separation in energy between the highest occupied molecular orbitals and the next highest filled molecular orbitals) as the metal varies from Cr to Mo to W.

Our experimental observations of various bulk and stoichiometric reduction reactions have led us to propose a unified mechanism for the overall reduction reactions of the $[CpM(NO)I_n]_2$ dimers which is presented in Scheme I for the case when M = Mo and n = 2. Nevertheless, confirmation of the exact natures of the various electron-transfer steps presented in this scheme as well as positive identification of the radical intermediates thus formed must await a detailed electrochemical study of these processes.

Despite the considerable insight into the overall reduction reaction (4) that has been gained during this work, some questions remain unanswered. The most intriguing of these is why the use of bulky phosphines such as P(*t*-Bu)$_3$ or PPh_3 during these reactions fails to produce any nitrosyl-containing products, even when such products (e.g., $CpM(NO)(PPh_3)_2$ (M = Cr, Mo)) are preparable by other synthetic routes.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L. and a graduate scholarship to A.D.H.

Registry No. $CpCr(NO)[P(OMe)_3]_2$, 100898-71-3; $CpMo(NO)[P(OMe)_3]_2$, 100898-72-4; $CpW(NO)[P(OMe)_3]_2$, 100898-73-5; $CpCr(NO)(PMePh_2)_2$, 100898-74-6; $CpMo(NO)(PMePh_2)_2$, 100898-75-7; $CpW(NO)(PMePh_2)_2$, 100898-76-8; $CpMo(NO)[P(n\text{-}Bu)_3]_2$, 100898-77-9; $CpMo(NO)(SbPh_3)_2$, 100898-78-0; $CpMo(NO)(Ph_2PCH_2CH_2PPh_2)$, 32842-38-9; $CpMo(NO)I_2(PMePh_2)$, 100898-79-1; $CpMo(NO)I_2[P(OMe)_3]$, 100898-80-4; $CpMo(NO)I_2(OPMePh_2)$, 100898-81-5; $[CpMo(NO)I(PMePh_2)_2]I$, 100898-82-6; $[CpMo(NO)I(Ph_2PCH_2CH_2PPh_2)]I$, 100908-90-5; $[CpCr(NO)I]_2$, 94090-65-0; $[CpMo(NO)I]_2$, 55836-28-7; $[CpW(NO)I_2]_2$, 71341-43-0; $[CpMo(NO)Br_2]_2$, 40671-96-3; $Na[H_2Al(OCH_2CH_2OCH_3)_2]$, 22722-98-1; $OPMePh_2$, 2129-89-7; $CpMo(NO)_2I$, 56403-79-3.

Catalytic Asymmetric Hydrogenation of Prochiral Enamides by Rhodium(I) Complexes Containing the Enantiomers of (*R**,*R**)-(±)-1,2-Phenylenebis(methylphenylphosphine) and Its Arsenic Isosteres

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Soluble (bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) complexes containing the enantiomers of (*R**,*R**)-(±)-1,2-phenylenebis(methylphenylphosphine) or their arsenic isosteres have been shown to be highly efficient catalysts for the asymmetric hydrogenation of a variety of prochiral *Z*-substituted enamide acids and esters, producing α-amino acid derivatives with optical yields as high as 94%. The enantioselectivity of the reaction, however, is remarkably dependent upon the nature of the β-substituent on the enamide–olefin bond. The catalyst containing the bis(tertiary arsine) out performed the corresponding phosphorus compound in several instances. Both ligands form rigid dissymmetric five-membered chelate rings in which the chirality is due solely to a pair of equivalent asymmetric tertiary phosphorus or arsenic donor groups. Hydrogenation of the catalyst precursor bis(tertiary phosphine) complexes in dichloromethane produces crystalline catalytic dimers of the type $[Rh_2(diphos)_2](PF_6)_2$ that have been assigned structures involving arene bridging on the basis of ^{31}P NMR spectroscopy. A ^1H NMR investigation of an isolated enamide complex of the bis(tertiary phosphine) has shown that hydrogenation of the minor diastereomer leads to the major amino acid product, thus supporting the view that it is the relative stabilities of intermediate product diastereomers that determines stereoselectivity in these systems. An unusual dynamic NMR behavior was observed for one of the diastereomers at temperatures below −50 °C, which has been rationalized in terms of a restricted rotation of one of the phosphorus–phenyl rings by the carbomethoxy group of the coordinated enamide.

The spectacular success of soluble rhodium(I) complexes containing chiral bis(diphenylphosphino)alkanes in catalyzing the asymmetric hydrogenation of prochiral enamides[1] has been attributed to the steric influence of a dissymmetric edge–face array of the four phenyl groups on the phosphorus donor atoms in the chelate ring.[2] In five-[2,3] and six-membered[4] alicyclic systems the preferred equatorial disposition of bulky substituents in the flexible chiral linkage between the donor atoms is responsible for a remarkable degree of control over the enantiomorphic ring conformation adopted, which in turn determines the chirality of the dissymmetric array of phenyl groups. It was therefore of interest to examine the properties of catalysts containing rigid chelate ring systems, where the dissymmetry can be associated directly with a pair of equivalent asymmetric phosphorus or arsenic donor groups.

In this paper we report the preparation of a pair of isostructural cationic rhodium(I) complexes containing an enantiomer of (*R**,*R**)-(±)-1,2-phenylenebis(methyl-

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Table I. Optical Yields of Amino Acids with Use of (−)-1 and (−)-2 as Catalyst Precursors under Nonoptimized Standard Conditions[a]

substrate	α-amino acid derivative	cat. precursor	optical yield, %
(*Z*)-PhCH:C(NHCOMe)CO_2H	*N*-acetyl-(*S*)-phenylalanine	(−)-1	79 (50)
		(−)-2	80 (49)
(*Z*)-PhCH:C(NHCOMe)CO_2Me	*N*-acetyl-(*S*)-phenylalanine methyl ester	(−)-1	*c* (51)
		(−)-2	*c* (16)
(*Z*)-PhCH:C(NHCOPh)CO_2H	*N*-benzoyl-(*S*)-phenylalanine	(−)-1	64 (33)
		(−)-2	77 (26)
(*Z*)-PhCH:C(NHCOPh)CO_2Et	*N*-benzoyl-(*S*)-phenylalanine ethyl ester	(−)-1	*c* (35)
		(−)-2	*c* (36)
CH_2:C(NHCOMe)CO_2H	*N*-acetyl-(*S*)-alanine	(−)-1	49 (50)
		(−)-2	23 (12)
(*Z*)-EtCH:C(NHCOPh)CO_2H	*N*-benzoyl-(*S*)-α-aminobutyric acid	(−)-1	79 (64)
		(−)-2	50 (57)
Me_2C:C(NHCOPh)CO_2H	*N*-benzoyl-(*S*)-valine	(−)-1	*d* (37)
		(−)-2	*d* (89)
(*Z*)-*i*-PrCH:C(NHCOMe)CO_2H	*N*-acetyl-(*S*)-leucine	(−)-1	94 (84)
		(−)-2	90 (9)
(*Z*)-*i*-PrCH:C(NHCOPh)CO_2H	*N*-benzoyl-(*S*)-leucine	(−)-1	90 (76)
		(−)-2	84 (21)

[a] All reactions were performed at 20 °C and 1 atm of H_2 for ethanol solutions (50 mL) containing 1 g (ca. 5 mmol) of substrate and 0.03 g (ca. 0.05 mmol) of catalyst precursor. [b] The value in parentheses is the optical yield in the absence of added triethylamine (ca. 10 mmol). The optical yields were calculated on the basis of the following literature values: *N*-acetyl-(*S*)-phenylalanine, $[\alpha]^{20}_D$ +46.0° (*c* 1.0, EtOH);[2] *N*-acetyl-(*S*)-phenylalanine methyl ester, $[\alpha]^{20}_D$ +16.4° (*c* 2.0, MeOH);[26] *N*-benzoyl-(*S*)-phenylalanine, $[\alpha]^{21}_D$ −40.3° (*c* 1.0, MeOH);[2] *N*-benzoyl-(*S*)-phenylalanine ethyl ester, $[\alpha]_D$ −42.7° (*c* 1, MeOH);[2] *N*-acetyl-(*R*)-alanine, $[\alpha]_D$ +66.3° (*c* 2, H_2O);[2] *N*-benzoyl-α-aminobutyric acid was converted into its sodium salt (by treatment with one equivalent of sodium hydroxide) for which $[\alpha]^{20}_D$ +30.7 (*c* 7.99, H_2O) is reported;[27] *N*-benzoyl-(*S*)-valine, +21.8° (*c* 4.9, 95% EtOH);[28] *N*-acetyl-(*S*)-leucine, $[\alpha]_D$ −23.2° (*c* 1, EtOH);[2] *N*-benzoyl-(*R*)-leucine, $[\alpha]_D$ +10.1° (*c* 2.0, MeOH).[2] [c] Reaction in presence of triethylamine not performed. [d] No reaction observed.

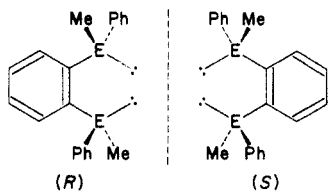

Figure 1. Enantiomerism in (*R**,*R**)-(±)-1,2-phenylenebis(methylphenylphosphine) (E = P) and in the corresponding bis(tertiary arsine) (E = As).

phenylphosphine), (*R**,*R**)-diph,[5] or its arsenic analogue, (*R**,*R**)-dias[6] (Figure 1), and compare the behavior of the two as catalysts for the asymmetric hydrogenation of a variety of prochiral *Z*-substituted enamide acids and esters.

Results and Discussion

The enantiomers of (*R**,*R**)-(±)-1,2-phenylenebis(methylphenylphosphine) and their arsenic isosteres were obtained as previously described.[5,6] The catalyst precursor complexes (−)-[Rh(NBD){[*R*-(*R**,*R**)]-diph}]PF_3·2Me_2CO [(−)-1] and (−)-[Rh(NBD){[*R*-(*R**,*R**)]-dias}]PF_6 [(−)-2] were isolated as highly crystalline orange solids (after recrystallization from acetone) by following the procedure of Schrock and Osborne,[7] for example

$$^1/_2[RhCl(NBD)]_2 \xrightarrow[2.\ [S\text{-}(R^*,R^*)\text{-diph}^8]{1.\ AgNO_3}{3.\ NH_4PF_6} [Rh(NBD)\{[R\text{-}(R^*,R^*)]\text{-diph}\}]PF_6$$
(−)-1

For precursor complex (−)-1, step 2 was performed at −78 °C in order to prevent the formation of [Rh{[*R*-(*R**,*R**)]-diph}$_2$]$^+$. Both (−)-1 and (−)-2 are air-stable.

Complexes (−)-1 and (−)-2 proved to be highly efficient compounds for the catalytic asymmetric hydrogenation of a wide range of prochiral enamides (see Table I). The results in Table I are not optimized: all reactions were run under 1 atm of hydrogen at 20 °C for solutions in ethanol (50 mL) containing substrate (1.0 g) and catalyst precursor (0.03 g). A significant substrate concentration effect was not evident: reduction of *N*-acetamidocinnamic acid at one-tenth of the usual concentration in the presence of (−)-1 gave an identical result to the above. Furthermore, identical optical yields were obtained with use of isolated (−)-[Rh_2\{[*R*-(*R**,*R**)]-diph}$_2$]$(PF_6)_2$ as catalyst precursor for this substrate. In tetrahydrofuran or dichloromethane solutions, however, the reaction did not proceed at all. In general, the addition of an equivalent of triethylamine to the reaction mixture led to a significant improvement in the optical yields of amino acid derivatives. The enantioselectivity of the reduction of (*Z*)-α-acetamido-β-isopropylacrylic acid by (−)-2 was increased from 9 to 90% by the addition of triethylamine, whereas α-benzamido-β,β-dimethylacrylic acid was not reduced in the presence of amine for either catalyst. Interestingly, the optical yield obtained in the hydrogenation of the latter tetrasubstituted olefin with (−)-2 is significantly higher than that previously obtained with use of any other chelating phosphine.[3,10,11] The optical yields obtained with the esters of the acrylic acids were similar to those found for the corresponding parent acid substrates. In general, the optical yields obtained with (−)-1 were higher than those found with the bis(tertiary arsine) containing catalyst (−)-2, but for several substrates (−)-2 out performed (−)-1. The bis(tertiary arsine) catalyst (−)-2 is much more effective for the reduction of prochiral enamides than the catalyst containing (+)- or (−)-diarsop (where diarsop = 2,3-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylarsino)butane]: the latter appears to be the only other optically active bis(tertiary arsine)-containing catalyst so far investigated.[12] The

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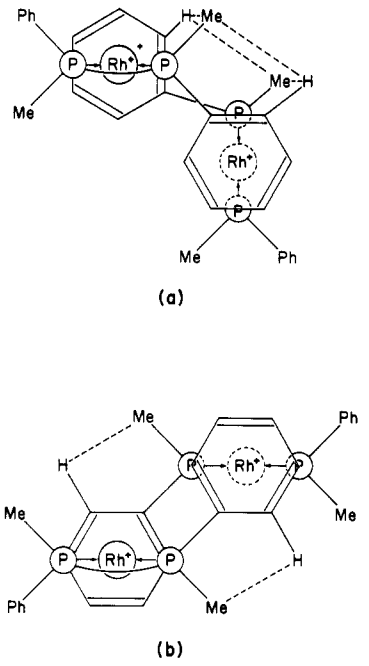

Figure 2. Representations of the proposed structures of cations in salts (−)-4 (a) and *meso*-4 (b).

unsymmetrical chelating mono(tertiary arsine) (*S*)-amars (where amars = *N*,*N*-dimethyl-1-[*o*-(diphenylarsino)-phenyl]ethylamine)[13] did not produce an effective rhodium(I) catalyst for the asymmetric reduction of prochiral ketones. The results of the asymmetric hydrogenation of enamides with this catalyst system do not appear to have been reported.

Reaction times varied over a wide range but were similar for both catalysts. For example, the hydrogenation of (*Z*)-α-acetamido-β-isopropyl-cinnamic acid with use of (−)-1 took ca. 25 min to complete, whereas 30 h was required to reduce (*Z*)-α-acetamido-*p*-acetoxycinnamic acid under the same conditions. In the presence of the catalyst derived from (−)-1 reduction of α-acetamidocinnamic acid took place at approximately twice the rate as the corresponding reaction involving the catalyst containing 1,2-bis(diphenylphosphino)ethane (precursor complex **3**), thus establishing (−)-1 as one of the most reactive five-membered chelate ring asymmetric hydrogenation catalysts hitherto studied.[3] It is evident from Table I that although the α-acylamino group appears to have only a small influence on the enantioselectivity of the reaction, the nature of the β-substituent is critical: selectivity increases in the order H < Me ≃ Ph < *i*-Pr.

Hydrogenation of (−)-1 in dichloromethane produced the light-sensitive, but air-stable, dimer (−)-4, which crystallized from hot dichloromethane as a solvate.

$$2[\underset{(-)\text{-}1}{\text{Rh(NBD)}\{[R\text{-}(R^*,R^*)]\text{-diph}\}}]\text{PF}_6 \xrightarrow[-\text{C}_7\text{H}_{12}]{\text{H}_2} \underset{(-)\text{-}4}{[\text{Rh}_2\{[R\text{-}(R^*,R^*)]\text{-diph}\}_2](\text{PF}_6)_2}$$

A structure involving η^6-arene bridging has been proposed for (−)-4 on the basis of ^{1}H and ^{31}P NMR data, and by comparison of the properties of this substance with those of other similar dimers, for example, $[Rh_2\{(R)\text{-Cycphos}\}_2](PF_6)_2$ (where Cycphos = 1,2-bis(diphenylphosphino)-1-cyclohexylethane),[3] $[Rh_2(dppe)_2](BF_4)_2$ (where dppe = 1,2-bis(diphenylphosphino)ethane),[14] and $[Rh_2\{(S)\text{-binap}\}_2](ClO_4)_2$ (where binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl).[15] The ^{31}P{^{1}H} NMR spectrum of dimer (−)-4 in dichloromethane-d_2 is consistent with the structure shown in Figure 2. Analysis of the spectrum with use of the program Davins[16] based on an AA′BB′XX′ spin system led to the following assignment: δ(A) 63.02, δ(B) 57.78, J_{AB} = 37.4 Hz, $J_{AB'}$ = −1.0 Hz, $J_{BB'}$ = 1.7 Hz, J_{AX} = 216.6 Hz, $J_{AX'}$ = 1.4 Hz, J_{BX} = 0.0 Hz, $J_{BX'}$ = 195.7 Hz, and $J_{XX'}$ = 2.7 Hz (Figure 3). These values, including that of J_{Rh-Rh}, are fully consistent with the proposed structure.[3] Differences between the calculated and observed spectrum may be attributed to the existence of a more complex spin system than that assumed in the simulation, but it was considered that a higher order analysis of the spectrum was not warranted. The presence of bridging phenyl groups is indicated by the multiplets in the region of δ 6.57 and 5.83 in the ^{1}H NMR spectrum.[3,14] Hydrogenation of the corresponding racemic precursor complex (±)-1 gave dimer *meso*-4, which was only slightly soluble in dichloromethane: the ^{31}P and ^{1}H NMR spectra of this complex are markedly different from

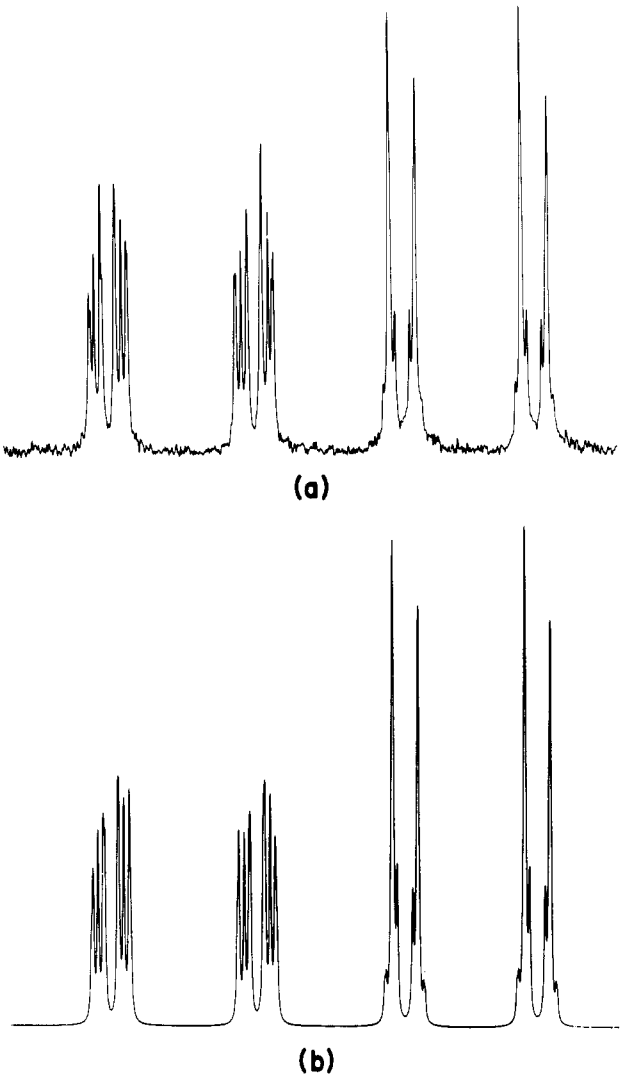

Figure 3. Observed (a) and simulated (b) ^{31}P{^{1}H} NMR spectrum of dimer (−)-4.

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Table II. Selected $^1H\{^{31}P\}$ NMR Spectral Data for Enamide Complex (±)-5

diasteromer	solv	temp, °C	chem shifts,[a] ppm δ(PMe)[b]	δ(COMe)	δ(CO_2Me)	δ(=CH)[c,d]
(±)-**5a**	CD_2Cl_2	25	2.00, 1.97	2.22	3.77	5.38 (2.5, 6.3)
(±)-**5b**	CD_2Cl_2	25	2.24, 2.04	2.22	3.13	6.46 (2.9, 5.3)
(±)-**5a**	CD_3OD	−20	2.13, 2.02	2.11	3.85	4.80 (2.6, 6.8)
(±)-**5b**	CD_3OD	−20	2.23, 2.33	2.07	3.46	5.66 (2.6, 6.2)

[a] Chemical shifts values quoted relative to Me_4Si for ca. 0.05 M solutions in the specified solvents at the temperatures indicated. [b] $^2J_{PH}$ = 10.2–10.5 Hz for all resonances. [c] Coupling constants (J_{RhH}, J_{PH}) parenthesized. [d] Complex multiplet for aromatic protons (and vinylic protons of free MAC) observed between 6.8 and 7.6 ppm.

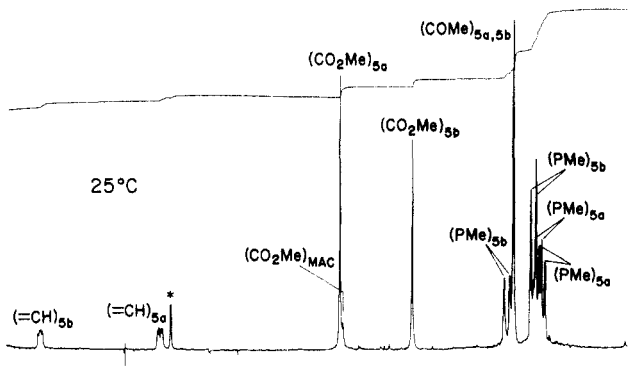

Figure 4. ^1H NMR spectrum of (±)-**5** in dichloromethane-d_2. Asterisked peak is due to solvent.

those of the corresponding optically active material. Whereas (−)-**4** exhibits ^{31}P NMR signals in acetone-d_6 with δ(A) 64.6 and δ(B) 59.3, the corresponding values for *meso*-**4** in the same solvent are δ(A) 64.5 and δ(B) 58.3. For both complexes in acetone-d_6, but not in dichloromethane-d_2 (only (−)-**4** is sufficiently soluble), a ^{31}P NMR signal due to the solvated monomer[17] was evident in the spectrum (ca. 25%) with δ(P) 64.4 (J_{RhP} = 200 Hz):

$$[Rh_2\{(R^*,R^*)\text{-diph}\}_2]^{2+} \rightleftharpoons 2[Rh\{(R^*,R^*)\text{-diph}\}(solvent)_2]^+$$

Molecular models of the two alternative η^6-arene-bridged diastereomers of **4** indicate that the structure of the meso dimer, viz., $[Rh_2\{[R\text{-}(R^*,R^*)]\text{-diph}\}\{[S\text{-}(R^*,R^*)]\text{-diph}\}]^{2+}$, may be more favorable on steric grounds than that of the corresponding racemic dication, which contains ligands of the same helicity (Figure 2). In the optically active compound steric interactions between the internal PMe groups and ortho aromatic protons of *both* η^6-aromatic rings are considerable: in the meso structure this interaction appears to be confined to ortho aromatic protons of the same ligand. No NMR evidence of the racemic dication was found in an acetone-d_6 solution of *meso*-**4** over the temperature range +20 to −60 °C. Thus, the meso compound, as well as possessing a higher lattice energy, is the thermodynamically favored species in solution when both enantiomers of the monomeric solvated cation are available for dimerization.

Hydrogenation of the corresponding bis(tertiary arsine) compounds (±)-**2** or (−)-**2** in dichloromethane led to the immediate deposition of metal.

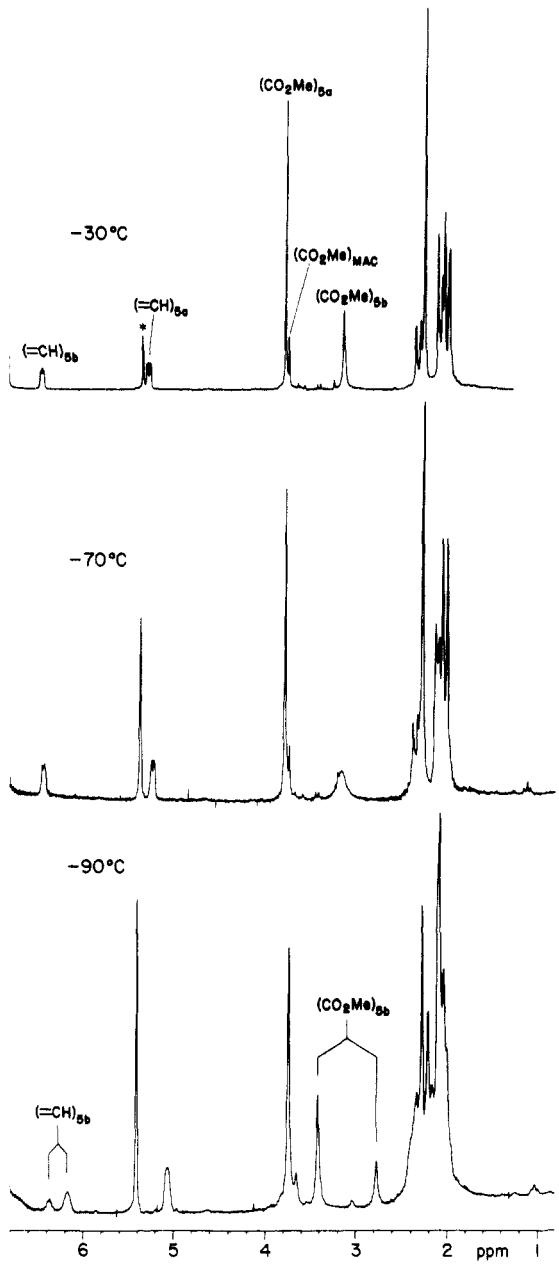

Figure 5. Variable-temperature ^1H NMR spectra of (±)-**5** in dichloromethane-d_2. Asterisked peak is due to solvent.

The catalytic behavior of dimer (−)-**4** toward the reduction of α-acetamidocinnamic acid or α-benzoylamidocinnamic acid is identical with that of the monomeric precursor (−)-**1** under similar conditions in ethanol. In acetone, a suspension of *meso*-**4** reacted rapidly with methyl α-acetamidocinnamate (MAC) to produce a blood-red solution from which highly crystalline clumps of needles of the maroon complex (±)-$[Rh\{(R^*,R^*)\text{-diph}\}\{(Z)\text{-PhCH:C(NHCOMe)CO}_2\text{Me}\}]PF_6$ [(±)-**5**] were isolated by the addition of diethyl ether. The corre-

(17) A considerable body of mechanistic information has been accumulated by Brown and co-workers on cationic bis(tertiary phosphine)-containing rhodium(I) catalyst precursors and their substrate adducts, notably with use of ^{31}P NMR spectroscopy.[18].

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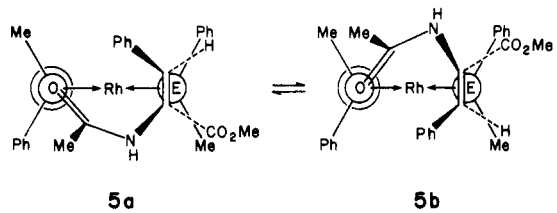
Table III. ^{31}P NMR Spectral Data for Enamide Complex (±)-5

	chem shifts,[a] ppm		coupling consts, Hz		
diastereomer	$\delta(P_A)$	$\delta(P_B)$	$J(P_AP_B)$	$J(RhP_A)$	$J(RhP_B)$
(±)-**5a**	61.53	50.14	41.7	158.5	156.2
(±)-**5b**	57.81	47.49	40.8	162.4	159.2

[a] Chemical shift values quoted relative to external 85% H_3PO_4 for ca. 0.05 M solutions in CD_2Cl_2 at 25 °C.



5a **5b**

Figure 6. Internal diastereomers of (±)-[Rh{(*R**,*R**)-diph}{(*Z*)-PhCH:C(NHCOMe)CO_2Me}]$^+$ [(±)-**5** (structures with *R*-phosphorus atoms shown)].

sponding cinnamic *acid* gave a *yellow* complex that could not be induced to crystallize.

The ^1H NMR spectrum of (±)-**5** in dichloromethane-d_2 at 25 °C contained resonances corresponding to a pair of diastereomers in the proportions of 1.2:1 (Figure 4). The relative proportions were determined accurately from the ^1H NMR spectrum of the mixture. A weak resonance (ca. 4%) corresponding to the CO_2*Me* group of free MAC was also evident in the spectrum. The minor diastereomer has been assigned structure **5b** (Figure 6) on the basis of a consideration of relative shielding patterns and variable-temperature ^1H NMR studies (see Figure 5). Assignments of the ^1H and ^{31}P NMR spectra of (±)-**5** in dichloromethane-d_2 at 25° C are given in Tables II and III, respectively. (The assignments are based on a wide experience of shielding patterns in 4-, 5-, and 6-coordinate complexes containing (*R**,*R**)-diph and related ligands, where the structures inferred from chemical shift data have been verified by X-ray crystal structure determinations.) At −90 °C the CO_2*Me* and the vinylic proton resonances of the minor diastereomer are each split into two resonances of unequal intensity (ca. 0.4:1), viz., δ 2.76, 3.41 and δ 6.35, 6.15, respectively. As evident from Figure 6, one of the *P*-phenyl groups is within close proximity of the CO_2Me group in diastereomer **5b**. The splitting of the CO_2*Me* resonance is consistent with a restriction of rotation of the phenyl ring adjacent to this group. The intramolecular nature of the process is confirmed by the observation of ^{103}Rh coupling to both the ^{31}P and vinylic proton nuclei in the dichloromethane-d_2 spectra at the fast-exchange limit. We believe this is the first direct evidence of conformational preferences of this type in such complexes. The possibility of cis/trans isomerization with respect to the carbonyl moiety of the ester group and the coordinated olefinic bond, as implied by the X-ray structure of a related [*S*-(*R**,*R**)]-chiraphos complex,[20] cannot be eliminated as an alternative explanation of the NMR behavior, but this phenomenon might have been anticipated to apply to *both* diastereomers. The activation barrier[19] for the process, ca. 43 kJ mol^{-1} for T_C = −60 °C, is consistent with either explanation. It is noteworthy that the high stereoselectivities found in reactions of similar

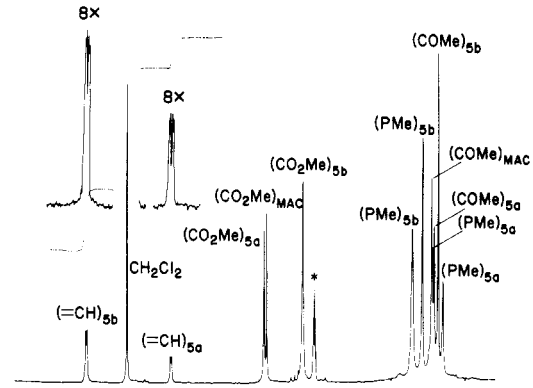


Figure 7. $^1H\{^{31}P\}$ NMR spectrum of (±)-**5** in methanol-d_4 at −20 °C. Asterisked peak is due to solvent.

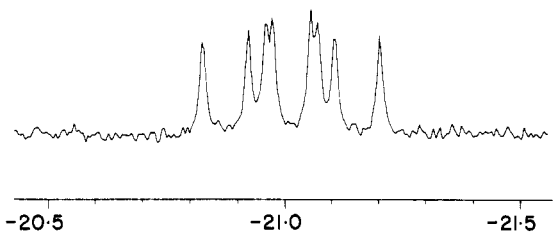


Figure 8. Multiplet due to Rh–H observed in ^1H NMR spectrum of (±)-**5** in methanol-d_4 after exposure to H_2 at −78 °C.

complexes containing chiral ligands with "symmetrical" donors, for example, [*S*-(*R**,*R**)]-chiraphos and related ligands,[2-4] have been rationalized in terms of "fixed" edge–face dissymmetric arrays of phenyl groups on the phosphorus donor atoms.

In methanol-d_4 cooling to −20 °C was required before the diastereomers of (±)-**5** were discernible in the ^1H NMR spectrum (Figure 7). The static spectrum showed a reversal in the intensities of **5a** and **5b** (**5a**:**5b** = 1:2.1). Resonances due to free MAC (ca. 25%) were also apparent in the methanol-d_4 spectrum. Cooling to −70 °C resulted in a broadening of the CO_2*Me* resonance due to **5b**, presumably because of restricted rotation of the type discussed above.

Exposure of a solution of (±)-**5** in methanol-d_4 at −78 °C to hydrogen caused a slight reduction in the intensity of the color of the solution, as well as the appearance of a *single* Rh–H absorption in the ^1H NMR spectrum at δ −21.04 with J_{RhH} = 29.3 Hz, J_{PH} = 26.7 Hz, and J_{PH} = 19.3 Hz (Figure 8). The failure to detect other diastereomeric hydrides may, however, have been due to a fortuitous coincidence of resonances: models of the reduced diastereomers suggest that the shielding differences of the hydridic proton in each compound due to the CO_2Me and CH_2Ph groups around the newly formed asymmetric carbon atoms may be very small indeed. The quality of the ^1H NMR spectrum at −78 °C in methanol-d_4 in the vinylic region, which is complicated by line broadening due to exchange, was not sufficient to determine if selective hydrogenation of one of the diastereomers had occurred upon addition of hydrogen.

Hydrogenation of MAC in dichloromethane in the presence of (±)-**1**, (±)-**4**, or (±)-**5** under the usual conditions (20 °C, 1 atm of H_2) proceeded very slowly, even though each of the complexes is soluble in the solvent. In the more polar coordinating solvents acetone or methanol, however, where there is evidence of substantial dissociation in solutions of each complex, catalytic activity is high. It was not possible to determine **5a**:**5b** from the ^1H or ^{31}P NMR spectra of (±)-**5** in methanol-d_4 at 20 °C because of exchange. The value of **5a**:**5b** = 1:1.56 at 20 °C was ob-

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tained, however, by extrapolation of the data obtained between −70 and −20 °C. Inspection of Figure 6 reveals that endo stereospecific hydrogenation of the major reactant diastereomer (**5b**) would produce an amino acid product of the opposite absolute configuration to that experimentally observed. Thus, as with the analogous [*S*-(*R**,*R**)]-chiraphos based catalyst, the predominant chiral product arises from the minor diastereomer of the rhodium enamide complex, and it is the relative stabilities of the intermediate product diastereomers (vis-à-vis reactant diastereomers) that determines the optical yields in systems of this type.[20] In the case of enamide complexes containing (*R*)- or (*S*)-binap[15] and various (*Z*)-α-acetamido- and α-benzamidocinnamic acids and methyl esters, one diastereomer only was observed by ^{31}P NMR spectroscopy for solutions of the complexes in a mixture of dichloromethane and methanol at −50 °C, but the stereochemistry of the coordinated enamide in the diastereomer was not correlated with the stereochemistry of the reduction product.

Conclusion

Soluble (bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) complexes containing the enantiomers of (*R**,*R**)-(±)-1,2-phenylenebis(methylphenylphosphine) or their arsenic isosteres have been found to be highly efficient catalysts for the asymmetric hydrogenation of a variety of prochiral *Z*-substituted enamide acids and esters. In several instances the bis(tertiary arsine) containing catalyst out performed the corresponding phosphorus compound. Our studies support the view that it is the relative stability of the intermediate product diastereomers that determines the enantioselectivity of the asymmetric hydrogenation and not the relative concentration of the reactant diastereomers at equilibrium. Thus, for an isolated catalyst–substrate adduct, we have conclusively shown that the minor reactant diastereomer at equilibrium leads to the major chiral product. It is also clear from the present work that rigid dissymmetric chelate rings containing equivalent pairs of asymmetric donor atoms are viable alternatives to ligand systems that transmit chirality through edge–face arrays of prochiral phenyl groups of diphenylphosphino donors. Moreover, rigid-backboned optically active bis(tertiary arsines) have been found to be highy effective catalysts for the asymmetric hydrogenation of prochiral enamides.

Experimental Section

General Comments. Preparations of catalyst precursors and derivatives were performed under a positive pressure of argon. ^1H and ^{31}P NMR spectra were recorded on a Bruker CXP 200 spectrometer operating at 200 (^1H) or 80.98 MHz (^{31}P). ^1H and ^{31}P NMR chemical shifts are reported as δ values relative to internal Me_4Si and external 85% H_3PO_4, respectively. Optical rotations were measured on the specified solutions in a 1-dm cell at 20 °C with a Perkin-Elmer Model 241 polarimeter. Elemental analyses were performed by staff within the Research School of Chemistry.

The ligands (*R**,*R**)-(±)-1,2-phenylenebis(methylphenylphosphine) and its arsenic analogue were prepared and resolved as described previously.[5,6] α-Acetamidocinnamic acid and α-acetamidoacrylic acid were purchased from Ega-Chemie and recrystallized before use. Ethyl α-benzamidocinnamate,[21] β,β-dimethyl-α-benzamidoacrylic acid,[22] and α-benzamidocrotonic acid[23] were prepared by literature methods. The oxazolone of α-acetamido-β-isopropylacrylic acid was prepared by the literature method[24] and then hydrolyzed to the acid. The remaining substituted (*Z*)-α-(acylamino)acrylic acid substrates were prepared by standard Erlenmeyer azlactone syntheses.[25]

[*SP*-4-[*R*-(*R,*R**)]-(Bicyclo[2.2.1]hepta-2,5-diene)[1,2-phenylenebis(methylphenylphosphine)]rhodium(I) Hexafluorophosphate Diacetone Solvate [(−)-1].** A mixture of $[RhCl(NBD)]_2$ (1.43 g, 3.1 mmol) and $AgNO_3$ (1.054 g, 6.2 mmol) in methanol (30 mL) was stirred for 30 min. The reaction mixture was cooled to −78 °C, and solid [*S*-(*R**,*R**)]-diph (2.0 g) was added. After 1 h the reaction mixture was allowed to warm to room temperature. The deep orange solution was separated from the AgCl by filtration, and the filtrate was carefully treated with aqueous NH_4PF_6 (2 g in 10 mL). The highly crystalline orange product was filtered off, washed with water, and dried. Recrystallization of this material from a small volume of acetone by the addition of diethyl ether gave the *diacetone solvate* as deep orange needles: mp 230–235 °C dec; yield 3.0 g (62%); $[\alpha]_D$ −203° (*c* 5.64, Me_2CO). Anal. Calcd for $C_{33}H_{40}F_6O_2P_3Rh$: C, 50.9; H, 5.2. Found: C, 50.8; H, 4.9. ^1H NMR (CD_2Cl_2): δ 1.78 (m, 2 H, H_7-NBD), 1.96 (filled-in d, $^2J_{PH} + {}^4J_{PH}$ = 18.4 Hz, J_{PRh} = 1.3 Hz, 6 H, PMe), 2.07 (s, 12 H, Me_2CO), 4.09 (m, 2 H, $H_{1,4}$-NBD), 5.28 (m, 2 H, $H_{2,5}$-NBD), 5.59 (m, 2 H, $H_{3,6}$-NBD), 7.30–7.62 (m, 14 H, aromatics).

[*SP*-4-(*R,*R**)]-(Bicyclo[2.2.1]hepta-2,5-diene)[1,2-phenylenebis(methylphenylphosphine)]rhodium(I) hexafluorophosphate diacetone solvate [(±)-1]** was prepared in the same way as the pure enantiomer, but with use of (±)-diph: deep orange needles; mp 230–235 °C dec; yield 75%. Anal. Calcd for $C_{33}H_{40}F_6O_2P_2Rh$: C, 50.9; H, 5.2. Found: C, 50.8; H, 4.9. ^1H NMR (CD_2Cl_2): identical with that of (−)-1.

[*SP*-4-[*R*-(*R,*R**)]]-(Bicyclo[2.2.1]hepta-2,5-diene[1,2-phenylenebis(methylphenylarsine)]rhodium(I) Hexafluorophosphate [(−)-2].** This compound was prepared and purified in a manner identical with that of the corresponding phosphorus compound, but without cooling before addition of [*S*-(*R**,*R**)]-dias (65% yield): mp 204–210 °C dec; $[\alpha]_D$ −278° (*c* 4.45, Me_2CO). Anal. Calcd for $C_{27}H_{28}As_2F_6PRh$: C, 43.2; H, 3.8. Found: C, 43.4; H, 3.8. ^1H NMR (CD_2Cl_2): δ 1.70 (d, *J* = 1.5 Hz, 2 H, H_7-NBD), 1.88 (d, J_{RhH} = 0.8 Hz, 6 H, AsMe), 4.14 (m, 2 H, $H_{1,4}$-NBD), 5.07 (m, 2 H, $H_{2,5}$-NBD), 5.38 (m, 2 H, $H_{3,6}$-NBD), 7.31–7.65 (m, 14 H, aromatics).

[*SP*-4]-(Bicyclo[2.2.1]hepta-2,5-diene)[1,2-bis(diphenylphosphino)ethane]rhodium(I) Hexafluorophosphate (3). This compound was prepared in 90% yield as for (−)-1 with use of the appropriate bis(tertiary phosphine); mp 210–215 °C dec. Anal. Calcd for $C_{33}H_{32}F_6P_3Rh$: C, 53.7; H, 4.4. Found: C, 54.0; H, 4.3.

(−)-[Rh_2{[*R*-(*R,*R**)]-diph}$_2$]$(PF_6)_2$·CH_2Cl_2 [(−)-4].** A solution of (−)-1 (2.0 g) in dichloromethane (10 mL) was stirred under H_2 (1 atm) for 15 h, during which time yellow needles of the pure dimer precipitated. The product crystallized from hot dichloromethane as needles: mp >230 °C; yield 1.59 g (49%); $[\alpha]_D$ −272° (*c* 1.8, CH_2Cl_2). Anal. Calcd for $C_{41}H_{42}Cl_2F_{12}P_6Rh_2$: C, 40.2; H, 3.5. Found: C, 39.5; H, 3.5. ^1H NMR (CD_2Cl_2): δ 2.40 (d of d, $^2J_{PH}$ = 9.7 Hz, $^3J_{RhH}$ = 1.3 Hz, 6 H, PMe), 2.41 (d of d, $^2J_{PH}$ = 10.6 Hz, $^3J_{RhH}$ = 1.1 Hz, 6 H, PMe), 5.28 (s, 2 H, CH_2Cl_2), 5.83 (t, *J* = 5.6 Hz, ca. 2 H, aromatics), 6.57 (t, *J* = 6.3 Hz, ca. 2 H, aromatics), 7.1–7.8 (m, ca. 24 H, aromatics).

[Rh_2{[*R*-(*R,*R**)]-diph}{[*S*-(*R**,*R**)]-diph}]$(PF_6)_2$·0.5CH_2Cl_2 (*meso*-4).** This compound was obtained similarly as small sparingly soluble prisms by hydrogenation of (±)-1 in dichloromethane: yield 90%; mp >230 °C. Anal. Calcd for $C_{40.5}H_{41}ClF_{12}P_6Rh_2$: C, 41.8; H, 3.5. Found: C, 41.7; H, 3.8. ^1H NMR (Me_2CO-d_6): δ 2.63 (d of d, $^2J_{PH}$ = 107 Hz, $^3J_{RhH}$ = 1.2 Hz, 6 H, PMe), 2.75 (d of d, $^2J_{PH}$ = 10.8 Hz, $^3J_{RhH}$ = 1.0 Hz, 6 H, PMe), 5.28 (s, 1 H, 0.5CH_2Cl_2), 6.46 (t, *J* = 7.1 Hz, ca. 2 H, aromatics), 6.66 (t, *J* = 6.3 Hz, ca. 2 H, aromatics), 7.5–8.3 (m, ca. 24 H,

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aromatics). Spectrum also contains P*Me* signal due to ca. 25% of [Rh{(*R**,*R**)-diph}(Me_2CO-d_6)$_2$]$^+$ at δ 2.24 (virtual triplet, $^2J_{PH}$ + $^4J_{PH}$ = 20.2 Hz, $^3J_{RhH}$ = 1.3 Hz).

[*SP*-4-(*R,*R**)]-(Methyl α-acetamidocinnamate)[1,2-phenylenebis(methylphenylphosphine)]rhodium(I) Hexafluorophosphate [(±)-5].** A suspension of *meso*-**4** (1.2 g) in acetone (20 mL) containing methyl α-acetamidocinnamate (0.44 g) was stirred until all of the dimer had dissolved (ca. 10 min). The addition of diethyl ether (40 mL) to the deep red solution produced the product as clumps of needles: mp 155–160 °C; yield 1.03 g (65%). Anal. Calcd for $C_{32}H_{33}F_6NO_3P_3Rh$: C, 48.7; H, 4.2; N, 1.8. Found: C, 48.9; H, 4.6; N, 1.6. ^1H and ^{31}P NMR (CD_2Cl_2): see Tables II and III.

Hydrogenation Procedure. Hydrogenation experiments were performed with use of a "Towers" atmospheric pressure microhydrogenation apparatus. The reaction vessel was charged with ca. 1 g (5 mmol) of substrate and ca. 0.03 g (0.05 mmol) of catalyst and then evacuated and flushed with argon before admission of solvent (ethanol, ca. 50 mL) and base (10 mmol if required) and exposure of the resulting solution to hydrogen. When gas uptake was complete, catalyst (−)-**1** was removed with use of Dowex 50W-X2 cation exchange resin in the acid form (200–400 mesh, 5–6 g). For experiments involving triethylamine or (−)-**2**, however, the extractive method of Riley and Shumate[3] was used. Optical yields were determined by comparison of optical rotations of product solutions after removal of catalyst with solutions of authentic specimens under the same conditions. The identity and chemical purity of the products were subsequently determined by ^1H NMR spectroscopy: isolated yields were >95%.

Identical results were obtained with use of (−)-**1** after it had been exposed to the atmosphere for 1 week. Dimer (−)-**4** performed identically to (−)-**1**.

Registry No. (−)-**1**, 100945-97-9; (±)-**1**, 101052-77-1; (−)-**2**, 100945-99-1; **3**, 60470-22-6; (−)-**4**, 100946-01-8; *meso*-**4**, 101052-79-3; (±)-**5a**, 101052-81-7; (±)-**5b**, 100946-03-0; $[RhCl(NBD)]_2$, 12257-42-0; [*S*-(*R**,*R**)]-diph, 72150-63-1; (±)-diph, 72091-01-1; [*S*-(*R**,*R**)]-dias, 57341-01-2; dppe, 1663-45-2; (*Z*)-PhCH=C(NHCOMe)CO_2H, 55065-02-6; (*Z*)-PhCH=C(NHCOMe)CO_2Me, 60676-51-9; (*Z*)-PhCH=C(NHCOPh)CO_2H, 26348-47-0; (*Z*)-PhCH=C(NHCOPh)CO_2Et, 26348-46-9; CH_2=C(NHCOMe)CO_2H, 5429-56-1; (*Z*)-EtCH=C(NHCOPh)CO_2H, 100928-37-8; Me_2C=C(NHCOPh)CO_2H, 1738-64-3; (*Z*)-*i*-PrCH=C(NHCOMe)CO_2H, 64896-30-6; (*Z*)-*i*-PrCH=C(NHCOPh)CO_2H, 64896-31-7; *N*-acetyl-(*S*)-phenylalanine, 2018-61-3; *N*-acetyl-(*S*)-phenylalanine methyl ester, 3618-96-0; *N*-benzoyl-(*S*)-phenylalanine, 2566-22-5; *N*-benzoyl-(*S*)-phenylalanine ethyl ester, 7200-18-2; *N*-acetyl-(*S*)-alanine, 97-69-8; *N*-benzoyl-(*S*)-α-aminobutyric acid, 87068-75-5; *N*-benzoyl-(*S*)-valine, 5699-79-6; *N*-acetyl-(*S*)-leucine, 1188-21-2; *N*-benzoyl-(*S*)-leucine, 1466-83-7.

Metal- and Alkoxide-Mediated Phosphorus–Oxygen Bond Cleavage in (η^5-Cyclopentadienyl)cobalt Phosphinite Ester Complexes

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Reaction of 2-pyridyl dimethylphosphinite (**1**) with 0.5 equiv of η^5-$CpCo(CH_2{=}CH_2)_2$ affords $Cp_2Co_2(\mu\text{-}PMe_2)(\mu\text{-}Opy)$ (**4**) in a 74% yield. Bridging phosphide **4** appears to arise by a formal oxidative addition across the phosphorus–oxygen bond of ligand **1**. Reaction of 4-*tert*-butylphenyl dimethylphosphinite (**6**) with $CpCo(CH_2{=}CH_2)_2$ affords $CpCo(CH_2{=}CH_2)(Me_2POAr)$ (**7**) in a 75–80% yield. Reactions of **7** with several allylic and homoallylic potassium alkoxides afford chelated unsaturated phosphinite ester complexes. Thermodynamic, kinetic, and photostationary diastereofacial selectivities are observed but the chelate stereochemistries are not assigned.

Introduction

We have been interested in developing a technology that would enable us to effect hydroxyl-directed organometallic reactions of unsaturated alcohols under *aprotic* conditions. In principle, the powerful stereochemical determinants that have added profound importance to hydroxyl-directed epoxidations[1] and hydrogenations[2] of olefins would become available to transition-metal-mediated olefin functionalizations other than simple redox processes.[3,4] The investigations began with attempts to chelate unsaturated dimethylphosphinite esters (Me_2POR, R = alkene) to a $Mo(CO)_4$ fragment.[5] Through efforts to solve a series of technical problems, we developed the alkoxide-triggered substitution reaction illustrated in eq 1. Although this reaction appeared to be potentially useful in both organic and inorganic synthesis with no immediately apparent limitations, the transition-metal chemistry of 2-pyridyl

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