The η^5-(σ-P,π-Arene) Chelating H-MOP Ligand in an Optically and Catalytically Active Rhodium(I) Complex

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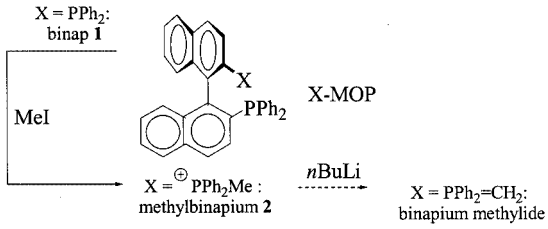
(*R*)-methylbinapium, a Hayashi-type phosphonium-MOP ligand, reacts with $[Rh(cod)_2][BF_4]$ in ethanol to afford the chiral mixed bis(monophosphane)rhodium(I) complex $[Rh(\eta^5$-H-MOP)$(MePh_2P)][BF_4]$. The constitutional and geometrical features of this complex have been determined by exhaustive ^1H, ^{11}B, ^{13}C, ^{31}P and ^{103}Rh 1-D, 2-D and NOE NMR spectroscopy and optical rotation measurements. The chelating η^5-(γ-phosphanyldiene) ligand character of H-MOP in this complex is an extension to Rh^I of similar coordination modes studied by Pregosin in the coordination sphere of Ru^{II}. The process of its formation relies on an enantiospecific reductive cleavage of a P^+–C bond, which is also reminiscent of Pregosin's P–C bond cleavages in the ruthenium series. The complex is a catalytic precursor for the hydrogenation of (Z)-α-acetamidocinnamic acid.

Introduction

According to the recent literature, the dogma stating that only chelating chiral *di*phosphane ligands can lead to high *ee*'s in reductive asymmetric catalysis has exceptions provided that the alternative *mono*phosphane ligands contain a resolved atropisomeric biaryl axis.[1] Monophosphite, monophosphonites and phosphoramidites of binaphthol are thus efficient ligands for the rhodium-catalyzed asymmetric hydrogenation of acrylic acid derivatives,[1,2] while Hayashi's X-MOP ligands (Scheme 1) are efficient ligands for the palladium-catalyzed reduction of allylic alcohols,[3] palladium-catalyzed hydrosilylation of olefins,[4] or rhodium-catalyzed arylation of imines.[5] The intriguing stereochemical efficiency of the X-MOP ligands is similar to that of the homoleptic binap ligand **1** (formally PPh_2-MOP).[6] This is assumed to mainly result from steric/electronic effects, but it might also be enhanced by the transient coordination of one or more C=C bonds of the naphthyl groups. Indeed, Pregosin's work definitely shows that binap and biphep can act as two-, four-, six-, or eight-electron donors in ruthenium(II) complexes.[7,8] On the other hand, binap- and MeO-biphep-ruthenium complexes have been reported to undergo selective hydrolytic P−C bond cleavage leading to complexes containing both a monophosphane H-MOP ligand and a diphenylphosphinoyl ligand.[9,10] In a few cases, the H-MOP ligand displays an η^4-coordination of one naphthyl substituent.[7,9]



Scheme 1. X-MOP ligands

Our initial goal was to look for chiral phosphoniophosphane ligands capable of providing hybrid chelation by primary P→$[Rh]^{\delta-}$ dative and secondary electrostatic $P^+\cdots[Rh]^{\delta-}$ interactions.[11] The results with "methyldiopium" as a ligand prototype suggested that the electrostatic interaction might be too loose due to the flexibility of the diopium skeleton.[12] The 1,1-binaphthyl core of **2**, a P^+-MOP ligand previously termed as "methylbinapium" (Scheme 1),[13] was therefore devised as a more rigid skeleton. The coordination chemistry of binapium **2** is, however, quite versatile.[12,13] While the methylbinapium skeleton is known to enter the coordination sphere of rhodium(I) as its ylide form (Scheme 1, X = PPh_2=CH_2),[14] the outcome of our attempts to introduce methylbinapium **2** (X = $^+PPh_2CH_3$) directly into the coordination sphere of rhodium(I) is here disclosed.

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Results and Discussion

Reactivity of Methylbinapium 2 with [Rh(cod)$_2$][BF$_4$]

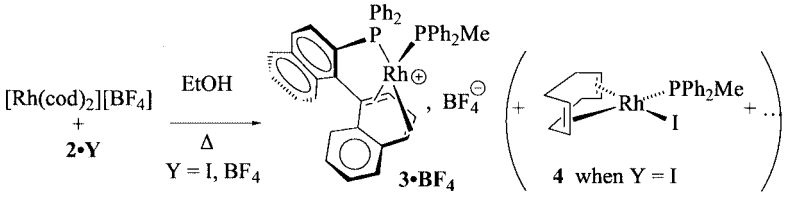
"(*R*)-methylbinapium" **2** was prepared by a one-step symmetry breaking of the parent C_2-symmetric diphosphane **1** with MeI.[13] The steric hindrance exerted by the phosphonium terminus towards the P^{III} terminus was illustrated by both the X-ray-crystal structure of binapium iodide **2·I**, and by its lack of reactivity toward electrophiles [e.g. MeI or Fe(CO)$_4$(NMe$_3$)].[13] It is therefore not surprising that **2·I** did not react with either [RhCl(cod)]$_2$ or [Rh(cod)$_2$][BF$_4$] under conventional conditions. Under harsher conditions, however, namely in boiling ethanol for two days, [Rh(cod)$_2$][BF$_4$] did react with a single equivalent of binapium iodide **2·I**. The expected product [RhI(cod)-(**2**)][BF$_4$] was not observed, but column chromatography allowed the separation of two complexes. An apolar complex was eluted first and assigned to structure **4** on the basis of its ^{1}H, ^{13}C and ^{31}P NMR spectroscopic data. The major polar complex was then eluted. Its ^{1}H and ^{31}P NMR spectra indicate the absence of both a cyclooctadiene ligand and any phosphonium group, and display two coupled nonequivalent P atoms at a rhodium center. The structure of this complex was later assigned as the H-MOP complex **3·BF$_4$** (Scheme 2, see below). Surprisingly, in the presence of two equivalents of **2·I**, the conversion of [Rh(cod)$_2$][BF$_4$] was much slower. This was ascribed to a harmful effect of the excess iodide ions competing with the hindered P^{III} center of **2**. Indeed, reaction of [Rh(cod)$_2$][BF$_4$] with the tetrafluoroborate salt **2·BF$_4$** proceeded more rapidly and more selectively: after refluxing for 20 h in ethanol, complex **3·BF$_4$** was the sole rhodium complex observed by ^{31}P NMR analysis of the crude material.

Structure Determination of Complex 3.

The major signal in the ES-MS spectrum at m/z = 741.2 is consistent with the parent cationic fragment [(MePh$_2$P)(H-MOP)Rh]$^+$. The complete multinuclear NMR assignment and the corresponding structure were determined in $CDCl_3$ solution. The ionic nature of the complex could be first refined as a [RhPP′]$^+$[BF$_4$]$^-$ form from the ^{11}B and ^{103}Rh NMR signals at δ = −0.59 ppm and −391 ppm (dd, $^1J_{PRh}$ = 199.6, $^1J_{P'Rh}$ = 206.0 Hz), respectively. The shielded ^{103}Rh signal is typical for a rhodium(I) complex in this environment.[15] The HMQC ^{1}H-^{31}P spectrum (Figure 1) displays a strong coupling of the ^{31}P/^{103}Rh ABX pattern [δ = 18.31 ppm (dd) and 57.39 ppm (dd), $^1J_{PRh}$ = 200, $^1J_{PRh}$ = 206, $^2J_{PP}$ = 39 Hz] with five inequivalent aromatic protons, and three equivalent shielded protons of a methylphosphane unit at δ = 1.50 ppm (d, $^2J_{PH}$ = 9 Hz). This observation supports a [Rh(PAr$_3$)(PAr$_2$Me)]$^+$ complexation pattern.

A weaker coupling of the ^{31}P nuclei also occurs with an intriguing ^{1}H nucleus at δ = 5.44 ppm. According to the ^{1}H-^{1}H COSY spectrum, this proton shows a $^3J_{H,H}$ coupling of 6.2 Hz with a proton whose signal appears at δ = 7.57 ppm, itself similarly coupled with a third proton (δ = 7.07 ppm). These latter three protons, referred to as H4, H3, and H2 (see Scheme 3), are also weakly coupled with ^{31}P nuclei ($J_{PH} \leq 1$ Hz). They were assigned to the protons of the η^4-diene-Rh moiety of a chelating H-MOP ligand. The η^4-coordination was confirmed by the high field resonance (δ = 97.3−105.5 ppm) of the corresponding carbon atoms C2, C3, C4 and C1, as well as by their $^1J_{RhC}$ values (c.a. 5 Hz). By contrast, the resonance at lower field of the adjacent C5 and C10 carbons (δ = 119.7 and 122.4 ppm) and the absence of coupling to the ^{103}Rh nucleus rule out the possibility of an η^6-coordination mode previously encountered in other cationic phosphane-rhodium complexes.[16] In the ruthenium series, due to the absence of $^1J_{RuC}$ information, it is more difficult to draw the line between η^4- and η^6-coordination. Nevertheless, in the related complex [Ru(η^5-H-MOP)(PPhEt$_2$)(PPh$_2$OH)]$^{2+}$[OTf]$_2$, which was assigned an η^4-diolefin structure, the effect of the proximate Ru atom on the uncoordinated C5 and C10 atoms was reported to result in chemical shifts of δ = 116.2 and 116.4 ppm, respectively. These are of the same order of magnitude as those of C5 and C10 in the rhodium complex **3**.[7] It is also worth noting that the η^4-coordination mode in **3** is consistent with a classical 16-electron count in the coordination sphere of phosphanylrhodium(I) complexes.

Although we were unable to isolate a crystal suitable for an X-ray diffraction analysis, the structure of the complex is probably very static, as indicated by VTP NMR analysis at 313 and 223 K: apart from a slight broadening, no significant shift nor decoalescence of the ^{1}H and ^{31}P signals was observed. ^{1}H-^{1}H NOE experiments allowed us to confirm the above topological assignment and to gain insights into the geometrical relationships between protons (Scheme 3). In particular, they show that in the preferred conformation, the methyl group is oriented towards the PPh$_2$ terminus of the naphthylphosphane ligand, while both phenyl rings of the methyldiphenylphosphane ligand are oriented towards the diene moiety. Although direct information on the conformation of the η^4-naphthyl group is not available, the absence of an NOE between the latter phenyl ring protons



Scheme 2. Reaction of methylbinapium **2** with [Rh(cod)$_2$][BF$_4$]

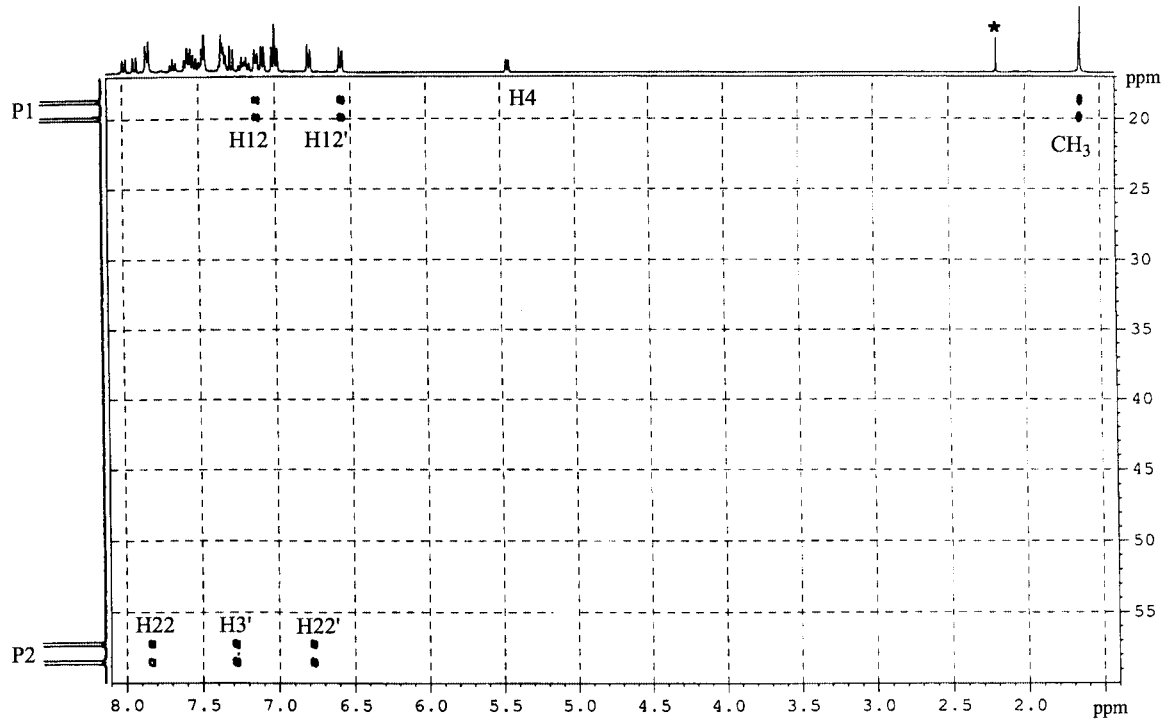
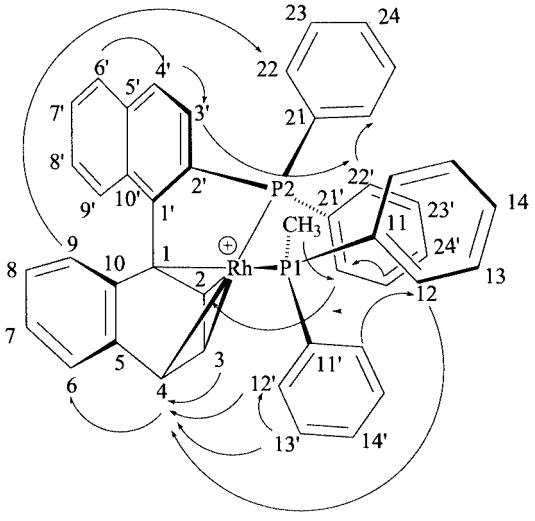


Figure 1. 400−162 MHz HMQC ^{1}H-^{31}P NMR spectrum of **3·BF$_4$** in $CDCl_3$ solution at 298 K; a weaker correlation of H4 with P1 and P2 is also seen at a lower threshold of the 2D plot (atom numbering in Scheme 3); *: residual acetone peak



Scheme 3. 3D structural assignment based on ^{1}H-^{1}H NOE experiments

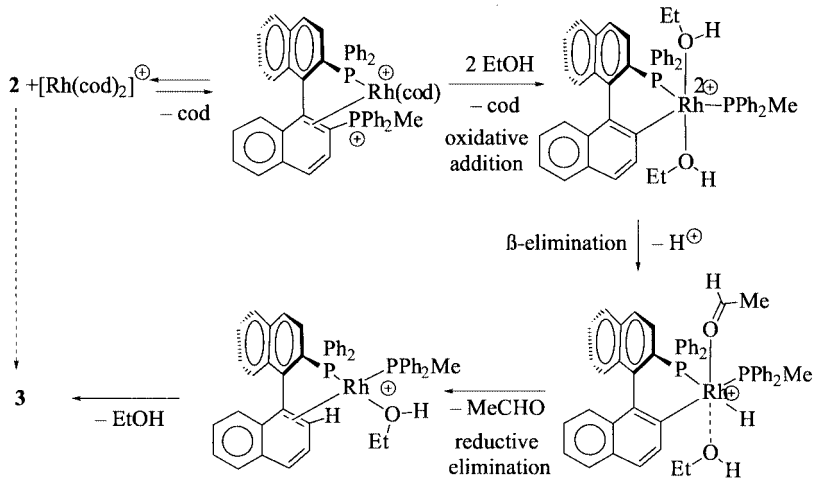
and the H6−H9 protons would be consistent with a folding along the C1···C4 axis. Such a folding (ca. 35°) was indeed reported to occur in the related complex [(η^4-naphthalene)RhCp].[17] Finally, NOE data also support a classical face-to-edge conformation of the phenyl substituents in both the $RhPPh_2$ units.

The optical rotation of complex **3·BF$_4$** is high: $[\alpha]_D^{25} = +175$ ($c = 0.1$, CH_2Cl_2). For comparison, the optical rotation of the enantiomerically pure complex [{(*R*)-binap}(cod)Rh][ClO_4] is $[\alpha]_D^{20} = +180$ ($c = 0.05$, CH_2Cl_2),[6] and that of free (*S*)-H-MOP prepared by Hayashi is $[\alpha]_D^{25} = +102$ ($c = 2.03$, $CHCl_3$).[18] The chiral information brought by the (*R*)-binapium reactant is therefore qualitatively preserved: the complex is enantiospecifically obtained as an enriched scalemic mixture.

In summary, the complex thus contains both an η^5-(σ-P, π-arene) (*S*)-H-MOP ligand and an independent η^1,σ-P methyldiphenylphosphane ligand. It provides a generalization to rhodium(I) of similar well-documented complexation patterns in ruthenium(II) complexes.[7−9] It is, however, worth noting that other chelating ω-phosphanylalkene ligands associated with an independent monophosphorus(III) ligand at a rhodium(I) center are known.[19]

Reaction Mechanism via Reductive P$^+$−C Bond Cleavage

The formation of complex **3** formally results from a complexation-reduction process. The reducing agent here is the ethanol solvent, which is also commonly used to convert rhodium(III) salts to rhodium(I) complexes.[24] A plausible mechanism involving elementary processes at Rh^I and Rh^{III} centers is depicted in Scheme 4. Starting from (*R*)-binapium, the final stereoselective reductive elimination would finally lead to an (*S*)-H-MOP ligand.[18] The overall P$^+$−C bond cleavage process is reducing in nature, and is therefore basically complementary to the related "acid-induced" and "solvent-induced" P−C bond cleavage processes identified by Pregosin in the coordination sphere of ruthenium complexes.[7] A related reductive P−C bond cleavage was also invoked in the coordination sphere of a rhodium complex converting PPh_3 to PPh_2(*n*-Pr) under hydrogen in the pres-

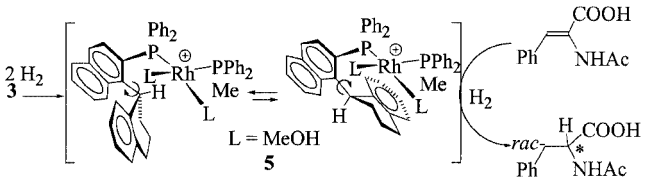


Scheme 4. Plausible mechanism for the formation of complex **3**

ence of propylene at 130 °C.[20] It is also worth noting that Hayashi recently reported a selective P^V-C bond cleavage by *n*BuLi in neutral $P(O)Ph_2$-MOP derivatives.[21]

Catalytic Hydrogenation with Complex 3

The chiral structure of complex **3** combines the essential features of classical $[P_2Rh(diene)]^+$ catalytic precursors for asymmetric hydrogenation of prochiral acrylic acid derivatives,[22] albeit in another connectivity pattern, $[P(Pdiene)Rh]^+$. These features prompted us to test complex **3** in a 1% catalytic ratio for the hydrogenation of (*Z*)-α-acetamidocinnamic acid, a reference substrate. Under 1 bar of hydrogen in methanol, the conversion into *N*-acetylphenylalanine reached only 6% after 40 h. Under 20 bar of hydrogen, however, the conversion reached 95%, although no significant enantioselectivity was obtained. According to the generally accepted mechanism for rhodium-catalyzed hydrogenation,[22] the η^4-diene moiety should be hydrogenated in situ to a putative (but likely) tetralinyl-substituted naphthylphosphane complex **5**. In this complex, the (*S*) configuration of the chiral carbon center should result from the initial (*S*)-configuration of the chirality axis of H-MOP (Scheme 5). The fate of the 1,1′-tetralinylnaphthtylphosphane ligand has been investigated by MM2 calculations. The latter suggest that, in contrast to H-MOP, this ligand no longer contains a frozen atropisomeric axis.[23] Both "atropisomers" are essentially isoenergetic,[23b] and the rotation barrier could be estimated at approx. 45 kcal·mol^{-1}.[23c] In qualitative accordance with the experimental observations, the same method applied to the parent H-MOP ligand affords a much higher barrier of about 130 kcal·mol^{-1}.[3,4] The 1,1′-tetralinylnaphthtylphosphane ligand can therefore be qualified as "weakly" chiral. The negligible *ee* is therefore consistent with all reports on the enantioselectivity control by monophosphane ligands bearing a remote chiral center on their backbone.[22]



Scheme 5. Catalytic hydrogenation of (*Z*)-α-acetamidocinnamic acid with complex **3** as precursor

Conclusion

The novelty of the above results comes from two points: (i) the η^5-(σ-P,π-arene) hetero-chelating behaviour of an atropisomeric biarylphosphane at a rhodium(I) center; (ii) a selective reductive P^+-C bond cleavage leading to a mixed bis(monophosphane)rhodium(I) complex. This peculiar organometallic chemistry and the preliminary catalytic results pave the way to more general studies of this type of complexes in other Rh-catalyzed processes, such as C–C bond forming reactions.[3,4,5]

Experimental Section

Reactions were carried out under a nitrogen atmosphere using Schlenk tube and vacuum line techniques. Ethanol was distilled over drierite. Dichloromethane was distilled over P_2O_5. (−)-(*R*)-Binap and methyl iodide were purchased from Fluka. Ammonium tetrafluoroborate was purchased from Aldrich. $[Rh(cod)_2][BF_4]$ was prepared from $[RhCl(cod)]_2$, itself prepared from cyclooctadiene and $RhCl_3{\cdot}3H_2O$ (Johnson–Mattey) according a modified described procedure (no carbonate was added).[24] NMR spectra were recorded in $CDCl_3$ solution, on Bruker AC 200 and AMX 400 spectrometers. Positive chemical shifts at low field are expressed in ppm relative to internal TMS for ^1H and ^{13}C, and external 85% H_3PO_4 in D_2O for ^{31}P. ^{103}Rh chemical shifts are given to high fre-

quency of Ξ(^{103}Rh) = 3.16 MHz. Optical rotations were measured in a 1-dm cell with a Perkin−Elmer 241 polarimeter.

Methylbinapium 2: (*R*)-Methylbinapium iodide **2·I** (m.p. 307−310 °C) was prepared in 97% yield from (*R*)-binap **1** according to described procedures.[13,14] The tetrafluoroborate salt **2·BF$_4$** was obtained quantitatively by metathesis of **2·I** and [NH$_4$][BF$_4$].

Complex 3·BF4: (*R*)-Binapium tetrafluoroborate **2·BF$_4$** (0.115 g, 0.16 mmol) and [Rh(cod)$_2$][BF$_4$] (0.065 g, 0.16 mmol) were mixed in ethanol (15 mL). The suspension was heated, and the resulting deep orange solution was refluxed for 20 h. The solvent was then evaporated under reduced pressure. ^{31}P NMR analysis of the crude material indicated the presence of complex **3·BF$_4$** along with traces of binapium oxide [^{31}P NMR (81 MHz, CDCl$_3$): δ = 26.52 (s, 1 P, MePh$_2$*P*$^+$), 31.67 (s, 1 P, Ph$_2$*P*=O)]. Further purification was achieved by chromatography over silica gel eluting with CH$_2$Cl$_2$/acetone mixtures of increasing polarity (from 100:0 to 80:20). The most colored fractions were collected and the solvents evaporated, leading to an orange solid (0.060 g, 45%) which was used for full spectroscopic analysis and optical rotation measurement. TLC (SiO$_2$, CH$_2$Cl$_2$/acetone 80:20) R_f = 0.60. (+)ES-MS: *m*/*z* = 741.2 with consistent isotopic pattern. $[\alpha]_D^{25}$ = +175, $[\alpha]_{578}^{25}$ = +202. $[\alpha]_{546}^{25}$ = +278 (c = 0.1, CH$_2$Cl$_2$). ^{11}B (128.4 MHz, CDCl$_3$): δ = −0.59 (q, $^1J_{FB}$ = 1.0 Hz, *B*F$_4$). Other NMR assignments were achieved with the help of ^{1}H{^{31}P}, ^{31}P{^{1}H}, ^{13}C{^{1}H}, ^{13}C{^{1}H, ^{31}P}, ^{1}H-^{31}P{^{1}H} HMQC, ^{31}P-^{103}Rh ^{1}J-HMQC, ^{1}H-^{13}C{^{31}P}, ^{1}H-^{1}H{^{31}P} GS-HMQC, ^{1}H-^{1}H GS-COSY45, ^{1}H{^{31}P} dpfgse TOCSY, and ^{1}H-^{1}H{^{31}P} dpfgse (t_m = 600 ms) NOE experiments.

^{31}P NMR (162 MHz, CDCl$_3$): δ = 57.89 (dd, $^1J_{PRh}$ = 206.0, $^2J_{PP}$ = 38.6 Hz, NaphtPh$_2$*P*), 19.28 (dd, $^1J_{PRh}$ = 199.6, $^2J_{PP}$ = 38.6 Hz, MePh$_2$*P*) ppm. ^{103}Rh NMR (12.6 MHz, CDCl$_3$): δ = −391 (dd, $^1J_{PRh}$ = 206.0, $^1J_{PRh}$ = 199.6 Hz, PP′*Rh*$^+$) ppm. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.63 (ddd, $^2J_{P1H}$ = 9.3 Hz, $^3J_{RhH}$ = 1.3 Hz, $^4J_{P2H}$ = 0.6 Hz, 3 H, P1C*H*$_3$), 5.44 (dt, $^3J_{H4H3}$ = 6.2 Hz, $^3J_{P1H4} \approx {}^2J_{P2H4} \approx$ 1 Hz, 1 H, *H*4), 6.56 (dd, $^3J_{H12'H13'}$ = 7.6, $^3J_{P1H12'}$ = 11.8 Hz, 2 H, *H*12′), 6.77 (dd, $^3J_{H22'H23'}$ = 7.7, $^3J_{P2H22'}$ = 12.0 Hz, 2 H, *H*22′), 7.00 (dt, $^3J_{H23'H22'} \approx {}^3J_{H23'H24'}$ = 7.6, $^4J_{P2H23'}$ = 1.3 Hz, 2 H, *H*23′), 7.00 (dt, $^3J_{H13'H12'} \approx {}^3J_{H13'H14'}$ = 7.6, $^4J_{P1H13'}$ = 1.3 Hz, 2 H, *H*13′), 7.07 (dd, $^3J_{H2H3}$ = 6.2 Hz, $^2J_{P1H2}$ = 0.7 Hz, 1 H, *H*2), 7.07 (dm, $^3J_{H9H8} \approx$ 7 Hz, 1 H, *H*9), 7.11 (dm, $^3J_{P1H12}$ = 11.8 Hz, 2 H, *H*12), 7.18 (ttd, $^3J_{H24'H23'}$ = 7.8, $^4J_{H24'H22'}$ = 1.3, $^3J_{P2H24'}$ = 1.8 Hz, 1 H, *H*24′), 7.21 (ttd, $^3J_{H14'H13'}$ = 7.5, $^4J_{H14'H12'}$ = 1.3, $^5J_{P1H14'}$ = 1.8 Hz, 1 H, *H*14′), 7.25 (dm, $^5J_{P2H24}$ = 2.0 Hz, 1 H, *H*24), 7.27 (dm, $^4J_{P2H23}$ = 2.0 Hz, 2 H, *H*23), 7.27 (dd, $^3J_{H3'H4'}$ = 8.4, $^3J_{P2H3'}$ = 8.5 Hz, 1 H, *H*3′), 7.33 (d, $^3J_{H6H7}$ = 7.2 Hz, 1 H, *H*6), 7.33 (m, 1 H, *H*14), 7.35 (dm, $^4J_{P1H13}$ = 2.0 Hz, 2 H, *H*13), 7.51 (t, $^3J_{H8H7} = {}^3J_{H8H9}$ = 7.2 Hz, 1 H, *H*8), 7.55 (m, 1 H, *H*8′), 7.57 (t, $^3J_{H3H2} \approx {}^3J_{H3H4}$ = 6.2 Hz, 1 H, *H*3), 7.57 (m, 1 H, *H*7), 7.66 (dt, $^3J_{H7'H6'} \approx {}^3J_{H7'H8'}$ = 8.3, $^4J_{H7'H9'}$ = 1.2 Hz, 1 H, *H*7′), 7.82 (dm, $^3J_{P2H22}$ = 7.8 Hz, 2 H, *H*22), 7.82 (d, $^3J_{H9'H8'}$ = 8.6 Hz, 1 H, *H*9′), 7.91 (dd, $^3J_{H4'H3'}$ = 8.4, $^4J_{P2H4'}$ = 1.6 Hz, 1 H, *H*4′), 7.98 (d, $^3J_{H6'H7'}$ = 8.3 Hz, 1 H, *H*6′) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 17.29 (ddd, $^1J_{PC}$ = 32, $^2J_{RhC}$ = 2, $^3J_{P2C}$ = 2 Hz, P1*C*H$_3$), 97.32 (ddd, $^1J_{RhC4}$ = 5, $^3J_{P1C4}$ = 4.8, $^3J_{P2C4}$ = 8.0 Hz, *C*4), 97.56 (ddd, $^1J_{RhC2}$ = 5, $^2J_{P1C2}$ = 4.0, $^2J_{P2C2}$ < 1 Hz, *C*2), 101.74 (ddd, $^1J_{RhC3}$ = 4, $^2J_{P1C3}$ < 1, $^2J_{P2C3}$ = 2.0 Hz, *C*3), 105.54 (ddd, $^1J_{RhC1}$ = 5, $^2J_{P1C1}$ = 10.4, $^2J_{P2C1}$ = 4.3 Hz, *C*1), 119.67 (s, *C*5),122.36 (s, *C*10), 122.90 (s, *C*9), 125.46 (s, *C*6), 126.44 (s, *C*9′), 127.71 (s, *C*3′), 128.78 (d, $^3J_{P1C13'}$ = 10.5 Hz, *C*13′), 128.78 (s, *C*6′), 128.97 (d, $^3J_{P2C23'}$ = 10.5 Hz, *C*23′), 128.94 (s, *C*8′),129.19 (d, $^3J_{P1C13}$ = 10.5 Hz, *C*13), 129.43 (s, *C*7′), 129.66 (s, *C*7), 129.69 (d, $^3J_{P2C23}$ = 11.5 Hz, *C*23), 129.84 (dd, $^1J_{P2C21}$ = 52, $^2J_{RhC21}$ = 3 Hz, *C*21), 130.08 (s, *C*8), 130.68 (d, $^4J_{P1C14}$ = 2.5 Hz, *C*14), 130.79 (d, $^4J_{P1C14'}$ = 2.5 Hz, *C*14′), 131.11 (d, $^4J_{P2C24'}$ = 2.0 Hz, *C*24′), 131.20 (d, $^2J_{P1C12}$ = 12.0 Hz, *C*12), 131.30 (d, $^1J_{P2C21'}$ = 48 Hz, *C*21′), 131.30 (s, *C*4′), 131.47 (d, $^3J_{P2C10'}$ = 15 Hz, *C*10′), 132.00 (d, $^2J_{P2C22'}$ = 11.5 Hz, *C*22′), 132.35 (d, $^4J_{P2C24}$ = 3 Hz, *C*22), 132.40 (d, $^2J_{P1C12'}$ = 12.0 Hz,; *C*12′), 132.50 (d, $^1J_{P1C11'}$ = 47.5 Hz, *C*11′), 134.44 (d, $^4J_{P2C5'}$ = 2.0 Hz, *C*5′), 134.72 (d, $^2J_{P2C22}$ = 13.5 Hz, *C*22), 137.62 (d, $^1J_{P1C11}$ = 46.2 Hz, *C*11), 142.27 (d, $^2J_{P2C1'}$ = 21.0 Hz, *C*1′), 146.21 (dd, $^1J_{P2C2'}$ = 49.0, $^2J_{P1C2'}$ = 3.0 Hz, *C*2′) ppm.

Hydrogenation Procedure: Complex **3·BF$_4$** (0.005 g, 0.006 mmol) and (*Z*)-α-acetamidocinnamic acid (0.123 g, 0.6 mmol) were placed in a glass vessel in a steel autoclave under 1 bar of nitrogen atmosphere. Methanol was then syringed in, and the autoclave was pressurized to 21 bar with hydrogen gas. After stirring at 25 °C for 40 h, the autoclave was opened and the solvent evaporated to dryness to give an orange solid. ^{1}H NMR analysis of the crude material in [D$_6$]DMSO indicated an exclusive 95% conversion of the staring material to *N*-acetylphenylalanine. The catalyst residue was removed by treatment with a 5 N aqueous NaOH solution and washing with Et$_2$O. After acidification with HCl, the aqueous layer was extracted with Et$_2$O. The organic layer was dried over MgSO$_4$ and the solvents evaporated giving a white powder (0.87 g) consisting in 95% *N*-acetylphenylalanine and 5% unchanged olefin according to ^{1}H NMR spectroscopy. $[\alpha]_D^{25}$ = +0.007 (*c* = 1, EtOH).

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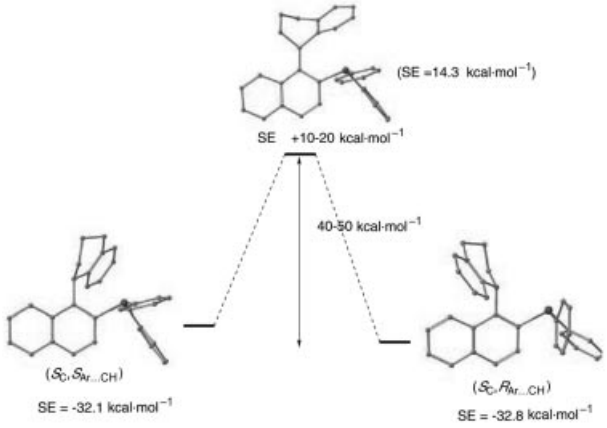

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