one metal center to the other. This, in turn, allows an intramolecular hydride transfer step that leads to aldehyde elimination.[5] In marked contrast to the initially proposed mechanism involving neutral bimetallic complexes, we have determined that the most active bimetallic catalyst species is not neutral, but rather dicationic.[6] The presence of a localized positive charge on each Rh center compensates for the strongly electron-donating et,ph-P4 phosphine ligand that would normally deactivate a *neutral* Rh center for hydroformylation catalysis. Indeed, when one starts with a neutral bimetallic precursor such as *rac*-$Rh_2(allyl)_2$(et,ph-P4), one generates a very poor bimetallic hydroformylation catalyst.[7]

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10.1021/ic010035f CCC: $20.00
Published on Web 08/15/2001

It is clear from these results that one wants to work with the pure *rac*-et,ph-P4 ligand and the associated bimetallic rhodium catalyst for hydroformylation. Our reported synthesis of et,ph-P4, however, generates a 1:1 mixture of *rac*- and *meso*-et,ph-P4 ligands.[3] The separation of these two ligand diastereomers, therefore, is a matter of considerable importance. Our previous work on Ni_2Cl_4(et,ph-P4) complexes had shown that the racemic and meso bimetallic complexes crystallized from THF with different crystal morphologies; the *meso*-Ni_2Cl_4(et,ph-P4), **2m**, complex readily loses some THF solvent of crystallization to turn opaque, while the *rac*-Ni_2Cl_4(et,ph-P4), **2r**, complex crystals remain clear.[3] This property of the crystals allowed us to separate small quantities of each bimetallic diastereomer for crystal structure determinations and to do a *very* small scale ligand isolation by cyanolysis of the bimetallic Ni_2Cl_4(et,ph-P4) complexes to release the et,ph-P4 ligand but only with about 45% yield.[3]

One separation strategy to obtain pure *meso*- and *rac*-et,ph-P4 ligands would involve production of a metal complex in which one diastereomer would be soluble in a suitable solvent, while the other would cleanly precipitate out allowing simple isolation of each in high yields and in larger quantities. The pure *meso*- and *rac*-et,ph-P4 ligands could then be released from the metal complex by use of a suitable reagent to give the pure ligand. Because nickel complexes had been successfully used to separate other diastereomeric mixtures in the past, we decided to concentrate our separation chemistry efforts on nickel et,ph-P4 complexes.[8]

We spent considerable time investigating the use of $Ni(NCS)_2$ as a separating agent, but this chemistry has proven to be surprisingly complex.[9] Although separations of the *rac*- and *meso*-et,ph-P4 ligands have been achieved using both $Ni(NCS)_2$ and $NiCl_2$, the previous procedures offered inconsistent and often low yields.[3,9] The original $NiCl_2$-based separation chemistry was, therefore, reexamined in order to optimize the yields.[3] We report here the straightforward $NiCl_2$-based route for the bulk separation and isolation of *rac*- and *meso*-et,ph-P4 ligands in pure diastereomeric form, along with the isolation and structural identification of the monometallic *trans*-Ni$(CN)_2(\eta^{2.5}$-et,ph-P4) intermediates from the cyanolysis step. An unusual *meso*- to *rac*-et,ph-P4 partial isomerization mediated by these monometallic Ni−cyanide complexes has also been observed.

Experimental Section

General Procedures. All manipulations were performed under inert atmosphere (argon or nitrogen), unless otherwise noted, with standard Schlenk or glovebox techniques. None of the nickel complexes reported are particularly oxygen-sensitive. NMR spectra were recorded on Bruker Avance-250 or ARX-300 instruments (δ ppm, ^{1}H TMS reference, ^{31}P 85% H_3PO_4 reference). IR spectra were run on a Perkin-Elmer 1760X FT-IR spectrometer using GRAMS/32 software (Galactic Industries). Oneida Research Services, Inc., Whitesboro, NY, performed the elemental analyses.

Solvents were dried and distilled under inert atmosphere from the appropriate drying agents as follows: tetrahydrofuran, diethyl ether, and hexane (potassium/benzophenone); dichloromethane (calcium hydride); ethanol and methanol (magnesium). Distilled (or deionized) water was degassed by purging with nitrogen gas for 20 min. NaCN and $NiCl_2\cdot 6H_2O$ were purchased from Aldrich Chemicals and used without further purification.

Synthesis of Ni_2Cl_4(et,ph-P4), 2m and 2r. A 125 mL EtOH solution of mixed *rac,meso*-et,ph-P4 ligand[3] (10.01 g, 0.0215 mol) was added dropwise to a rapidly stirred clear green solution of $NiCl_2\cdot 6H_2O$ (10.24 g, 0.0431 mol) in 135 mL of EtOH. The solution turned dark red as the ligand solution was added. An orange precipitate began to form after the addition was complete. After the mixture was stirred for 24 h, the orange precipitate was collected by filtration and washed with three ca. 30 mL portions of EtOH to give 7.32 g (94% yield) of *meso*-Ni_2Cl_4(et,ph-P4), **2m**. Yields are typically 90−96%. The filtrate was concentrated down to a dark red amorphous solid of mainly *rac*-Ni_2Cl_4(et,ph-P4), **2r**. Spectroscopic properties have already been reported.[3]

Isolation of *rac*-et,ph-P4, 1r. A Schlenk flask containing *rac*-Ni_2Cl_4(et,ph-P4), **2r** (2.0 g, 2.77 mmol), was charged with a solution of NaCN (18.1 g, 0.369 mol, 133 equiv) in 125 mL of H_2O and 50 mL of MeOH. The resulting orange solution was stirred slowly for 3 h, during which it became increasingly red. The flask was then charged with more NaCN (20.4 g, 0.416 mol, 150 equiv), and the solution was allowed to slowly stir until all the NaCN dissolved (ca. 15 min). This two-step cyanide addition allows any *meso*-et,ph-P4 ligand impurities present to be partially isomerized to *rac*-et,ph-P4 ligand giving slightly higher yields. The free *rac*-et,ph-P4 ligand was then extracted into three 100 mL portions of benzene. The slightly yellow extracted solution was then passed through a small neutral alumina column to remove the yellow color, which is the monometallic Ni complex *trans,rac*-Ni$(CN)_2(\eta^{2.5}$-et,ph-P4), **3r**. The colorless solution was then concentrated to yield a clear viscous oil (1.16 g, 2.50 mmol, 85%) of free *rac*-et,ph-P4 ligand. Yields are typically 75−87%, and the purity level, based on ^{31}P NMR, is typically greater than 95%. ^{31}P{^{1}H} NMR (C_6D_6): −25.5 (P_{int}, J_{P-P} = 10.2, 12.1 Hz), −18.4 (P_{ext}, J_{P-P} = 10.2, 12.1 Hz). Computer-simulated coupling constants based on an AXX′A′ spin system: $J_{P_{int}-P_{ext}}$ = 22.5 Hz, $J_{P_{int}-P_{int}}$ = 109.5 Hz.[3] ^{31}P{^{1}H} NMR is included in Supporting Information.

Isolation of *meso*-et,ph-P4, 1m. A Schlenk flask was charged with 40 mL of H_2O, 20 mL of MeOH and NaCN (2.0 g, 0.408 mol, 393 equiv). To the white cyanide suspension, 30 mL of a brown 50/50 solution of H_2O and MeOH containing *meso*-Ni_2Cl_4(et,ph-P4) (0.75 g, 1.04 mmol) was added dropwise with rapid stirring. Upon addition, the cyanide suspension turned light orange. After slow overnight stirring, the free *meso*-et,ph-P4 ligand was then extracted into three 75 mL portions of hexane. The slightly yellow extracted solution was then passed through a small neutral alumina column to remove the light yellow color. The colorless solution was then concentrated to yield a cloudy, highly viscous oil (0.30 g, 0.647 mmol, 62% yield) that is *meso*-et,ph-P4 ligand. Yields are typically 45−65%, and the purity level, based on ^{31}P NMR, is typically only about 75−85% because of partial isomerization of *meso*-et,ph-P4 ligand to *rac*-et,ph-P4. Shorter reaction times give less isomerization to *racemic* ligand, but there is also less ligand released from nickel giving lower yields of free ligand. Recrystallization of the extracted crude ligand (0.30 g, 0.647 mmol) from hexane (ca. 25 mL) provided 99% pure meso ligand as a white powder, based on ^{31}P NMR, (0.25 g, 0.539 mmol, 51% yield). Yields after recrystallization are typically 30−60%, and purity is greater than 98%. ^{31}P{^{1}H} NMR (C_6D_6): −26.2 (P_{int}, J_{P-P} = 10.4, 12.2 Hz), −18.3 (P_{ext}, J_{P-P} = 10.4, 12.2 Hz).[3]

Isolation of Impure *rac*-et,ph-P4 from *meso*-Ni_2Cl_4(et,ph-P4). A Schlenk flask was charged with *meso*-Ni_2Cl_4(et,ph-P4) (1.0 g, 1.385 mmol) and 20 mL of H_2O. After the mixture was stirred for 1 h to dissolve the *meso*-Ni_2Cl_4(et,ph-P4), a 10 mL H_2O solution of NaCN (0.35 g, 7.14 mmol, 5.2 equiv) was added dropwise with stirring. During the addition, an orange precipitate formed, which was *rac,trans*-Ni$(CN)_2(\eta^2$-et,ph-P4). MeOH (20 mL) was added to dissolve the precipitate. More NaCN was added (3.50 g, 0.0714 mol, 52 equiv) to free the ligand. The ligand was extracted with three 50 mL portions of benzene. The slightly yellow extracted solution was then passed through a neutral alumina column to remove the yellow tint. The colorless solution was concentrated to yield a clear viscous liquid (0.41 g, 0.875 mmol, 70% yield). Yields are typically 60−75% (mixture of 1:1 to 1.4:1 *rac*- to *meso*-et,ph-P4 ligand).

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***rac,trans*-[Ni(CN)$_2$($\eta^{2.5}$-et,ph-P4)], 3r. Method A (THF Solvate).** This complex was a byproduct of the et,ph-P4 extraction from *rac*-Ni_2Cl_4(et,ph-P4) using a benzene/H_2O/NaCN reflux system for 30 min.[3] Yellow **3r** remained in the benzene phase and was isolated on a neutral alumina column and then removed by elution with THF. After slow evaporation of the THF solvent, orange-yellow crystals of **3r**·THF were obtained.

3r. Method B (H_2O Solvate). NaCN (0.11 g, 2.08 mmol, 3 equiv) in 10 mL of H_2O was added dropwise without stirring to a Schlenk flask containing *rac*-Ni_2Cl_4(et,ph-P4) (0.50 g, 0.693 mmol) in 10 mL of H_2O. After the addition, the flask was slowly swirled for 30 s. The orange solid that formed was filtered (0.23 g, 0.400 mmol, 58%), rinsed with ca. 2 mL of H_2O, and redissolved in H_2O/MeOH. Stirring during cyanide addition limits the amount of precipitate that forms. Slow evaporation yielded orange clusters of crystals of **3r**·H_2O. Anal. Calcd (found) for $C_{27}H_{44}N_2O_2P_4Ni$ (water present by X-ray): C, 53.05 (53.80); H, 7.26 (6.95); N, 4.58 (4.58). $^{31}P\{^1H\}$ NMR (C_6D_6): 43.0 ($2P_{ext}$, s), −14.7 ($2P_{int}$, s). IR (KBr): ν_{CN} = 2096 cm^{-1} (sharp and strong).

***meso,trans*-[Ni(CN)$_2$($\eta^{2.5}$-et,ph-P4)], 3m (H_2O Solvate).** NaCN (0.11 g, 2.08 mmol, 3 equiv) in 10 mL of H_2O was added abruptly to a Schlenk flask containing *meso*-Ni_2Cl_4(et,ph-P4) (0.50 g, 0.693 mmol) in 10 mL of H_2O. The flask was slowly swirled for 5 s. The orange solid that formed was filtered (0.22 g, 0.382 mmol, 55%), rinsed with ca. 2 mL of H_2O, and redissolved in a 3:1 H_2O/MeOH mixture. The quick addition of cyanide to **2m** causes more precipitation of **3m** and minimizes the isomerization to **3r**. Slow evaporation produced two crystal morphologies, yellow needles and orange clusters. The vast majority of them were yellow needles, which were determined through X-ray crystallography to be **3m**·H_2O. The orange clusters were **3r**·H_2O. Anal. Calcd (found) for $C_{27}H_{42}N_2OP_4Ni$ (water present by X-ray): C, 54.67 (54.18); H, 7.14 (6.95); N, 4.72 (4.58); P, 20.89 (22.54). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): −16.2 (P3), 12.8 (P1), 47.5 (P4, d, J_{P2-P4} = 219 Hz), 68.9 (P2, d, J_{P2-P4} = 219 Hz). ^{31}P resonances were broad and no further coupling could be determined. IR (KBr): ν_{CN} = 2119 cm^{-1} (sharp and strong).

X-ray Crystallography. Suitable crystals (all air-stable) were mounted on glass fibers using epoxy. Data collection was performed on Enraf-Nonius CAD4 and Nonius Kappa CCD diffractometers using Cu Kα and Mo Kα radiation and graphite crystal monochromators. Structure solving was done using the Enraf-Nonius Molin and Bruker ShelXTL program sets on DEC Alpha or PC computers. Both structures were solved using MULTAN direct methods program set and refined by using full-matrix least-squares refinement. The hydrogen atoms were not refined but included in the calculations at fixed positions with $B = 1.3B_{eq}$ for their bonded atoms. Compound **3r** had a disordered THF that could only be partially modeled. Because the oxygen atom could not be uniquely identified, all atoms were refined as carbons. There are two independent molecules in the asymmetric unit for **3m** and one water solvent associated with each. Key crystal and data collection information is presented in Table 1. Full crystal data, experimental details, and positional and thermal parameters for **3r** and **3m** are given in Supporting Information as CIF files.

Results and Discussion

***rac*- and *meso*-Ni_2Cl_4(et,ph-P4).** Treating the mixed et,ph-P4 ligand with 2 equiv of $NiCl_2$·$6H_2O$ produces the bimetallic nickel complexes *meso*- and *rac*-Ni_2Cl_4(et,ph-P4), **2m** and **2r**, in almost quantitative yield. Both diastereomeric bimetallic complexes have symmetrical, chelated, bridged, open-mode type structures (i.e., nonbonded Ni···Ni separations of 6.272(1) and 5.417(1) Å).[3] In the original work, the synthesis was performed in EtOH solvent, but the concentrations of the bimetallic complexes formed were not optimized to get the cleanest possible separation. We had to resort to recrystallizations from THF that gave *rac*- and *meso*-Ni_2Cl_4(et,ph-P4) crystals with different morphologies. Picking out single crystals under a microscope allowed us to get pure **2r** and **2m**. This is clearly not suitable for larger-scale separations.

Table 1. Key Crystallographic Data for *rac*- and *meso*-Ni(CN)$_2$($\eta^{2.5}$-et,ph-P4), **3r** and **3m**

	3r·THF	**3m**·H_2O
formula	$C_{31}H_{48}N_2NiOP_4$	$C_{27}H_{42}N_2NiOP_4$
fw	647.35	593.22
T, K	296 K	120 K
diffractometer	CAD4	Kappa-CCD
λ, Å	1.541 84 (Cu)	0.710 73 (Mo)
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	15.128(2)	8.4310(2)
b, Å	11.085(2)	18.5593(3)
c, Å	20.663(2)	19.7142(4)
α, deg	90	95.2808(8)
β, deg	98.78(2)	94.3847(7)
γ, deg	90	99.5244(10)
V, Å^3	3402(1)	3016.08(11)
Z	4	4
ρ_{calcd}, g cm^{-1}	1.256	1.306
μ, cm^{-1}	2.80 (Cu)	0.878 (Mo)
$R(F_o)^a$	0.063	0.049
$R_w(F_o^2)^b$	0.084	0.099

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

The volume of EtOH used and the concentration of the nickel complexes are quite important because the *meso*-Ni_2Cl_4(et,ph-P4) complex precipitates as an orange powder and is only slightly less soluble than *rac*-Ni_2Cl_4(et,ph-P4). The current work has optimized these factors to give nearly quantitative separation of **2m** and **2r** after rapid stirring for 24 h. The yield of isolated *meso*-Ni_2Cl_4(et,ph-P4) solid obtained by vacuum filtration was always greater than 90%. The filtrate, which contains *rac*-Ni_2Cl_4(et,ph-P4), was concentrated down to a black amorphous tarry substance that still contains some EtOH, so the yield cannot be accurately determined.

After experimentation with numerous solvents and $NiCl_2$ and et,ph-P4 ligand concentrations, it was determined that the optimal solvent for the separation of *meso*- and *rac*-Ni_2Cl_4(et,ph-P4) is EtOH (although MeOH works almost as well). A total of 260 mL of EtOH solvent is required for each 10 g of mixed et,ph-P4 ligand used. Interestingly, at higher Ni/P4 ligand concentrations, no separation occurs. Instead, the concentrated solution remains black and tarry with no precipitate formation. The highly complex ^{31}P NMR spectrum of this concentrated solution contains coordinated and uncoordinated resonances and is unlike any other mono- or bimetallic P4 complex that we have characterized. This may be due to the formation of partially coordinated, low-symmetry nickel-et,ph-P4 oligomeric chains. Fortunately, addition of the appropriate amount of EtOH solvent and overnight stirring do lead to the formation of well-defined *meso*- and *rac*-Ni_2Cl_4(et,ph-P4) and produce the desired separation.

Cyanolysis of *rac*-Ni_2Cl_4(et,ph-P4). Reaction of Ni_2Cl_4(et,ph-P4) with excess CN^- is a convenient method for removing the nickel centers from the ligand. The previous published cyanolysis procedure for **2r** only produced a 45% yield of *rac*-et,ph-P4 ligand.[3] This original separation chemistry employed heating, lower concentrations of cyanide, and H_2O/benzene as a mixed solvent system. All these factors contributed to the low yield and have now been corrected to provide an optimized procedure for obtaining pure *rac*-et,ph-P4.

Heating during the cyanolysis procedure is not needed, as the strongly σ-donating cyanide anions readily displace the phosphine ligands, even a strongly coordinating, chelating, mainly alkylated phosphine like et,ph-P4. Heating also has the undesirable effect of promoting the decomposition of NaCN.[10,11]

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Not surprisingly, higher concentrations of CN^- promote better yields for the liberation of the et,ph-P4 ligand. The low yields of isolated **1r** in the previous work[3] resulted from the formation of a stable monometallic nickel complex, *rac,trans*-$Ni(CN)_2$-($\eta^{2.5}$-et,ph-P4), **3r**, which will be discussed more fully below. The stability of this intermediate complex requires higher concentrations of CN^- in order to fully liberate the *rac*-et,ph-P4 ligand. Extensive experimentation with differing concentrations of CN^- has resulted in a procedure that employs two separate CN^- additions. The first addition of 133 equiv serves to cleanly release one of the nickel centers from **2** to produce *trans*-$Ni(CN)_2$($\eta^{2.5}$-et,ph-P4) and orange, square-planar $[Ni(CN)_4]^{2-}$. Addition of another 150 equiv of CN^- frees the remaining nickel center to give free *rac*-et,ph-P4 ligand. The higher cyanide ion concentration also favors the formation of the pentacyano-complex $[Ni(CN)_5]^{3-}$ as evidenced by the solution turning from orange to red.

For the intermediate monometallic complex **3r** to efficiently react with CN^-, it must be completely dissolved. The *rac,trans*-$Ni(CN)_2$($\eta^{2.5}$-et,ph-P4) is insoluble in H_2O but is soluble in MeOH. Therefore, a 2.5:1 ratio of H_2O/MeOH is employed, which keeps *rac,trans*-$Ni(CN)_2$($\eta^{2.5}$-et,ph-P4) in solution. The removal of the free ligand from the H_2O/MeOH solvent is achieved via extractions with benzene. Hexane can also be employed to extract the ligand; however, yields are 20−30% lower. The use of a H_2O/MeOH mixed solvent to keep **3r** dissolved, along with a second CN^- addition, gives consistent and good to excellent isolated yields of the *rac*-et,ph-P4 ligand.

Cyanolysis of *meso*-Ni_2Cl_4(et,ph-P4). The removal of the nickel from **2m** through cyanolysis is more difficult because of an unexpected partial *meso*- to *rac*-et,ph-P4 ligand isomerization side reaction that will be discussed below. Although **1m** is not particularly useful as a ligand for dirhodium-catalyzed hydroformylation, it is potentially useful in other applications. To minimize the *meso*- to *rac*-et,ph-P4 isomerization, a 1:1 H_2O/MeOH solution of *meso*-Ni_2Cl_4(et,ph-P4), **2m**, is added dropwise to a well-stirred, saturated NaCN solution in 2:1 H_2O/MeOH. When **2m** is added, it quickly reacts with cyanide to form a mixture of $[Ni(CN)_4]^{2-}$ and $[Ni(CN)_5]^{3-}$, along with free *meso*-et,ph-P4, **1m**. The CN^- saturation of the aqueous layer aids the extraction process and increases the yield of the isolated **1m** by 5−10%.

Benzene and hexane are both suitable solvents for the extraction of **1m**, but it is considerably more soluble in the aqueous phase than **1r**. The yield, therefore, of meso P4 ligand from the aqueous extraction process is correspondingly lower: 45−65% for **1m**, compared to 75−87% for **1r**. The meso ligand is evident in ^{31}P NMR spectra of the aqueous layer both before and after the extraction. In addition, the purity of the extracted *meso*-et,ph-P4 is typically lower than that of **1r** because of the meso to rac ligand isomerization that occurs. Recrystallization of the extracted *meso*-et,ph-P4 ligand from hexane, however, does provide pure **1m**, typically in isolated yields of 30−60%. The $^{31}P\{^1H\}$ NMR spectra of mixed et,ph-P4, **1m**, and **1r** are available in Supporting Information.

***meso,trans*- and *rac,trans*-[$Ni(CN)_2$($\eta^{2.5}$-et,ph-P4)], 3m and 3r.** During our original studies into the cyanolysis of the *rac*-Ni_2Cl_4(et,ph-P4) solution, a two-phase H_2O/benzene solvent system was used.[3] A distinct yellow color almost always rapidly appeared in the organic phase, and when this occurred, low yields of the isolated et,ph-P4-ligand resulted. Concentration of the yellow benzene solution yielded orange-yellow crystals, which were recrystallized from THF. A single-crystal structural determination revealed the presence of monometallic *rac,trans*-$Ni(CN)_2$($\eta^{2.5}$-et,ph-P4). More reproducible production of these monometallic intermediates in the cyanolysis procedure is obtained via the use of only 3 equiv of CN^- in the cyanolysis of *rac*- or *meso*-Ni_2Cl_4(et,ph-P4) allowing the isolation and recrystallization of *rac,trans*- and *meso,trans*-$Ni(CN)_2$($\eta^{2.5}$-et,ph-P4), **3r** and **3m**, in 55% yield, both of which have been structurally characterized.

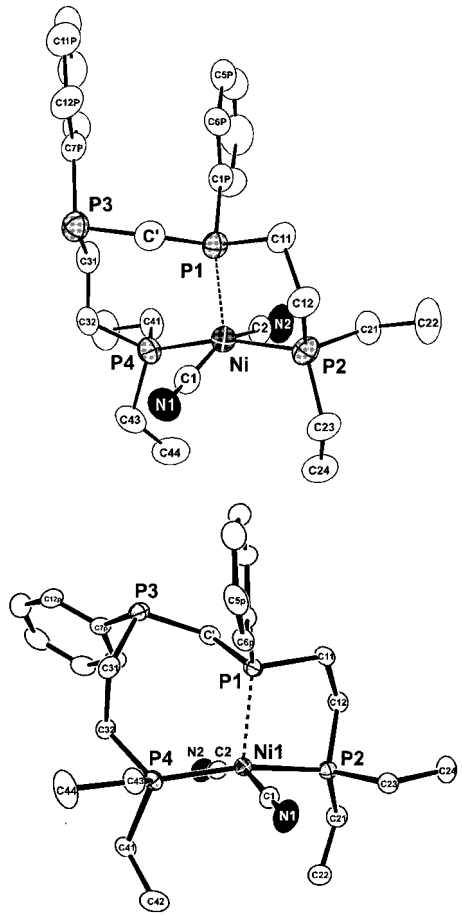


Figure 1. ORTEP plots of *rac*-$Ni(CN)_2$($\eta^{2.5}$-et,ph-P4), **3r** (top), and the corresponding meso complex, **3m** (bottom). Hydrogen atoms are omitted for clarity. The carbon and nitrogen atoms in **3m** were refined isotropically.

The structures (Figure 1) show that these monometallic complexes have square-pyramidal coordination geometries with two basal cyanide ligands trans to one another on the Ni(+2) center. The other two basal coordination sites are occupied by the external phosphorus atoms of the trans-spanning et,ph-P4 ligand, which forms a 10-membered ring system about the nickel center. Trans-spanning phosphine ligand−metal complexes are relatively well-known.[12] Most have been characterized with group 8−10 metals,[13] but at least one Mo complex is known.[14] Our system is unusual in that one of the internal phosphorus atoms of the et,ph-P4 ligand forms a longer and weaker Ni−P interaction (Ni−P1 = 2.395(2) Å for **3r**, 2.3526(9) Å for **3m**)

(11) Kramer, V. W. U.S. Patent 2,773,752, 1957.

(12) Compare: Bessel, C. A.; Aggarwal, P.; Marschilok, A. C.; Takeuchi, K. J. *Chem. Rev.* **2001**, *101*, 1031−1066.

(13) Compare: (a) Kapoor, P. N.; Pregosin, P. S.; Venanzi, L. M. *Helv. Chim. Acta* **1982**, *65*, 654−660. (b) Elding, L. I.; Kellenberger, B.; Venanzi, L. M. *Helv. Chim. Acta* **1983**, *66*, 1676−1690. (c) Kapoor, P. N. *J. Organomet. Chem.* **1988**, *341*, 363−366. (d) Tani, K.; Yabuta, M.; Nakamura, S.; Yamagata, T. *J. Chem. Soc., Dalton Trans.* **1993**, 2781−2789. (e) Gray, G. M.; Varshney, A.; Duffey, C. H. *Organometallics* **1995**, *14*, 238−244.

(14) Gray, G. M.; Duffey, C. H. *Organometallics* **1994**, *13*, 1542−1544.

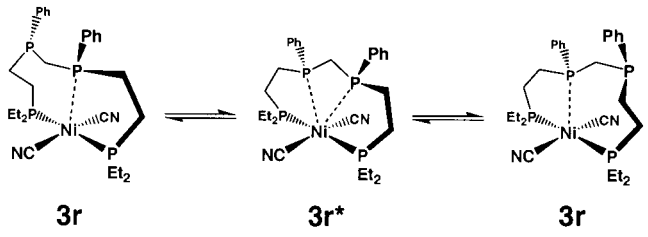
Table 2. Selected Bond Distances (Å) and Angles (deg) for *rac*,*trans*- and *meso*,*trans*-Ni(CN)$_2$(η^2-et,ph-P4), **3r** and **3m**

	3r	**3m**
Ni−P1	2.395(2)	2.3526(9)
Ni−P2	2.183(2)	2.1900(9)
Ni−P4	2.186(2)	2.1829(9)
Ni−C1	1.876(7)	1.865(3)
Ni−C2	1.859(7)	1.880(3)
N1−C1	1.164(7)	1.163(4)
N2−C2	1.156(7)	1.149(4)
P1−Ni−P2	87.54(7)	88.07(3)
P1−Ni−P4	105.67(7)	102.93(3)
P1−Ni−C1	94.6(2)	106.69(10)
P1−Ni−C2	107.3(2)	97.36(10)
P2−Ni−P4	165.48(8)	167.58(3)
P2−Ni−C1	85.6(2)	91.82(10)
P2−Ni−C2	91.9(2)	86.85(9)
P4−Ni−C1	87.3(2)	90.51(10)
P4−Ni−C2	89.9(2)	86.04(9)
C1−Ni−C2	157.9(3)	155.86(13)
Ni−C1−N1	176.0(3)	177.4(3)
Ni−C2−N2	178.7(3)	178.0(3)
P1−C′−P3	122.1(3)	115.82(16)

with the apical coordination site. Weak apical interactions in Ni(+2) complexes with phosphine ligands have been reported before by several groups.[15] This weaker apical phosphine coordination is why we designate the coordination of the et,ph-P4 ligand as $\eta^{2.5}$. Selected bond distances and angles for *rac*,*trans*- and *meso*,*trans*-[Ni(CN)$_2$($\eta^{2.5}$-et,ph-P4)] are listed in Table 2.

The compound *trans*-Ni(CN)$_2$($\eta^{2.5}$-et,ph-P4) can be described as a partially liberated monometallic complex in which the cyanide anions have only displaced one nickel center, with the ligand rearranging to an $\eta^{2.5}$-coordination mode. The solubility of this complex in organic solvents limits further attack of aqueous cyanide ion and nicely explains the relatively low yield of isolated et,ph-P4 ligand in the original H_2O/benzene solvent cyanolysis procedures. The IR spectrum has a strong absorption at 2096 cm^{-1} for **3r** and 2119 cm^{-1} for **3m**, characteristic of the C≡N stretches.

In the solid state, **3r** contains four inequivalent phosphorus nuclei. This is *not* the case, however, in solution where the room-temperature ^{31}P{^{1}H} NMR spectrum only shows two sharp singlets. These singlets are produced from a temperature-dependent solution fluxional process where the weak apical Ni−P bond is easily broken. At room temperature, the ligand on the molecule is rapidly wagging in solution so both internal phosphorus atoms alternate in their weak bonding interactions with the metal center. This generates an average symmetrical structure, **3r***, that yields the simple singlets observed for both the internal and external phosphorus atoms. The −14.7 ppm resonance corresponds to the internal phosphines and lies almost exactly intermediate between the uncoordinated P3 resonance (−23.5 ppm) and the weak apically coordinated P1 atom in **3m** (15.8 ppm). The exchange between the internal phosphorus atoms can be slowed, but not stopped, by lowering the temperature to −80 °C. New resonances are observed in the ^{31}P{^{1}H} NMR at −80 °C, but the coupling constants could not be obtained because of line broadening, probably caused by partial precipitation of the complex at this low temperature.



The room-temperature solution ^{31}P NMR spectrum of the meso monometallic complex **3m**, on the other hand, shows four somewhat broad resonances indicating an $\eta^{2.5}$-*meso*-et,ph-P4-bound static structure consistent with that seen in the ORTEP plot (Figure 1). The uncoordinated lone pair on phosphorus atom P3 in **3m** is oriented almost completely opposite from the nickel center and cannot coordinate easily to the metal. This is in marked contrast to the P3 lone pair in **3r**, which, on the basis of the dynamic NMR behavior, can very readily coordinate and dissociate. The somewhat broad nature of the ^{31}P resonance for **3m** probably indicates some fluxional behavior but on a rather different time scale relative to **3r**. This stereochemical difference leads to a rather unusual reaction in the case of Ni(NCS)$_2$ in which we see a nickel-mediated selective sulfur transfer reaction from thiocyanate to the racemic P3 phosphorus atom to produce a P═S group. This thiocyanate sulfur transfer chemistry is not seen for the meso mono- or bimetallic Ni-et,ph-P4 ligand complexes.[9] This is one reason we abandoned the Ni(NCS)$_2$-based et,ph-P4 separation procedures and concentrated on the much cleaner $NiCl_2$ chemistry.

Isomerization of *meso*- to *rac*-et,ph-P4. During the investigation of the cyanolysis of the *meso*-Ni_2Cl_4(et,ph-P4) to produce pure *meso*-et,ph-P4, **1m**, unexpectedly high amounts of racemic ligand were occasionally obtained (50−70% racemic ligand), although the starting Ni_2Cl_4(et,ph-P4) complex used was pure meso based on ^{31}P NMR spectra. There turns out to be an isomerization pathway available that can partially convert **3m** to **3r** during the cyanolysis. The monometallic intermediate **3r** appears to be thermodynamically favored over **3m**, and that, coupled with a kinetically accessible pathway, allows isomerization from *meso*- to *rac*-et,ph-P4. The question naturally arose whether it would be possible to isolate pure *rac*-et,ph-P4 ligand (**1r**) from *meso*-Ni_2Cl_4(et,ph-P4), **2m**. This could represent a useful pathway for producing more of the valuable *rac*-et,ph-P4 ligand.

Slow dropwise addition of NaCN to **2m** in H_2O provides the optimal condition to form the maximum amount of the *rac*,-*trans*-Ni(CN)$_2$($\eta^{2.5}$-et,ph-P4), **3r**, intermediate. During the addition, **3r** forms as an orange precipitate. Further addition of NaCN to this solution frees the et,ph-P4 ligand. However, the highest conversion achieved was only 70:30 racemic to meso. This ratio appears to be thermodynamically controlled for this Ni-based system. We have observed complete meso to racemic ligand isomerization in the case of reacting Rh(+1) complexes (1 equiv of [Rh(nbd)$_2$](BF$_4$) (nbd = norbornadiene) or 0.5 equiv of Rh$_2$(μ-Cl)$_2$(CO)$_4$) with 1 equiv of mixed or *meso*-et,ph-P4 ligand in CH_2Cl_2. The monometallic racemic Rh(+3) complex [*rac*-RhCl$_2$(η^4-et,ph-P4)]$^+$ is produced in nearly quantitative yield.[16] This selective metal-assisted stereochemical isomerization is highly unusual and is the first reported example for a phosphine ligand.

(15) (a) Stalick, J. K.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 1084. (b) Stalick, J. K.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 1090. (c) Raymond, K. N.; Corfield, P. W. R.; Ibers, J. A. *Inorg. Chem.* **1968**, *7*, 1362. (d) Hirshfeld, F. L.; Hope, H. *Acta Crystallogr., Sect. B* **1980**, *B36*, 406. (e) Allen, D. W.; Mann, F. G.; Millar, I. T.; Powell, H. M.; Watkins, D. J. *J. Chem. Soc. D* **1969**, 1004. (f) Hope, H.; Olmstead, M. M.; Power, P. P.; Viggiano, M. *Inorg. Chem.* **1984**, *23*, 326,

(16) Hunt, C., Jr.; Fronczek, F. R.; Billodeaux, D. R.; Stanley, G. G. *Inorg. Chem.*, in press.

The stronger Rh−P bonding and increased Rh(+3) octahedral coordination environment that allows full η^4-*rac*-et,ph-P4 coordination to the metal center provide a considerably greater thermodynamic impetus for isomerizing the meso to racemic ligand. The meso ligand cannot readily coordinate in an η^4-fashion to a single metal center. Molecular modeling studies showed that the η^4-*meso*-et,ph-P4 coordination was 13 kcal/mol higher in energy relative to that of the monometallic racemic ligand complex.[16] Unfortunately, the [*rac*-$RhCl_2$(η^4-et,ph-P4)]$^+$ complex is extremely robust, and we have not yet been able to release the *rac*-et,ph-P4 ligand or convert it into an active bimetallic catalyst precursor complex.

The current work strongly suggests that the formation of the *rac*,*trans*- and *meso*,*trans*-$Ni(CN)_2$($\eta^{2.5}$-et,ph-P4) intermediates promotes the partial isomerization of the meso to the racemic ligand diastereomer during the cyanolysis procedure. Increasing the CN^- concentration minimizes the amount and/or lifetime of **3m** limiting the meso to racemic ligand isomerization which is important if one wants to isolate *meso*-et,ph-P4. The bimetallic complex *meso*-Ni_2Cl_4(et,ph-P4), **2m**, is stable in cyanide-free solutions and does not show any tendency to isomerize. Similarly, free *meso*-et,ph-P4 ligand is not isomerized simply by cyanide in solution. The stereochemical inversion of the one internal meso phosphorus atom is most likely tied into the trans-spanning structure present in **3m**. The presence of filled d_{z^2} and empty p_z orbitals on the Ni(+2) center and their ability to interact with the internal phosphorus atoms of the et,ph-P4 ligand in **3** should assist the inversion of the one internal phosphorus center to form the somewhat better coordinating *rac*-et,ph-P4 ligand. The ^{31}P NMR spectrum of pure **3m** shows little evidence of conversion from **3m** to **3r** in solution at room temperature, arguing for the active role of CN^- anions in conjunction with **3m** for this isomerization process.

Acknowledgment. This work was supported by the National Science Foundation (Grants CHE-92-01051 and CHE-97-00526).

Supporting Information Available: CIF files for **3r** and **3m** and $^{31}P\{^1H\}$ NMR spectra of mixed, *rac*-, and *meso*-et,ph-P4 ligands. This material is available free of charge via the Internet at http://pubs.acs.org.

IC010035F