Enantioselective Catalysis. 6. The Catalytic Hydrogenation of α-(Acetylamino)cinnamic Acid with Rhodium(I)–Bis(phosphine) Complexes. On the Origin of the Enantioselection[1]

Ulrich Nagel* and Bernhard Rieger[2]

University of Tuebingen, Institute of Inorganic Chemistry, Auf der Morgenstelle 18, D-7400 Tuebingen 1, FRG

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From the ligands[1] the rhodium complex [(P*R*,3*R*,4*R*,P′*S*)-*tert*-butoxycarbonyl-3,4-bis(benzylphenylphosphino)pyrrolidine-*P*,*P*′](1,5-cyclooctadiene)rhodium tetrafluoroborate (**2**) and the three diastereomeric complexes [(P*S*,3*R*,4*R*,P′*S*)-, (P*R*,3*R*,4*R*,P′*R*)-, and (P*R*,3*R*,4*R*,P′*S*)-1-*tert*-butoxycarbonyl-3,4-bis(methylphenylphosphino)pyrrolidine-*P*,*P*′](1,5-cyclooctadiene)rhodium tetrafluoroborate (**3**–**5**) were prepared. With the hydrogenation of α-(acetylamino)cinnamic acid and its methyl ester as model reactions, the pressure dependence of the catalytic activity and enantioselectivity of these complexes was studied. The three isomers **3**, **4**, and **5** demonstrate completely different catalytic behavior. They give optical yields between 20 and 90%. The conclusion is drawn that the high enantioselectivities obtained with the rigid rhodium complexes of bis(diphenylphosphino) ligands are mainly due to the influence of the axially situated phenyl groups at the phosphorus atoms. The equatorially situated phenyl groups play a minor role.

Introduction

Catalytic hydrogenation was the first preparatively useful enantioselective catalysis. Optically active rhodium[3] and ruthenium[4] complexes have found many applications as catalysts for this reaction. Much work has been carried out on the mechanism of the asymmetric hydrogenation of *N*-acyldehydroamino acids with rhodium complexes of 1,2-diphosphino ligands. In particular Brown[5] and Halpern[6] have clarified the mechanistic course of this reaction. They used either Dipamp[7] or Chiraphos[8] complexes as catalysts. These authors demonstrated that the activation of the hydrogen molecule is both the rate- and selectivity-determining step, provided the hydrogen pressure is not too high (about 1 atm) and the temperature is not below room temperature.

All complexes of diphosphino ligands show a chiral array of the four groups R^1–R^4 (Figure 1) attached to the phosphorus atoms. It has been known for a long time that the handedness of this array determines the configuration of the prevailing product.[8,9] Which of the details of this chiral array controls the selectivity remains unknown.[6] To obtain information on this topic, we synthesized three diastereomeric ligands with one methyl and one phenyl group at each phosphorus atom. In contrast to complexes of 1,2-phenylenebis(methylphenylphosphine),[10] the chiral backbone of these ligands fixes the chiral array A as shown in Figure 1. In the rhodium complexes **3**, **4**, and **5** all possible arrangements of two methylphenylphosphino groups are realized.

For the discussion of our results we assume the reader's familiarity with the mechanistic work of Halpern.[6] On the basis of his work the catalytic cycle of the hydrogenation reaction (Figure 2) consists of four fundamental steps: (1) the complexation of the substrate, (2) the activation of the hydrogen molecule, (3) the formation of the σ-alkyl complex, and (4) the reductive elimination of the product. Obviously, only the rate of the second step depends on the hydrogen pressure. There are two limiting cases. In the limit of low hydrogen pressure the rate constant of the second step becomes identical with the overall rate constant. The catalytic reaction shows a linear relationship between the rate of the reaction and the hydrogen pressure. The optical yield is independent of the hydrogen pressure. This case is fully realized with complex **1** (Figure 3) for a pressure up to 75 atm. As far as we know there is only one other example[11] for a linear relationship up to 75 atm in the literature. In the limit of high hydrogen pressure, the overall rate constant and the optical yield are independent of the hydrogen pressure. The first step is now irreversible and controls the enantioselection[6] but not necessarily the overall rate constant.

Results and Discussion

For the interpretation of our results we assume without experimental proof that the mechanistic picture described above is also valid for our complexes **1**–**5**. In our eyes this is reasonable because all ligands in consideration are 1,2-bis(phosphines), the metal is rhodium, and the substrate is α-(acetylamino)cinnamic acid in all cases.

Synthesis of the Catalysts. In previous papers[1,12] we described the syntheses of the complex [(3*R*,4*R*)-1-*tert*-butoxycarbonyl-3,4-bis(diphenylphosphino)pyrrolidine-*P*,*P*′](1,5-cyclooctadiene)rhodium tetrafluoroborate (**1**), of the ligand (P*R*,3*R*,4*R*,P′*S*)-1-*tert*-butoxycarbonyl-3,4-bis(benzylphenylphosphino)pyrrolidine, and of the three diastereomeric ligands (P*R*,3*R*,4*R*,P′*R*)-, (P*S*,3*R*,4*R*,P′*S*)-, and (P*R*,3*R*,4*R*,P′*S*)-1-*tert*-butoxycarbonyl-3,4-bis(methylphenylphosphino)pyrrolidine. From these ligands we have now prepared the corresponding rhodium complexes **2**, **3**, **4**, and **5** by the reaction with $[(COD)_2Rh]BF_4$ (cf. Figure 3). The synthesis of pure complex **3** met with

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(2) Current address: Zentralforschung Polymerchemie, BASF AG, D-6700 Ludwigshafen, FRG.
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Table I. Results of the Catalytic Hydrogenations[a]

no.	cat.	substr	substr/cat.	*p*, atm	*T*, °C	to., s^{-1}	oy, %
1	**2**	acid	200	1	22	0.02	74.5
2	**2**	acid	200	2	22	0.07	75.5
3	**2**	acid	2000	20	22	0.41	77.0
4	**2**	acid	2000	30	22		77.4
5	**2**	acid	2000	75	22	0.65	78.0
6	**2**	ester	2000	75	22		18.0
7	**3**	acid	100	1	22	0.01	64.0
8	**3**	acid	100	1	60		76.0
9	**3**	acid	1014	12.5	22	0.23	64.9
10	**3**	acid	2000	30	22	0.54	61.4
11	**3**	acid	2000	75	22	1.31	59.4
12	**3**	ester	2000	75	22		62.0
13	**4**	acid	100	1	22	0.05	34.1
14	**4**	acid	100	1	60		26.0
15	**4**	acid	100	2	22	0.06	31.7
16	**4**	acid	2000	30	22	0.08	26.6
17	**4**	acid	2000	50	22		26.5
18	**4**	acid	2000	67	22	0.09	26.4
19	**4**	acid	2000	75	22	0.09	26.4
20	**4**	ester	2000	75	22		21.0
21	**5**	acid	200	1	22	0.08	20.9
22	**5**	acid	100	1	22		20.9
23	**5**	acid	100	1	60		36.0
24	**5**	acid	200	2	22	0.14	22.8
25	**5**	acid	2000	20	22	0.44	
26	**5**	acid	2000	30	22		35.5
27	**5**	acid	2000	50	22	0.51	39.2
28	**5**	acid	2000	75	22	0.53	42.4
29	**5**	ester	2000	75	22	0.20	91.0

[a] Substrates: α-(acetylamino)cinnamic acid, α-(acetylamino)cinnamic acid methyl ester. The substrate to catalyst ratio is molar; the substrate concentration was 0.1 mol/L in all cases. to. = turnover number. After a small variable induction period in all cases the rate of hydrogen uptake was constant. oy = optical yield (100 times the optical rotation of the product divided by the optical rotation of the pure substance).

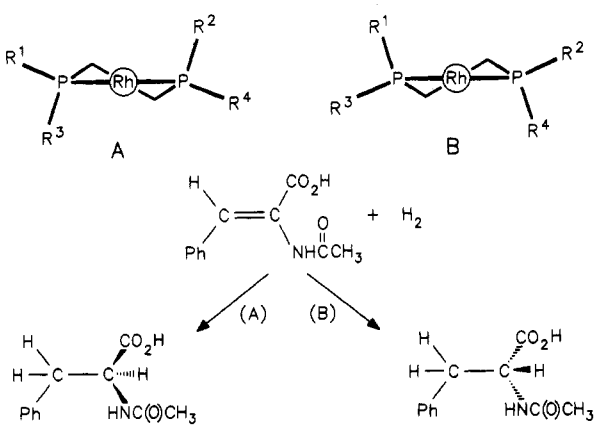

Figure 1. Schematic front view of two rhodium complexes. Only the chelating 1,2-diphosphine ligand is shown. Complex A corresponds to a λ-chelate and complex B to a δ-chelate ring. During catalysis complex A yields an excess of (*S*)-*N*-acylamino acid in the hydrogenation product and B favors the opposite enantiomer. The groups R^1 to R^4 are arbitrary.

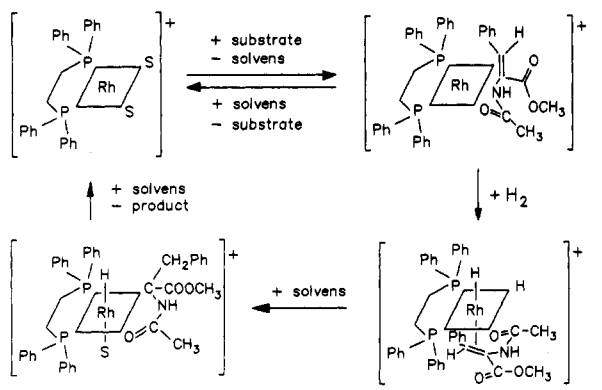

Figure 2. Catalytic cycle for the nonchiral catalyst [Rh(diphos)$^+$].

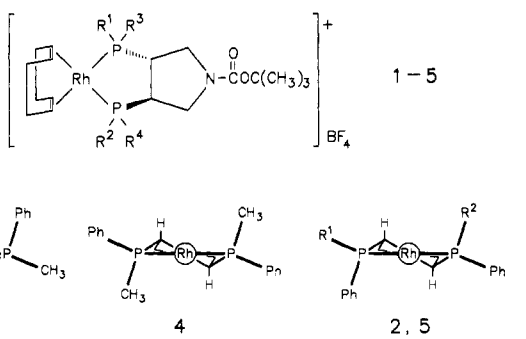

Figure 3. Rhodium complexes **1**–**5**: **1**, $R^1 = R^2 = R^3 = R^4$ = Ph; **2**, $R^1 = R^2 = CH_2Ph$, $R^3 = R^4$ = Ph; **3**, $R^1 = R^4 = CH_3$, $R^2 = R^3$ = Ph; **4**, $R^1 = R^4$ = Ph, $R^2 = R^3 = CH_3$; **5**; $R^1 = R^2 = CH_3$, $R^3 = R^4$ = Ph;

difficulty. The stoichiometric reaction between the ligand and $[(COD)_2Rh]BF_4$ led to a mixture of two components. Both show a doublet in their $^{31}P\{^1H\}$ NMR spectrum. The desired complex **3** exhibits a coupling constant of 151 Hz between the phosphorus and the rhodium atoms. The nature of the second rhodium species, with a coupling constant of 134 Hz, could not be determined. Throughout the course of the catalytic reaction the second complex remains inert. The catalytic activity depends only on the amount of complex **3** present, which could be determined by $^{31}P\{^1H\}$ NMR spectroscopy. The enantiomeric excess is independent of the purity of complex **3**. To demonstrate this we investigated the catalytic hydrogenation using (P*R*,3*R*,4*R*,P′*R*)-1-*tert*-butoxycarbonyl-3,4-bis(methylphenylphosphino)pyrrolidine[13] and either $[(COD)_2Rh]BF_4$ or $[(COD)RhCl]_2$ as catalytic precursors. In all cases neither the catalytic activity nor the enantiomeric excess

(13) For nomenclatory reasons the (P*R*,3*R*,4*R*,P′*R*) ligand gives the (P*S*,3*R*,4*R*,P′*S*) complex.

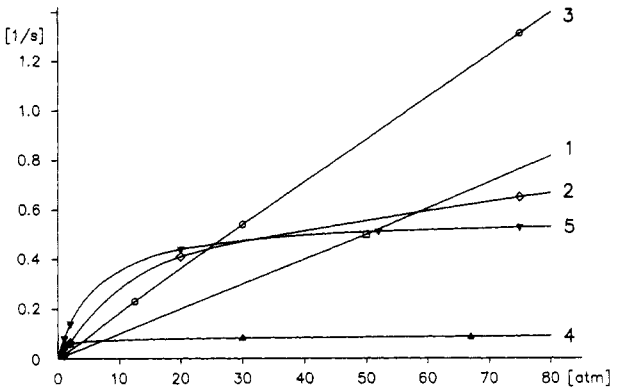

Figure 4. Dependence of the rate (turnover/$[Rh]_{total}$, s^{-1}) on the H_2 pressure (atm) for the 1–5 catalyzed hydrogenation of α-(acetylamino)cinnamic acid at room temperature (22 °C).

depend on the nature of the catalyst precursor.

Catalytic Hydrogenations. Pressure Dependence of Turnover Numbers. As substrates for the catalytic hydrogenations we used α-(acetylamino)cinnamic acid and its methyl ester. The experimental results are summarized in Table I. The dependence of the turnover numbers on the hydrogen pressure for the acid as the substrate and complexes 1–5 as catalysts is shown in Figure 4. Complex 1 is added for comparison only. In particular, the three diastereomeric complexes 3–5 with their differently positioned phenyl groups show a remarkably different reactivity toward hydrogen. A plot of the turnover numbers vs the hydrogen pressure at room temperature is nearly linear for the complex with the axial phenyl groups, 3. The deviation from linearity is very small and is not significant. The slope for catalyst 3 is 1.7 times that for catalyst 1. This difference may result from the higher basicity and the lower steric demand of the methylphenyl ligand in 3. According to the mechanism depicted in Figure 2 for both ligands the hydrogen activation is the rate-limiting step in the catalytic cycle. At high hydrogen pressure catalyst 3 is very active (1.31 s^{-1}), which implies that the rate of all other steps in the catalytic cycle is equal or greater than this number.

For the complex with the axial methyl groups, 4, the same plot shows no dependence of the turnover number on the hydrogen pressure above 10 atm. The observed rate (0.09 s^{-1}) is very low for such a high hydrogen pressure (75 atm), 15 times lower then for isomer 3 (Table I, entries 11 and 19). We assume that the reductive elimination of the product (step 4, Figure 2) is now the turnover limiting step. The reason is as follows: The first step in the catalytic cycle, the coordination of the substrate, can be excluded because the overall rate is independent of the substrate concentration. Step two can be excluded because the rate is independent of the hydrogen pressure. Step three, the transfer of the first hydrogen atom, is most likely very fast since a dihydride was never observed.[6] If we assume the mechanism depicted in Figure 2 is correct, this leaves only step four as the rate-determining step. This conclusion seems quite probable because it has already been shown[6] that for Dipamp as the ligand in a rhodium complex step four becomes rate-determinating below −25 °C.

At 1 atm of hydrogen pressure the hydrogenation using catalyst 4 (with axial methyl groups) is 5 times faster than the hydrogenation using catalyst 3 (with axial phenyl groups) (Table I, entries 7 and 13). Therefore, the rate constant of hydrogen activation of isomer 4 is at least 5 times greater then that of isomer 3.

A possible explanation of the different reactivities of the isomers 3 and 4 is as follows: The basicity of the two ligands should be the same. The higher reactivity of the isomer 4 (with axial methyl groups) toward hydrogen, which is combined with a smaller tendency to reductive elimination, is due to the decreased steric hindrance in the axial position compared with the bulkier axial phenyl groups of complex 3. This seems plausible because upon addition of the hydrogen molecule, the coordination number of the rhodium atom increases from 4 to 6. The coordination geometry changes from square planar to octahedral. Because the activation of the hydrogen molecule involves a late transition state,[6] the octahedral complex is a good model for this transition state. In the square-planar complex, the axial groups attached to the phosphorus atoms of the ligands have little influence on the stability of the complex. In the octahedral complex this is quite different. Here the apical positions are occupied. These positions are in close contact with the axial groups in the ligand. Therefore, large axial groups tend to destabilize the octahedral complex. They retard the oxidative addition of hydrogen (Figure 2, step 2) and enhance the reductive elimination (Figure 2, step 4). Even if there is no dihydride involved,[14] this argument still holds, since hydrogen activation then leads directly to the hydride alkyl complex. This species posesses octahedral geometry, with one of the coordination sites occupied by a solvent molecule.

The turnover numbers for the nonsymmetrical complexes 2 and 5, each with one axial and one equatorial phenyl group, increase with hydrogen pressure, but the relationship is not linear. Up to 20 atm of hydrogen the isomers 2 and 5 are more active catalysts than isomer 3. But with rising pressure complex 3 becomes the most active isomer. The interpretation of the kinetic behavior of complexes 2 and 5 is very difficult. The lack of C_2 symmetry makes the two phosphorus atoms different. Trans to a given phosphorus atom, either the olefin moiety or the amide oxygen atom of the substrate can coordinate. This increases the number of kinetic parameters by twofold. With 2 or 5 as catalysts it was not possible to realize either of the limiting cases in the rate law: linear dependence on the hydrogen pressure at low pressure or no dependence at high pressure. Two axial phenyl groups promote the limiting case of low hydrogen pressure (up to 75 atm) and two axial methyl groups the limiting case of high hydrogen pressure (down to 10 atm). With the mixed complexes 2 and 5 the first limiting case must exist below and the second above the pressure ranges used (1–75 atm).

Pressure, Temperature, and Substrate Dependence of Enantiomeric Excess. In all known rhodium complexes of optically active diphosphines, the conformation of the chelating ligand determines the prevailing product configuration.[9] As already mentioned a λ-chelate gives the (*S*)-enantiomer and a δ-chelate the (*R*)-enantiomer. This rule holds for catalysts 1–5 as well. The different configurations at the phosphorus atoms of 2–5 influence only the extent of the enantiomeric excess. The influence of the configuration of the carbon skeleton dominates in all cases we have tested. The dependence of the optical yield (oy) on the hydrogen pressure for complexes 1–5 is shown in Figure 5. All possibilities are realized: no dependence (1) and decrease (3, 4) or increase (2, 5) in hydrogen pressure. An increase of the oy with hydrogen pressure was to our knowledge never observed before. In the mechanistic picture delineated by Halpern,[6,15] it can be explained if we assume that the first step of the catalytic cycle (Figure 2) is more selective than the second.

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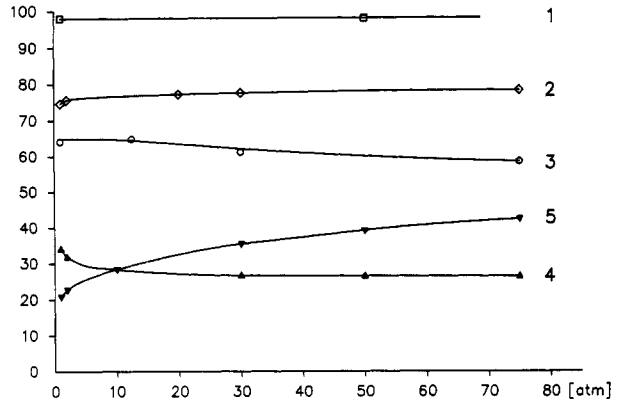

Figure 5. Dependence of the optical yield (percent) on the H_2 pressure (atm) for the 1–5 catalyzed hydrogenation of α-(acetylamino)cinnamic acid at room temperature (22 °C).

Again the comparison of the three diastereomeric complexes 3–5 is most interesting. At all hydrogen pressures used, catalyst 3, with two axial phenyl groups, gives the higher enantiomeric excess. For catalyst 3 (axial phenyl groups) at pressures up to 75 atm, the rate-determining step is the hydrogen activation (see above) as is the case[6] for Chiraphos and Dipamp at 1 atm. We assume that for this catalyst the activation of hydrogen is also the enantioselecting step. It has been shown that for complexes of Chiraphos and Dipamp this conclusion is valid.[6] Only at high pressures does the oy decrease. As already shown[6] this is due to an increasing influence of the first step of the catalytic cycle. In other words, the equilibrium of the two diastereomeric substrate complexes is established too slowly compared with the increasing rate of the second step.

Catalyst 4, the complex with two axial methyl groups, gives the lowest optical yield above 10 atm of hydrogen pressure. This catalyst adds the hydrogen molecule faster than our other catalysts (see above). At pressures above 10 atm, the optical yield is no longer dependent on the hydrogen pressure and probably is only determined through the ratio of the rate constants for the formation of the two diastereomeric substrate complexes. This ratio normally is close to unity,[6] and the observed oy is small (20%). Such a behavior is consistent with the limiting case of high hydrogen pressure mentioned above and discussed by Halpern.[6] On decreasing hydrogen pressure, the oy rises as expected because the more selective addition of the hydrogen molecule gains influence.

Because the complex with one axial and one equatorial phenyl group, 5, shows a increasing optical yield with increasing hydrogen pressure, it gives the lowest optical yield below 10 atm. As for the kinetic data, the interpretation of the enantioselectivity of the asymmetric catalysts 2 and 5 is very difficult. The higher optical yield of the more bulky complex 2 compared with 5 for the hydrogenation of α-(acetylamino)cinnamic acid (Table I, entries 1–5 and 21–28) is as expected. Surprisingly for the ester the order is reversed. The less bulky catalyst 5 is much more selective (Table I, entries 6 and 29). The asymmetric catalysts can be very selective. We feel a prediction of their enantioselectivity is not possible.

In a few cases (ligands 3–5) we also studied the temperature influence on the enantiomeric excess. The catalysts with at least one axial phenyl group (3, 5) show an increase of oy with raising temperature (Table I, entries 7, 8 and 22, 23). The catalyst without an axial phenyl group 4, however, shows a decrease in oy with increasing temperature (Table I, entries 13 and 14). This is as expected because for catalysts 3 and 5 rising temperature shifts the kinetic control toward the more enantioselective oxidative addition of hydrogen.[6] For isomer 4 at 1 atm, this reaction step has only a small influence on its kinetic behavior.

It is known[16] that rhodium complexes of 1,2-bis(methylphenylphosphino)ethane give only moderate optical yields (22% ee for α-(benzoylamino)cinnamic acid as substrate). This result correlates well with our findings for complex 4 (26–34% ee, depending on the hydrogen pressure; Table I, entries 13–20). We assume that in the complex of 1,2-bis(methylphenylphosphino)ethane the large phenyl groups are disposed in equatorial positions in the crowded enantioselecting step and the smaller methyl groups take axial positions. This is the same geometry as in complex 4.

It is also known[6] that with Chiraphos or Dipamp as ligands α-(acetylamino)cinnamic acid methyl ester coordinates to the rhodium complex in two diastereomeric forms. The ratio of the two diastereomers is greater than 20/1 for Chiraphos and 10/1 for Dipamp. But the minor diastereomer yields the prevailing enantiomer of the product (ee about 95%). A possible explanation is as follows: In the square-planar rhodium(I) complex the equatorial phenyl groups control the stability of the diastereomeric substrate complexes.[1] The axial groups have little influence. In the octahedral dihydrido complex, as mentioned above, the axial phenyl groups dominate with their influence on the stereochemistry. The axial phenyl groups direct the reaction (during hydrogen activation) in the opposite sense compared with that of the equatorial phenyl groups (substrate equilibrium). This is as expected because the handedness of the chiral array of the two axial groups is opposite to the handedness of the array of the two equatorial groups. (For example the axial groups R^2 and R^3 in A are on the right side up and on the left side down; on the other hand the equatorial groups R^1 and R^4 in A are left side up and right side down; see Figure 1.)

Conclusion

We have shown that different stereoisomers of a ligand deeply influence the catalytic behavior of their rhodium complexes. A rhodium complex with a phosphine ligand, which bears phenyl groups axial and methyl groups equatorial, gives higher optical yields than its counterpart with the methyl groups axial and the phenyl groups equatorial. If we assume that the large phenyl groups have more influence on the enantioselection than the small methyl groups, we can conclude that the contribution of the axial groups to the enantioselection is greater than that of the equatorial groups.

We feel that to build a good catalyst for the hydrogenation of *N*-acylacrylic acid derivatives, it is necessary to have two large groups in the chelating diphosphine as axial as possible. How this is achieved does not matter. If the skeleton of the ligand is very rigid, the equatorial groups can be small.

Experimental Section

General Procedures. All reactions were carried out under argon atmosphere in dry solvents. ^1H NMR spectra were recorded with a JEOL FX 90 spectrometer. ^{31}P NMR spectra were recorded with a Varian FT 80 or a Bruker AC 200 spectrometer. IR spectra were recorded with a Perkin-Elmer 325 spectrometer. Optical rotation measurements were carried out with a Zeiss LEP A2 polarimeter; the $[\alpha]_D$ numbers were calculated from the $[\alpha]_{578}$ and $[\alpha]_{546}$ numbers. All hydrogenations were carried out in stainless-steel autoclaves with a volume of 50 or 80 mL (Roth KG,

(16) Horner, L.; Simons, G. *Z. Naturforsch., B*; **1983**, *39B*, 512.

D-7500 Karlsruhe). Hydrogen (Linde high purity grade 99.999%) and α-(Acetylamino)cinnamic acid (Fluka) were used as purchased. α-(Acetylamino)cinnamic acid methyl ester,[7] $[(COD)RhCl]_2$,[17] $[(COD)_2Rh]BF_4$,[18] (P*S*,3*R*,4*R*,P′*S*)-, (P*R*,3*R*,4*R*,P′*R*)-, and (P*R*,3*R*,4*R*,P′*S*)-1-*tert*-butoxycarbonyl-3,4-bis(methylphenylphosphino)pyrrolidine, and (P*R*,3*R*,4*R*,P′*S*)-1-*tert*-butoxycarbonyl-3,4-bis(benzylphenylphosphino)pyrrolidine[1] were prepared according to reported procedures.

Preparation of the Catalysts. To a solution of 0.61 mmol of the respective carefully dried 3,4-bis(phosphino)pyrrolidine in 15 mL of CH_2Cl_2 were added 0.25 g (0.60 mmol) of $[(COD)_2Rh]BF_4$. The resulting yellow-red solution was filtered over Kieselguhr. The solvent was removed and the residue dried under vacuum.

[(P*R*,3*R*,4*R*,P′*S*)-1-*tert*-Butoxycarbonyl-3,4-bis(benzylphenylphosphino)pyrrolidine-*P*,*P*′](1,5-cyclooctadiene)rhodium tetrafluoroborate (2): IR (KBr) 1690 (C=O), 1435 (P—Ph), 1385 (P—CH_2Ph), 1000–1150 (BF_4) cm^{-1}; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 26.85 (d, $J_{P,Rh}$ = 144 Hz, first rotamer,[19] the two different P atoms are not resolved), 26.55 (d, $J_{P,Rh}$ = 143 Hz, second rotamer). Anal. Calcd for $C_{43}H_{51}BF_4NO_2P_2Rh\cdot CH_2Cl_2$: C, 55.60; H, 5.62; N, 1.47. Found: C, 55.80; H, 5.98; N, 1.43.

[(P*S*,3*R*,4*R*,P′*S*)-1-*tert*-Butoxycarbonyl-3,4-bis(methylphenylphosphino)pyrrolidine-*P*,*P*′](1,5-cyclooctadiene)rhodium tetrafluoroborate (3): IR (KBr) 1690 (C=O), 1435 (P—Ph), 1390 (P—Me), 1000–1150 (BF_4) cm^{-1}; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 21.11 (d, $J_{Rh,P}$ = 151.6 Hz, no rotamers resolved).

[(P*R*,3*R*,4*R*,P′*R*)-1-*tert*-Butoxycarbonyl-3,4-bis(methylphenylphosphino)pyrrolidine-*P*,*P*′](1,5-cyclooctadiene)rhodium tetrafluoroborate (4): IR (KBr) 1690 (C=O), 1435 (P—Ph), 1390 (P—Me), 1000–1150 (BF_4) cm^{-1}; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 18.00 (d, $J_{Rh,P}$ = 147.8 Hz, first rotamer), 17.70 (d, $J_{Rh,P}$ = 147.6 Hz, second rotamer).

[(P*R*,3*R*,4*R*,P′*S*)-1-*tert*-Butoxycarbonyl-3,4-bis(methylphenylphosphino)pyrrolidine-*P*,*P*′](1,5-cyclooctadiene)rhodium tetrafluoroborate (5): IR (KBr) 1690 (C=O), 1435 (P—Ph), 1390 (P—Me), 1000–1150 (BF_4) cm^{-1}; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 23.75, 20.48 (ABX spin system, $J_{P(a),P(b)}$ = 12.4 Hz, $J_{P(a),Rh}$ = 143.4 Hz, $J_{P(b),Rh}$ = 153.9 Hz, first rotamer), 24.07, 20.17 (ABX spin system, $J_{P(a),P(b)}$ = 12.4 Hz, $J_{P(a),Rh}$ = 143.9 Hz, $J_{P(b),Rh}$ = 153.4 Hz, second rotamer). Anal. Calcd for $C_{31}H_{43}BF_4NO_2P_2Rh\cdot 1.5CH_2Cl_2$: C, 46.43; H, 5.52; N, 1.67. Found: C, 46.70; H, 5.98; N, 1.85.

Catalytic Hydrogenations. The substrate, as a catalyst either complexes 1–5 or $[(COD)_2Rh]BF_4$ or $[(COD)RhCl]_2$, and the ligand were weighed out, placed in the autoclave, and dissolved in 30–50 mL of methanol. The autoclave was closed, thoroughly evacuated, and flushed at least three times with 1 atm of argon to ensure a completely oxygen-free environment. The evacuated autoclave was filled with hydrogen and the reaction started with rapid stirring. At 1 and 2 atm the pressure was kept constant and the hydrogen uptake was measured. At higher pressures the volume was kept constant and the pressure drop (typically 10%) was measured. With α-(acetylamino)cinnamic acid as the substrate the workup was as reported.[12] With the ester as the substrate the reaction mixture was evaporated and the residue was chromatographed in diethyl ether over silica. In all cases the quantitative hydrogenation was confirmed with a ^1H NMR spectrum. The optical yield was determined by comparison with the specific rotations of the pure enantiomers [(*S*)-*N*-acetylphenylalanine, $[\alpha]_D^{22}$ = 47.4 (*c* = 1.0, 95% EtOH);[20] (*S*)-*N*-acetylphenylalanine methyl ester, $[\alpha]_D^{22}$ = 15.9 (*c* = 2.0, CH_3OH)[21]].

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Reactions of Dianionic Carbonylmetalates with Heteroallenes: Reduction of Carbonyl Sulfide, Isothiocyanates, Isocyanates, and Carbodiimides by Group 6 and 8 Carbonylmetalates[1]

Gary R. Lee[2a] and N. John Cooper*[,2b]

Departments of Chemistry, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138, and University of Pittsburgh, Pittsburgh, Pennsylvania 15260

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Dianionic carbonylmetalates of the group 6 and group 8 metals can reduce a number of heteroallenes X=C=Y to coordinated C≡X ligands, provided X is a first-row element (N or O) which can form a strong triple bond with C. Thus $Na_2[M(CO)_4]$ (M = Fe, Ru) and $Na_2[M(CO)_5]$ (M = Cr, W) react readily with COS to give $[M(CO)_5]$ (M = Fe, Ru) and $[M(CO)_6]$ (M = Cr, W) in good yield, as established by absorbance mode IR for Fe and W and by isolation of the known derivatives $[M(CO)_4I_2]$ (M = Fe, Ru) and $[N(n\text{-}Bu)_4][M(CO)_5Br]$ (M = Cr, W), while CS_2 does not give thiocarbonyl complexes with $Na_2[W(CO)_5]$ or $Na_2[Fe(CO)_4]$. It is suggested on the basis of IR and stoichiometry that the COS reductions are reductive disproportionations leading to thiocarbonate formation. Isothiocyanates RNCS (R = Ph, Me) give moderate yields of the corresponding isonitrile complexes $[M(CO)_4(CNR)]$ with $Na_2[Fe(CO)_4]$, but not with $Na_2[Ru(CO)_4]$. A similar reaction of PhNCS with $Na_2[Cr(CO)_5]$ gives low yields of $[Cr(CO)_5(CNPh)]$, but $[W(CO)_5(CNPh)]$ can only be isolated after addition of oxalyl chloride to the intermediate isothiocyanate complex. Reduction of PhNCO with $Na_2[W(CO)_5]$ leads to 84% and 5% solution yields of $[W(CO)_6]$ and $[W(CO)_5(CNPh)]$, respectively, consistent with control of the reduction of unsymmetrical heteroallenes by the relative triple bond strengths in the product C≡X ligands (C≡O > C≡N > C≡S).

We have previously reported that dianionic carbonylmetalates characteristically induce reductive disproportionation of carbon dioxide to coordinated carbon monoxide and carbonate,[3] and we have also established, in the

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