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Intermediates in Homogeneous Catalytic Hydrogenation. The Crystal and Molecular Structure of the Methyl(Z)-α-Acetamodicinnamate Adduct of 1,2-Bis-(diphenylphosphino)ethanerhodium(I)

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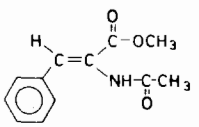
The use of chiral homogeneous catalysts to effect the asymmetric hydrogenation of prochiral olefins, with high optical yields, constitutes one of the most impressive achievements to date in catalytic selectivity [1, 2]. Notably high optical yields (approaching 100%) have been attained with α-amidoacrylic- and α-amidocinnamic-acid derivatives as substrates, for example methyl(Z)-α-acetamidocinnamate (MAC, *1*), using cationic rhodium catalysts containing chiral chelating diphosphine ligands, including either ring or backbone substituted derivatives of 1,2-bis(diphenylphosphino)-ethane $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, abbreviated DIPHOS], *e.g.*, $[(o\text{-}CH_3OC_6H_4)(C_6H_5)PCH_2CH_2P(C_6H_5)(o\text{-}CH_3OC_6H_4)]$ (DIPAMP) [3], $[(C_6H_5)_2PCH(CH_3)CH(CH_3)P(C_6H_5)_2]$ (CHIRAPHOS) [4] and $[(C_6H_5)_2PCH(CH_3)CH_2P(C_6H_5)_2]$ (PROPHOS) [5].



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A rational understanding of the factors that influence stereoselectivity in these and related systems must rest ultimately upon a mechanistic description that encompasses the interception and structural characterization of the substrate-containing catalytic intermediate which determines the stereochemistry of the process. We now report the successful isolation of such an intermediate, $[Rh(DIPHOS)(MAC)]^+$ (*2*), in the hydrogenation of *1* with a cationic rhodium catalyst containing the prototype DIPHOS ligand, and the determination of its structure by single crystal X-ray crystallography. Evidence also is presented that the essential structural features of *2* extend to the corresponding intermediates in catalyst systems involving chiral derivatives of DIPHOS, notably DIPAMP.

We have previously reported that the catalyst precursor, $[Rh(DIPHOS)(Norbornadiene)]^+$, reacts rapidly with H_2 in methanolic solution according to eqn. 1, and that the resulting cationic rhodium complex ($[Rh(DIPHOS)]^+$, presumably solvent-coordinated in methanol solution, *i.e.*, $[Rh(DIPHOS)(CH_3OH)_2]^+$) is a homogeneous catalyst for the hydrogenation of olefinic substrates according to the mechanistic scheme of eqns. 2 and 3 [6]. The present report describes the isolation of the BF_4^- salt of the $[Rh(DIPHOS)(C{=}C)]^+$ intermediate for the substrate MAC (*i.e.*, of *2*) and the determination of its crystal and molecular structure by single crystal X-ray crystallography.

$$[Rh(DIPHOS)(Norbornadiene)]^+ + 2H_2 \longrightarrow [Rh(DIPHOS)]^+ + Norbornane \quad (1)$$

$$[Rh(DIPHOS)]^+ + \rangle C{=}C\langle \rightleftharpoons [Rh(DIPHOS)(\rangle C{=}C\langle)]^+ \quad (2)$$
(Rapid equilibrium)

$$[Rh(DIPHOS)(\rangle C{=}C\langle)]^+ + H_2 \longrightarrow [Rh(DIPHOS)]^+ + H\text{–}C\text{–}C\text{–}H \quad (3)$$
(Rate-determining)

The addition of MAC to a methanolic solution of $[Rh(DIPHOS)]^+$ resulted in the formation of a 1:1 adduct (*2*) (λ_{max} 473 nm, ϵ_{max} 2.18×10^3 M^{-1} cm^{-1}; λ_{min} 427 nm, ϵ_{min} 1.87×10^3 M^{-1} cm^{-1}). Spectral titrations, similar to those described earlier for related adducts [6], yielded a value of 5.3×10^3 M^{-1} for the binding constant, *i.e.*, for the equilibrium constant (K_4) of reaction (4), at 25 °C. The role of *2* as an intermediate in the catalytic hydrogenation of MAC was confirmed by demonstrating that *2* reacts with H_2 to yield N-acetylphenylalanine methyl ester ($MACH_2$) and to regenerate $[Rh(DIPHOS)]^+$ according to the stoichiometry of eqn. 5 and the rate law of eqn. 6 where $k_6 = 1.0 \times 10^2$ M^{-1} sec^{-1} at 25 °C.

$$[Rh(DIPHOS)]^+ + MAC \overset{K_4}{\rightleftharpoons} [Rh(DIPHOS)(MAC)]^+ \quad (4)$$
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$$[Rh(DIPHOS)(MAC)]^+ + H_2 \overset{k_5}{\longrightarrow} [Rh(DIPHOS)]^+ + MACH_2 \quad (5)$$

$$-d[Rh(DIPHOS)(MAC)^+]/dt = k_5[Rh(DIPHOS)(MAC)^+][H_2] \quad (6)$$

$[Rh(DIPHOS)(MAC)][BF_4]$ was prepared by adding 0.2 g of $[Rh_2(DIPHOS)_2][BF_4]_2$ and 0.1 g MAC to 10 ml of warm methanol, and stirring until the mixture dissolved. Diethyl ether was added

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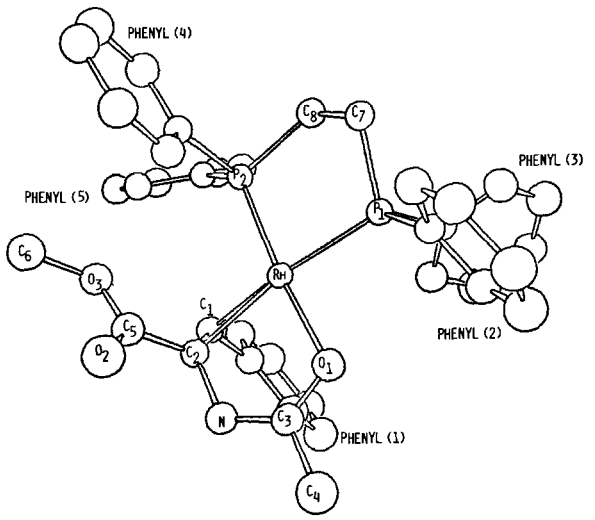

Fig. 1. Structure of [Rh(DIPHOS)(MAC)]$^+$.

slowly until the solution turned slightly cloudy, followed by addition of just enough methanol to clarify the solution. Red crystals of [Rh(DIPHOS)(MAC)] [BF_4] were grown by diffusing diethyl ether into the solution over a period of *ca.* 20 hr.

The X-ray analysis was performed on a crystal of [Rh(DIPHOS)(MAC)] [BF_4] of approximate dimensions, 0.23 X 0.23 X 0.48 mm. *Crystal Data:* M = 807.4; space group $P2_1/c$; a = 9.616(3), b = 15.843 (5), c = 27.095(6) Å, β = 115.75(2)°; Z = 4; ρ_{calc} = 1.442 g cm^{-3}; ρ_{obsd} = 1.437 g cm^{-3}. Three dimensional intensity data were collected on a Picker FACS I diffractometer, equipped with a graphite monochromator, using MoKα radiation (0.71069 Å). A total of 5435 reflections (sin θ/λ = 0.538) were collected, of which 3919 with $F^2 \geqslant 3\sigma_{F^2}$ were used in the refinement. No significant intensity change was observed during the data collection. The structure was solved by the MULTAN procedure (October 1973 version) and full-matrix least-square refinement, using unionized scattering factors, treating the phenyl groups as rigid bodies (with 1.395 Å C–C bond lengths) and the hydrogen atoms as fixed contributions at normal positions (0.95 Å C–H bond lengths and normal geometries), except for the N-bonded H atom which was neglected. Anisotropic thermal parameters were used for the other atoms. The refinement led to final values of R = 0.049, R_W = 0.059 and S = 2.0.

The structure of the [Rh(DIPHOS)(MAC)]$^+$ cation is depicted in Fig. 1 and selected bond lengths and bond angles are listed in Table I. The most significant feature of the structure (confirming an earlier suggestion [2]) pertains to the chelation of the MAC substrate which is coordinated to the Rh atom *through the oxygen atom of the amide carbonyl,* as

TABLE I. Selected Bond Lengths and Bond Angles.

Bond Lengths (Å)		Bond Angles (deg)	
Rh–P(1)	2.271(2)	P(1)–Rh–P(2)	83.0(1)
Rh–P(2)	2.228(2)	P(1)–Rh–O(1)	88.9(2)
Rh–O(1)	2.113(5)	P(1)–Rh–C(1)	153.3(2)
Rh–C(1)	2.246(6)	P(1)–Rh–C(2)	166.1(2)
Rh–C(2)	2.195(8)	P(2)–Rh–O(1)	168.8(2)
P(1)–C(7)	1.818(7)	P(2)–Rh–C(1)	92.0(2)
P(1)–C(Ph_2)	1.809(5)	P(2)–Rh–C(2)	109.6(2)
P(1)–C(Ph_3)	1.819(5)	O(1)–Rh–C(1)	98.7(2)
P(2)–C(8)	1.837(8)	O(1)–Rh–C(2)	77.8(2)
P(2)–C(Ph_4)	1.828(4)	C(1)–Rh–C(2)	36.2(3)
P(2)–C(Ph_5)	1.836(5)	Rh–P(1)–C(7)	110.4(2)
C(1)–C(2)	1.382(12)	Rh–P(1)–C(Ph_2)	113.8(2)
C(1)–C(Ph_1)	1.481(8)	Rh–P(1)–C(Ph_3)	113.8(2)
C(2)–N	1.443(9)	Rh–P(2)–C(8)	110.6(2)
C(2)–C(5)	1.498(11)	Rh–P(2)–C(Ph_4)	112.7(2)
C(3)–N	1.334(9)	Rh–P(2)–C(Ph_5)	121.3(2)
C(3)–O(1)	1.248(8)	Rh–C(1)–C(2)	69.9(4)
C(3)–C(4)	1.495(12)	Rh–C(1)–C(Ph_1)	110.1(5)
C(5)–O(2)	1.191(8)	C(2)–C(1)–C(Ph_1)	131.7(6)
C(5)–O(3)	1.345(8)	Rh–C(2)–N	106.0(4)
C(6)–O(3)	1.441(8)	Rh–C(2)–C(1)	73.9(5)
C(7)–O(8)	1.524(9)	Rh–C(2)–C(5)	110.4(4)
		N–C(2)–C(1)	124.7(6)
		N–C(2)–C(5)	109.7(7)
		C(1)–C(2)–C(5)	122.2(6)
		O(1)–C(3)–N	121.5(7)
		O(1)–C(3)–C(4)	120.0(7)
		N–C(3)–C(4)	118.4(8)
		O(2)–C(5)–O(3)	123.5(7)
		O(2)–C(5)–C(2)	123.7(7)
		P(2)–C(8)–C(7)	108.3(6)
		Rh–O(1)–C(3)	114.8(4)
		C(5)–O(3)–C(6)	116.6(7)
		C(2)–N–C(3)	119.5(7)

well as through normal symmetrical (η^2) coordination of the C=C bond. Together with the normal chelation of the DIPHOS ligand, the overall coordination around the Rh atom thus corresponds to an idealized square planar arrangement of ligands (C=C, O, 2P). Bond lengths and angles are unexceptional.

The contribution of the amide carbonyl to the binding of MAC to the Rh atom is reflected in the large enhancement of the binding constant of the substrate (*i.e.*, of K_4) by the amide group; thus, in methanol solution, K_4 = 5.3 X 10^3 M^{-1} for MAC *vs. ca.* 20 M^{-1} for *trans*-cinnamic acid. The solid state structure of [Rh(DIPHOS)(MAC)]$^+$ (Fig. 1) also is consistent with the NMR spectrum of the corresponding species (50% ^{13}C-enriched at the C=C α-carbon atom) in methanol solution (Fig. 2): ^{31}P *NMR:* P_A, δ 56.9 (with ^{13}C satellites); P_B, δ 71.6; J_{Rh-P_A} = 157 Hz; J_{Rh-P_B} = 160 Hz; $J_{^{13}C-P_A}$ = 20.5; $J_{^{13}C-P_B}$ < 2 Hz. $J_{P_A-P_B}$ = 38 Hz. ^{13}C *NMR:* C_α, δ 86.8; J_{Rh-C_α} = 7 Hz; $J_{P_A-C_\alpha}$ = 20.5 Hz (the assignments

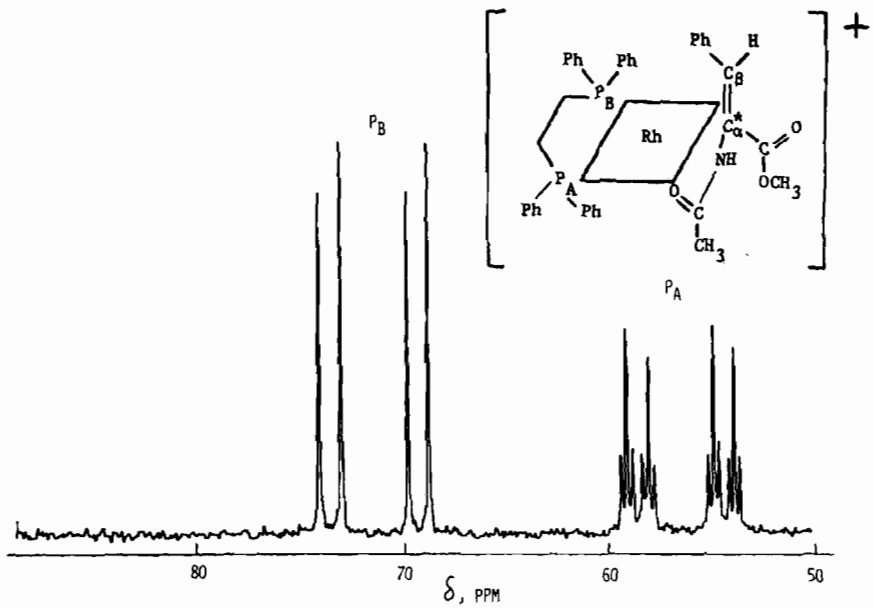

Fig. 2. 36.4 MHz ^{31}P proton-decoupled spectrum of [Rh(DIPHOS)(MAC)]$^+$ (50% ^{13}C-enriched at C_α) in methanol at −40 °C (see text for interpretation and parameters).

of P_A and P_B are based on the usual assumption that the larger P–^{13}C coupling is associated with the *trans*-related ligand pair). Similar ^{31}P NMR spectra (but without ^{13}C-labelling) have previously been reported for some related adducts, *e.g.*, [Rh(DIPHOS)(Z-α-benzamidocinnamic acid)]$^+$, and have been interpreted in terms of similar structures [7].

The enhancement of the binding of the substrate to the Rh by the amido-substituent undoubtedly contributes to the stereoselectivity exhibited by chiral catalysts derived from [Rh(DIPHOS)]$^+$, *e.g.*, [Rh(DIPAMP)]$^+$. In this connection, the intermediates corresponding to (*2*) are crucial in determining the stereochemistry of the hydrogenation reaction, since the usual mechanism (*i.e.*, oxidative addition of H_2, migratory insertion of the olefin, and reductive elimination of the saturated product), which almost certainly applies to the present catalyst, results in hydrogen addition to the Rh-coordinated olefin face. Unfortunately, while we have been able to prepare chiral variants of (*2*), *e.g.*, [Rh(DIPAMP)(MAC)][BF_4], attempts (which are continuing) to obtain single crystals suitable for X-ray diffraction have thus far been unsuccessful. A number of comparisons, however, strongly suggest that the structural features (*i.e.*, coordination about the Rh atom) of [Rh(DIPHOS)(MAC)]$^+$ (*2*) and [Rh(DIPAMP)(MAC)]$^+$ (*3*) are essentially similar. These comparisons include, (a) binding constants (*i.e.*, K_4) of MAC to [Rh(DIPHOS)]$^+$ and [Rh(DIPAMP)]$^+$ in methanol, 5.3 × 10^3 M^{-1} and 2.5 × 10^4 M^{-1}, respectively (the difference being in the direction expected due to the electronic influence of the methoxy substituents of DIPAMP), (b) the ^1H, ^{13}C and ^{31}P NMR spectra of *2* and *3* in methanol solution (which reveal only one diastereoisomer of *3*), and (c) the EXAFS spectra of solid [Rh(DIPHOS)(MAC)][BF_4] and [Rh(DIPAMP)(MAC)][BF_4], both of which correspond to the Rh coordination environment revealed by the X-ray structure of the former [8].

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