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Interaction of Cinchonidine and 1-Phenyl-1,2-Propanedione on the Surface of a Chirally Modified Pt/Al$_2$O$_3$ Hydrogenation Catalyst

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Enantioselective hydrogenation of 1-phenyl-1,2-propanedione (PPD) over cinchona-modified oxide-supported
platinum catalysts represents an extension to the well-known Orito reaction with methyl and ethyl pyruvates
(EtPy) as typical substrates for the asymmetric reduction. In this paper, the adsorption of PPD and cinchonidine
on a Pt catalyst was studied by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The
catalyst preparation and the adsorption of the reactant and modifier were carried out according to the procedure
generally used in catalysis under actual reaction conditions. The catalysts with adsorbed species were analyzed
ex situ. The selective deposition of cinchonidine and PPD on the metal surface was confirmed by parallel
experiments with alumina samples and by analyzing the platinum adsorption sites with carbon monoxide as
a probe molecule. Among the IR visible adsorbed species, η^1(O2)-configuration of PPD was found as the
most populated on Pt surface under the conditions of ex situ measurements. New data on the mutual interactions
among cinchonidine, PPD, and the Pt catalyst are presented. Tilted π-bonded cinchonidine was detected on
the surface under the modifier concentration profile used for obtaining high enantioselectivity in the
hydrogenation of PPD. Hydrogen bonding between adsorbed cinchonidine and PPD was also detected.

Introduction

The mechanism of asymmetric induction over chirally modified heterogeneous catalysts is a subject of intensive ongoing investigation.[1–4] Such catalyst systems, exemplified by supported platinum-based hydrogenation catalysts modified by cinchona alkaloids, provide promising means for cost-efficient preparation of chiral compounds. In particular, the asymmetric hydrogenation of prochiral ketoesters[1–4] (Orito reaction[5]) and diketones[1] to the corresponding chiral lactates and hydroxyketones has received considerable attention. In earlier investigations, various surface science techniques, including near-edge absorption fine structure spectroscopy (NEXAFS),[6,7] scanning tunneling microscopy (STM),[7–9] X-ray photoelectron spectroscopy (XPS),[7,10,11] low-energy electron diffraction (LEED),[11] electrochemical polarization,[12] reflection–absorption infrared spectroscopy (RAIRS),[13–15] surface-enhanced Raman spectroscopy (SERS),[15–17] attenuated total reflection infrared spectroscopy (ATR-IR),[18–20] and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)[21] have been applied to reveal important details on the adsorption behavior of cinchona alkaloids on platinum. Nevertheless, the mechanisms of enantiodifferentiation operating in these catalyst systems have remained unclear and even disputed. Several earlier studies focusing on the modifier adsorption state,[6–9,11–19,21] modifier-reactant interaction on the catalyst surface,[16,20,22–24] reactant[24–33] and solvent decomposition[18,19,34] have been reported. It should

be mentioned that the solvent effect is essential for establishing the transition-state structure and the molecular mechanism which describe the surface reaction. This was particularly emphasized in earlier studies and attributed to the solubility of the reactants and modifiers and to interactions between the solvent, reactants, modifiers and surfaces.[35]

Several models have been proposed to describe the origin of enantioselectivity over the chirally modified metal catalysts under the hydrogen exposure conditions. The first attempt to rationalize the effect of surface chiral modification by Wells and co-workers suggested non-closely packed adsorption of the modifier to form a chiral chemical environment on the surface.[36] The origin of enantioselectivity within the Wells model, also known as the template model, was assigned to the favorable adsorption of one of the faces of the prochiral reactant. Later, Augustine proposed the operation of nucleophilic attack of the ketone carbonyl by the quinuclidine-N of the cinchona alkaloid.[37] Recently, Sun and co-workers have revised the Augustine's interaction model by modeling the possible zwitterionic adduct between cinchonidine and pyruvate molecule.[38]

The most discussed of the hitherto proposed mechanisms is the chiral pocket model by Baiker.[39] Here, the H-bonding interaction between the quinuclidine-N$^+$−H moiety of a single protonated modifier adsorbed on the surface and a reactant molecule serves as the chiral discrimination mechanism. Recently, McBreen and co-workers developed a two-point H-bonding model where an interaction of chemisorption induced aromatic C−H donor functionality and keto-carbonyl is accompanied by a second H-bonding interaction between the quinuclidine function and ester carbonyl.[40] In addition to the surface adsorption models, a chemical shielding model based on the formation of a complex between the modifier and reactant

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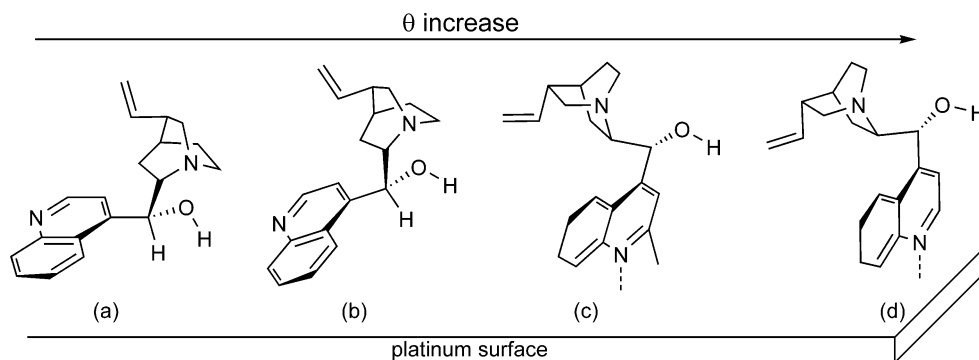§ Laboratory of Industrial Chemistry, Åbo Akademi University.
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Figure 1. The adsorption modes of cinchonidine: (a) parallel π-bonded; (b) tilted π-bonded; (c) α-H-abstracted quinolyl; (d) quinoline-N-lone-pair-bonded.

in the liquid phase has been proposed by Margitfalvi and co-workers.[41] Moreover, the formation of 1:1 and 2:1 cinchona alkaloid−ketopantolactone complexes were recently detected in the liquid phase by NMR techniques.[42]

The majority of the earlier mechanistic models utilizes the chiral modifier with its anchoring part parallel to the metal surface for construction of the one-to-one modifier-substrate intermediates. For cinchona alkaloids, three different adsorption modes have been identified on metal surfaces: π-bonded, α-H-abstracted and quinoline-N-lone-pair-bonded.[13,19] These have been designated as a, c, and d in Figure 1. Here, we aim to elucidate which of the adsorbed species potentially are involved in the enantioselection step of the PPD hydrogenation. Enantioselective hydrogenation of PPD over cinchona-modified oxide-supported platinum similarly to the other vicinal diketones[43] or aromatic ketones[44,45] requires higher alkaloid concentrations than routinely employed for ethyl pyruvate hydrogenation. Thus, for obtaining a noticeable effect of chiral modification, a cinchonidine-to-surface platinum molar ratio 1:10 must be applied (ee = 8%, ethyl acetate).[1,46] The maximum enantiomeric excess obtained with n(mod)/n(Pt$_{surf}$) ratio of 2−3:1 in aprotic solvents[1] is gradually decreasing by increase in the modifier concentration. The enantioselective hydrogenation of EtPy is highly sensitive to even trace amounts of chiral modifiers.[47,48] An investigation of the system with n(mod)/n(Pt$_{surf}$) ratio of 1 : 300 has resulted in noticeable enantiomeric excess of (R)-ethyl lactate (ee = 31%).[47] Moreover, a saturation type dependence for enantioselectivity as a function of modifier concentration has been detected for α-ketoesters.[47] The highest enantiomeric excess in toluene was obtained with n(mod)/n(Pt$_{surf}$) ratio of 1:3−4,[47,49] being slightly higher than the modifier concentration essential for observing ee in the hydrogenation of PPD. It is thus evident that the optimal modifier concentrations are different in the two cases. The saturation type dependence is indicative of a strong adsorption of the chiral modifier on Pt surface while the maximum type dependence suggests competitive adsorption with gradual displacement of the adsorbed species responsible for the enantioselection by other species on the catalyst surface. The adsorption of alkaloids from solutions of very low concentration has been found to be irreversible.[12] This very well explains the saturation type dependence in the hydrogenation of ethyl pyruvate. The species active in the enantioselection of PPD hydrogenation start to populate the Pt surface at a considerably higher modifier concentration and is considered to be weaker bonded than the parallel π-bonded species. Yet, due to their instability under the actual catalytic conditions an α-H-abstracted quinolyl species cannot be considered for being responsible for enantioselection, on account of their instability under the actual catalytic
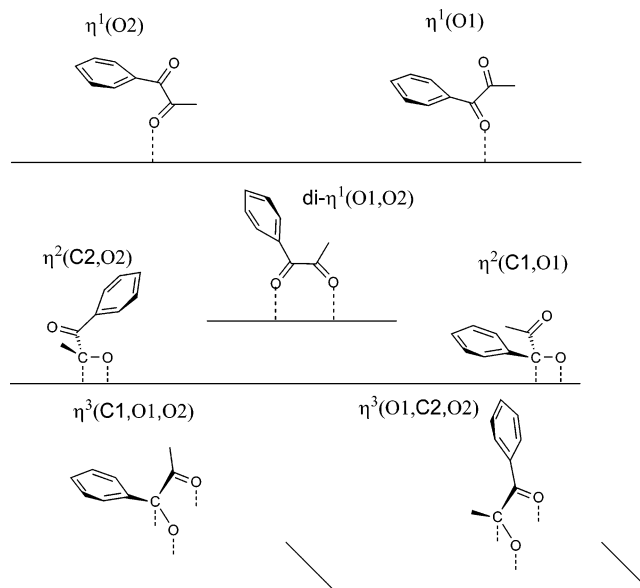

Figure 2. PPD adsorption modes.

conditions. Quinolyl adsorbed cinchonidine is hydrogenated upon exposure to hydrogen and converted to a quinoline-N-lone-pair-bonded species.[19] The latter are weakly adsorbed and therefore most likely act as spectator species.

Thus, it is obvious, that on the saturation scale, a link is missing between the parallel adsorbed and N-lone-pair-bonded cinchonidine species. This adsorption mode was modeled by Vargas et al. for cinchonidine adsorbed on a Pt cluster of 31 atoms.[50] The adsorption mode is referred to as tilted mode in ref 50, while in the IR literature this expression is used to refer to the quinoline-N-lone-pair-bonded mode with quinoline moiety almost perpendicular to the surface. In the present paper, we follow the terminology of Vargas.[50] The quinoline-surface tilting angle was found to be 28°. In the π-bonded tilted mode, the quinoline-N and C(8′) mainly interact with Pt resulting in a strong rehybridization of the above-mentioned atoms while the C(3′)−C(6′) quinoline part practically retains its sp^2 character (Figure 1b). The calculated adsorption energy of the tilted mode of (1S)-(quinolinyl)ethanol is considerably lower than that of the parallel mode (152.0 and 220.2 kJ/mol, respectively), being still rather high.

The second part of the present paper aims to address the adsorption geometry of 1-phenyl-1,2-propanedione on the Pt/Al$_2$O$_3$ catalyst (PPD, Figure 2). Although the mechanism of PPD interaction with transition metal surfaces has not been studied earlier experimentally, the adsorption of various carbonyl

compounds, including acetone,[51−55] acetophenone,[56] butane-2,3-dione,[57] and methyl pyruvate[58] has been the subject of several IR investigations. Moreover, the adsorption of PPD on Pt was recently studied by theoretical methods and discussed in the context of regioselectivity of PPD hydrogenation.[59] Parallel η^2-adsorption of the carbonyl group adjacent to the phenyl ring and accompanying flat bridge(30) adsorption of aromatic group results in the most stable PPD adsorption mode on Pt. In the present paper we address the less stable configurations of PPD on the platinum surface as an implication of the possible reactant−reactant lateral repulsive interactions under the high concentration of PPD, and following destabilization of the adsorbed structure.

The consideration of PPD adsorption on Pt is complicated by the presence in the molecule of two nonequivalent carbonyl groups and the phenyl aromatic ring. Two main adsorption modes can be anticipated for the carbonyl groups of PPD (Figure 2): 1) In the first mode, the π-electrons of C=O interact with the metal d bands. The adsorption geometry of this complex is close to parallel to the platinum surface (η^2); 2) In the second mode, the bonding is dominated by an oxygen lone pair (η^1). Here, the carbonyl group is inclined to the surface normal. The formation of a strongly adsorbed α-diketone in di-η^2-configuration can be considered unlikely[57] due to its highly strained structure that would result from the required sp^3 hybridization of the two carbonyl carbons.

Experimental Section

General Considerations. Nicolet 460 Protégé spectrometer equipped with a diffuse-reflectance attachment was used to analyze the samples of adsorbates. The DRIFT spectra were recorded at room temperature with co-addition of 200 scans and at a resolution of 4 cm^{-1}. The catalyst samples were irradiated in a quartz reactor supplied with a KBr window. Background spectrum of KBr was recorded each time before the measurement. All spectra reported here have been corrected by subtraction of the platinum catalyst and KBr window traces. The adsorption of CO (10−15 Torr) was performed at room temperature. Details of the catalytic hydrogenation experiments, X-ray structure determination and computational methodology are available as Supporting Information.

Sample Preparation. A 5% Pt/Al$_2$O$_3$ catalyst (Strem Chemicals, 78−1660, BET specific surface area: 95 m^2/g, average metal particle size: 2.5 nm (hydrogen chemisorption), 6.5 nm (TEM), 8.3 nm (XRD), dispersion 40% (H$_2$ chemisorption), the mean catalyst particle size 18.2 μm (Malvern)) was activated in a hydrogen flow (AGA, 99.999%, 100 cm^3/min) at 400 °C for 2 h. The detailed catalyst characterization has been described in previous publications.[60,61] Dichloromethane (Fluka, ≥99.5%) was used as received. The adsorption of CO (10−15 Torr) was performed at room temperature. Platinum catalyst was saturated under the solutions of cinchonidine (Aldrich, 96%) and cinchonine (Aldrich, 98%) at two different concentrations. The modifier concentration in bulk of 0.34 mmol dm^{-3} was found as optimal for achieving high enantioselectivity in the heterogeneous hydrogenation of PPD.[46] Almost 50-fold higher concentration (15.0 mmol dm^{-3}) was chosen to discriminate between the different adsorption modes. The adsorption of 11-triethylsilyl-10,11-dihydrocinchonidine (11-TES-10,11-DH-CD)[62] from a solution in dichloromethane was studied at a concentration of 15.0 mmol dm^{-3}. The adsorption of 1-phenyl-1,2-propanedione (Aldrich, 22303-4, 99%) was performed from the solution concentration of 50 mmol dm^{-3} in accordance with the experimental conditions for catalytic hydrogenation. The

organic compounds were adsorbed from 20 mL solutions in dichloromethane (Fluka, ≥99.5%). After stirring overnight, the liquid phase was decanted, the catalyst was filtered, washed with 15 mL of dichloromethane and evacuated at room-temperature prior to the measurment. The analytical sample, referred to as "Pt/CD/PPD" in this manuscript, was prepared by treatment of the activated catalyst with a solution of cinchonidine in dichloromethane (0.34 mmol dm^{-3}) followed by filtration and drying and the subsequent treatment of the sample obtained with a solution of PPD in dichloromethane (50 mmol dm^{-3}). Pretreatment of the spent catalyst and details of catalytic experiments are available as Supporting Information.

Results

First, we demonstrate that chiral modifiers and PPD are selectively deposited on the metal surface. The modifier can be adsorbed from solution on alumina.[63] Hence, the washing of the catalyst with small amount of the solvent was applied both during the preparation of the catalyst and alumina samples in order to remove the possibly physisorbed organic molecules from the metal and the support. In order to distinguish between the adsorption on the metal surface and on alumina support, samples of Al$_2$O$_3$ were subjected to analogous treatment with organic solutes and studied by DRIFTS (Supporting Information). The spectra of pure alumina was subtracted from the original spectra (Figure S3), and the result was carefully examined for the presence of characteristic absorbance bands. Consequently, we tentatively assume that, under the sample preparation conditions, PPD and the chiral modifier are not adsorbed on the support, since no characteristic vibrations were observed in the alumina samples.

Adsorption of Carbon Monoxide. Adsorption of carbon monoxide on the samples studied in this paper was performed to ensure the presence of organic molecules on the metal surface and to control the availability of the adsorption sites. The utilization of small gas molecules as spectroscopic probes is a well-known technique for characterization of various surfaces.[64,65] Carbon monoxide is overwhelmingly the most widely used probe molecule for infrared studies. Gaseous carbon monoxide usually gives the absorption band at 2143 cm^{-1} which is shifted to lower frequencies for CO chemisorbed on the metal surface. In the case of metallic Pt species, the C−O stretch appears within the region of 2130−2000 cm^{-1}, which is characteristic for linearly adsorbed CO.[66]

The adsorption of carbon monoxide on metal surface from a gas phase is challenging, as shown by Baiker et al.[67] In the present study, CO was successfully adsorbed on a dry Pt/Al$_2$O$_3$ sample from the gas phase. Under the conditions described in the experimental section, the vibration frequency of the CO adsorbed on the platinum surface is 2090 cm^{-1} (Supporting Information). The band position of adsorbed CO is known to be sensitive to the molecular environment. In contrast to the IR band position of CO adsorbed on a clean platinum surface, the corresponding band for CO adsorbed on Pt in the presence of dichloromethane is observed at 2084 cm^{-1}.

Interesting results were obtained when CO was adsorbed on Pt surface previously treated with CD solutions in dichloromethane. Two different concentrations of the alkaloid solutions were used for the platinum modification. In both cases, the spectrum of CO adsorbed on the Pt surface reveals a single broad band at approximately 2045−2039 cm^{-1}. The red shift is characteristic of the strong electron-donative interaction of quinoline moiety of the modifier with the platinum d-bands. The observations are in line with the previous reports.[14,68]

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It is noteworthy that the CO band is shifted to a slightly lower wavenumber when the catalyst is treated with the lower concentration solution and band broadening of the latter is observed. This phenomenon can originate from two different adsorption modes of the modifier at the different saturation levels.

The adsorption of CO on Pt treated with PPD solutions in dichloromethane was studied and the results were compared with those obtained for the CO adsorption on the Pt/CD/PPD catalyst samples (Table S1, Supporting Information). The latter corresponds to the catalyst employed under the actual catalytic conditions for enantioselective hydrogenation of PPD.[61] Evaluation of the IR spectra for v_{CO} in the Pt/PPD sample reveals a slight difference in the position of the CO vibrational band as compared to the spectrum of the Pt/CD/PPD catalyst. The difference in the CO band positions is rather substantial. The Pt/PPD sample lacking a pre-adsorbed modifier, corresponding to the actual hydrogenation catalyst under racemic conditions, is characterized by the adsorbed CO vibration frequency of 2067 cm^{-1}, whereas the spectrum of the Pt/CD/PPD sample with pre-adsorbed CD has the CO band at 2059 cm^{-1}. Coverage of the Pt surface with CD decreases the amount of active sites available for reaction with subsequent decrease in the amount of adsorption sites.

Adsorption of CO on the samples obtained from the reaction quenched after both 1 and 45 min resulted in CO absorption bands at 2063 and 2064 cm^{-1}, respectively. In the spectrum of the sample treated for 45 min, the CO vibration band appears as a very small and broad signal, whereas the aliphatic C−H vibration bands in the 2800−3000 cm^{-1} region assigned to the reactant, product, and modifier molecules are intense and sharp. This can be taken as evidence for the Pt adsorption sites having a high occupation by organic molecules, resulting in a decrease of the CO adsorption.

It was interesting to compare the Δv_{CO} of co-adsorbates of different nature as the PPD molecule can interact with the platinum surface by means of an O-lone-pair, C=O and/or the phenyl π-electron systems. Thus, for benzene co-adsorption with CO, a red shift Δv_{CO} of 40 cm^{-1} was detected, which is characteristic for the π-adsorption.[69] Adsorption of ammonia or water, which coordinatively bind to the platinum via lone-pairs, has resulted in Δv_{CO} of 25 and 15 cm^{-1}, respectively.[69] Hence, Δv_{CO} of 23 cm^{-1} upon adsorption of PPD is more consistent with the O-lone-pair interaction with the platinum (η^1(O) adsorption mode).

Liquid Phase Interactions. One-to-one and two-to-one complexes between the ether derivatives of cinchona alkaloids and ketopantolactone were recently detected in the liquid phase by NMR techniques.[42] Therefore, in the present study, one-to-one molar mixture of cinchonidine and PPD solution was examined in dichloromethane for potential liquid phase interactions. IR spectra of the individual compounds were recorded and compared with those of the mixture. Eventual hydrogen bonding or the formation of a supramolecular shielding complex between the modifier and PPD should be easily recognized by trace of the carbonyl group vibrational frequency, which tends to be red-shifted by 30−100 cm^{-1} upon interaction. A comparison of the IR spectra of a PPD solution and the PPD−CD mixture shows that both IR traces have strong absorption bands corresponding to the carbonyl groups at 1716 and 1676 cm^{-1} (C2=O2 and C1=O1, respectively) indicating no interaction between CD and PPD in the liquid phase (Spectrum is available as Supporting Information).
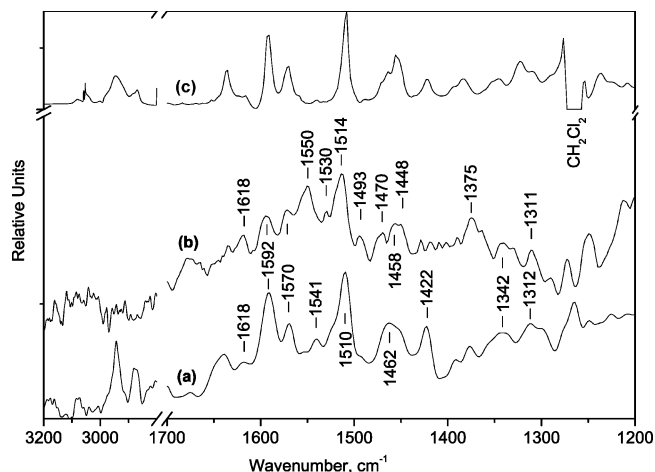

Figure 3. DRIFT spectra of the platinum catalyst: (a) CD adsorption on 5% Pt/Al$_2$O$_3$ from 15 mM solution in dichloromethane; (b) CD adsorption on 5% Pt/Al$_2$O$_3$ from 0.34 mM solution in dichloromethane; and (c) transmission spectra of CD solution in dichloromethane.

Adsorption of the Modifier. The adsorption of cinchonidine on platinum has been extensively studied by infrared spectroscopy.[13−19,21] In the present work, the assignment of the peaks follows that of two earlier publications.[15,19] The IR spectrum of CD adsorbed on Pt/Al$_2$O$_3$ from the solution concentration of 15 mmol dm^{-3} resembles the corresponding spectrum of CD in solution (Figure 3). Peaks and shoulders can be observed at 1636, 1618, 1592, 1570, 1541, 1510, 1460, 1422, 1342, and 1312 cm^{-1}. A scaled transmission spectrum of 0.1 M solution of CD in dichloromethane is also given for comparison. The negative peak at 1270−1260 cm^{-1} is a result of absorption of uncompensated solvent. The strong absorption of alumina skeleton vibrations substantially increases the noise below 1200 cm^{-1} making the analysis of lower wavenumber vibrations unfeasible. A list of band assignments for the cinchonidine surface peaks is provided in Table 1. The 1600−1500 cm^{-1} region is useful in providing information on the adsorption mode of CD on metal surfaces. In the spectrum of the low concentration sample, the in-plane vibration of quinoline moiety at 1592 cm^{-1} is not very pronounced indicating the presence of a π-bonded species. The band at 1570 cm^{-1} is not intense, while the band at 1550 cm^{-1} is a new feature in the low concentration IR trace. Another difference is the absence of a quinoline in-plane deformation peak at 1422 cm^{-1} in the spectrum of low concentration sample and the occurrence of a fairly intense signal at 1375 cm^{-1}.

In our earlier work, the highest enantiomeric excesses (approaching 70% ee) in the hydrogenation of PPD over Pt/Al$_2$O$_3$ have been obtained by using 11-(triethylsilyl)-10,11-dihydrocinchonidine (11-TES-10,11-DHCD) as the chiral modifier.[62] This compound, prepared by hydrosilylation of the vinylic double bond of cinchonidine,[62] contains a bulky substituent in a distal position from the adsorbing quinoline anchor part of the modifier. Considering that for a bulkier compound (for X-ray structure, see Figure 4) a tilted adsorption mode might be hindered, the adsorption of 11-TES-10,11-DHCD was studied at a higher concentration. The IR spectra of the two adsorbed modifiers, CD and 11-TES-10,11-DHCD, are represented in Figure 5. The IR trace of 11-TES-10,11-DHCD adsorbed on platinum has the same quinoline and quinuclidine features. The band at 1236 cm^{-1} results from the Si−C symmetric deformations, while the intense set of peaks below 3000 cm^{-1} corresponds to the CH$_3$ and CH$_2$ stretching vibrations of the silane part of the molecule.
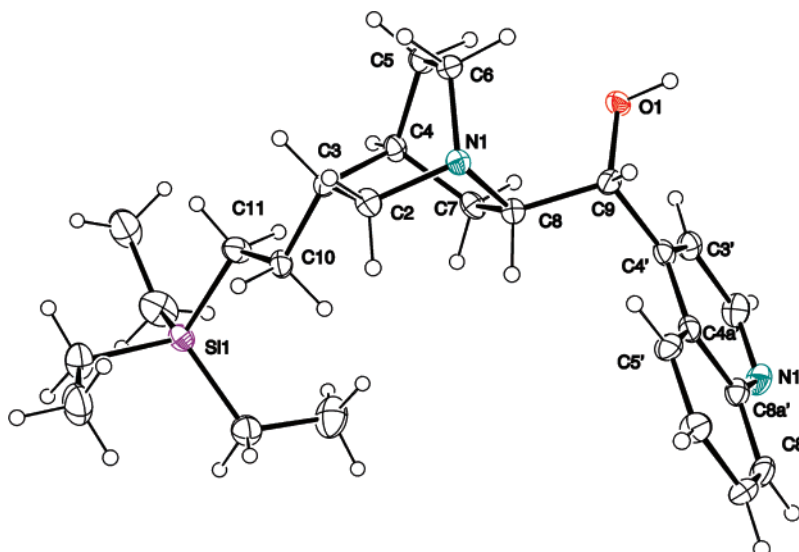
Figure 4. Molecular structure of 11-triethylsilyl-10,11-dihydrocinchonidine. Thermal ellipsoids are drawn at 30% probability level. The synthesis of this compound has been described in our earlier work,[62] while this is the first report of its molecular structure. For discussion and parameters, see Supporting Information.

TABLE 1: Assignment of Frequencies (cm^{-1}) from IR Spectra of Cinchonidine Adsorbed on Pt/Al$_2$O$_3$ and Dissolved in CH$_2$Cl$_2$[a]

CD in CH$_2$Cl$_2$	high conc. on Pt/Al$_2$O$_3$	low conc. on Pt/Al$_2$O$_3$	(19)	assignment[15,19]
1636(m)	1637			vinyl C=C stretch
1616(w)	1618	1618	1610	Q ip C=C ring def + Q C−H ip bend
1590(m)	1592	1593	1590	Q ip C=C ring def + Q C−H ip bend
1569(m)	1570	1571	1570	Q ip C=C ring def + Q C−H ip bend
		1550		tilted π−bonded
	1541	1530	1530	α−quinolyl
1508(m)	1510	1514	1511	Q ip ring def + Q C−H ip bend
1465(w)	1462(br)	1470	1458	QN C(7)H$_2$ oop scissor
1456(m)	1462(br)	1458	1458	QN C(5)H$_2$ oop scissor
		1448		QN C(6)H$_2$ oop scissor
1422(w)	1422		1421	Q ip ring def
1390(sh)	1392			C8−C9 stretching
1383(m)	1378	1375		Q ring stretch + CH ip bend
1345(w)	1342	1342		Q ring stretch + QN C(8)H wag
1323(w)			1318	QN CH$_2$ wag + Q ip ring def
1308(sh)	1312	1311		QN CH and CH$_2$ wag

[a] Experimental intensities: s = strong, m = medium, w = weak, vw = very weak. Comments: sh, peak shoulder; br, broad; ip, in plane; oop, out of plane; def, deformation; QN, quinuclidine; Q, quinoline.

Adsorption of PPD. The solid-phase IR spectra of PPD has been studied in detail by Fausto and co-workers.[70] Electron diffraction investigation revealed that PPD is a nonplanar molecule, with the dihedral angle formed by the two carbonyl groups of 129.9° and the phenyl ring residing nearly coplanar to the adjacent carbonyl.[71] The fingerprint region of the IR spectrum of PPD adsorbed on Pt/Al$_2$O$_3$ is shown in Figure 6, with PPD vibration bands observed at 1710, 1678, 1599, 1451, 1415, 1344, and 1310 cm^{-1}. Assignment of the peaks is presented in Table 2. The broad hump between 1530 and 1580 cm^{-1} originates from the carbonaceous species on the platinum surface. A red shift of v(C2=O2) of the adsorbed diketone is observed when compared with the corresponding vibration in bulk. This shift is characteristic of η^1 adsorption state of carbonyl compounds on transition metal surfaces.[51−58] Interestingly, the adsorption of PPD on Pt/Al$_2$O$_3$ does not lead to a discernible shift in v(C1=O1). In the spectrum of adsorbed PPD, new bands appear at 1433 and 1392 cm^{-1}. These could be assigned to an antisymmetric CH$_3$ bending in the di-η^1 adsorption mode in analogy with butane-2,3-dione adsorption (Table 3).[57] The absence of a methyl group C−H stretch in the 3000−2800 cm^{-1} region, however, does not support this hypothesis. Yet C−H

TABLE 2: Assignment of the PPD Vibrations[a]

Xe matrix 20 K[70]	solution in CH$_2$Cl$_2$	on Pt/Al$_2$O$_3$	on CD/ Pt/Al$_2$O$_3$	assignment
1717	1716(s)	1710	1671	C2=O2 str.
1677	1676(s)	1678	1681+ 1649	C1=O1 str.
1599	1597(m)	1599	1598	C−C ring def
1580	1579(w)	[b]	[b]	C−C ring def
1450	1450(m)	1451	1453	arom C−H ip bend
1416	1418(w)	1415	1415	CH$_3$ as bend
1354	1356(m)	1344	1346	CH$_3$ s bend
1319	1319(w)	1310	1323	arom C−H ip bend

[a] Experimental intensities: s = strong, m = medium, w = weak, vw = very weak. Comments: arom, aromatic; as, asymmetric; br, broad; def, deformation; ip, in plane; oop, out of plane; s, symmetric; sh, peak shoulder; str, stretching. [b] Shadowed by hump of carbonaceous species.

stretching vibrations of a phenyl group at 3050−3090 cm^{-1} are not developed which argues against the assignment to a di-η^1 or η^2 mode of adsorption.

Pre-modification of the catalyst surface with cinchonidine and the subsequent adsorption of PPD gives rise to some interesting
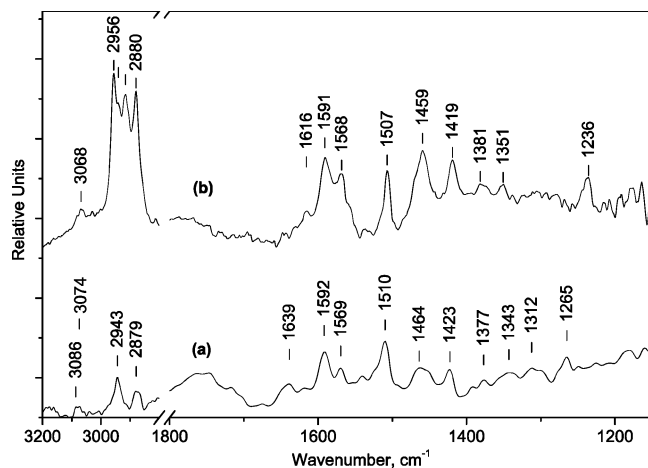
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Figure 5. DRIFT spectra of the platinum catalyst: (a) CD adsorption on 5% Pt/Al₂O₃ from 15 mM solution in dichloromethane; (b) 11-TES-10,11-DHCD adsorption on 5% Pt/Al₂O₃ from 15 mM solution in dichloromethane.

TABLE 3: Main Vibrations of Butane-2,3-dione (BD) Adsorbed on Ni (111)[57]

		BD[57]		
	liquid[60]	η^1 on Ni (111)	η^2 on Ni (111)	di-η^1 on Ni (111)
v(CH₃)	3010			
v(CH₃)	2999			2914
v(CH₃)	2935			2881
v(CO)	1715	1722[a]	1720[a]	
δ_{as}(CH₃)	n.o.			1438
δ_{as}(CH₃)	1419		1420	1387
δ_s(CH₃)	1352		1367	

[a] Carbonyl not attached to the surface.

observations: Both carbonyl bands are red-shifted to broad bands at 1682 and 1649 cm⁻¹ (Figure 6, spectrum b). The low-frequency shift of the C=O stretching suggests that the carbonyl groups are the proton acceptor sites of the intermolecular hydrogen bond.[73] The assignment of these bands is obvious by comparison with the IR spectra of the samples of exhausted catalysts (Figure 7). Two separate peaks are distinguishable at 1681 and 1671 cm⁻¹ after treatment of the reaction mixture with hydrogen for 1 min. The band at 1681 cm⁻¹ is a shoulder of a more pronounced peak at 1671 cm⁻¹, which is opposite to the situation with the catalytic sample before the reaction (Figure 6, spectrum b). During the reaction, the peak at 1648 cm⁻¹ is almost disappearing, while the feature at 1681−1671 cm⁻¹ is clear even after 45 min of reaction. The kinetics of PPD hydrogenation over Pt in dichloromethane have been studied thoroughly.[61] Hydrogenation of the C1=O1 keto group next to the phenyl ring proceeds with a higher rate resulting in a regioselectivity of 12:1 under optimal catalyst/modifier conditions. Hence, the bands at 1648 and 1681 cm⁻¹ can be assigned to hydrogen-bonded-with-cinchonidine and free C1=O1 carbonyl groups, respectively. The peak at 1671 cm⁻¹ is a new feature in the PPD and CD mixture spectrum and can be assigned to the C2=O2 carbonyl group involved in H-bonding with cinchonidine. Interestingly, the unperturbed C2=O2 carbonyl band at 1710 cm⁻¹ is missing from the spectrum of cinchonidine with PPD co-adsorbed on platinum while the C1=O1 carbonyl exists in two distinguishable forms when adsorbed on the pre-modified catalyst. This phenomenon will be discussed in the following section.

The set of bands below the 3000 cm⁻¹ region, belonging to the C−H stretch of the accumulating products, and the peaks
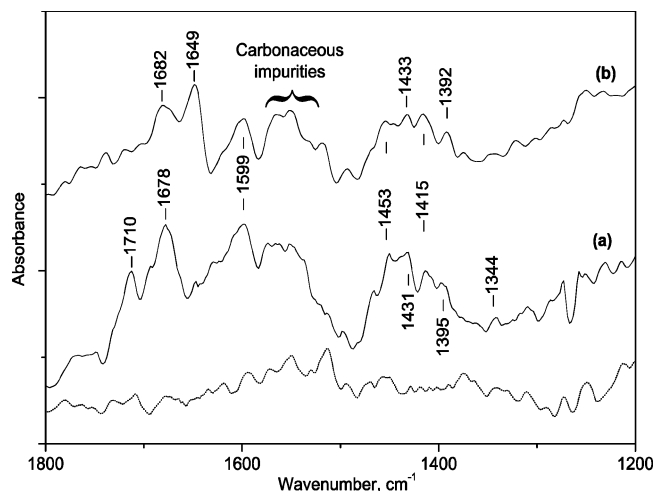

Figure 6. Adsorption of PPD on unmodified (a) and cinchonidine-modified (b) Pt/Al₂O₃ catalyst. The spectrum of low concentration cinchonidine on platinum is depicted by dotted line.
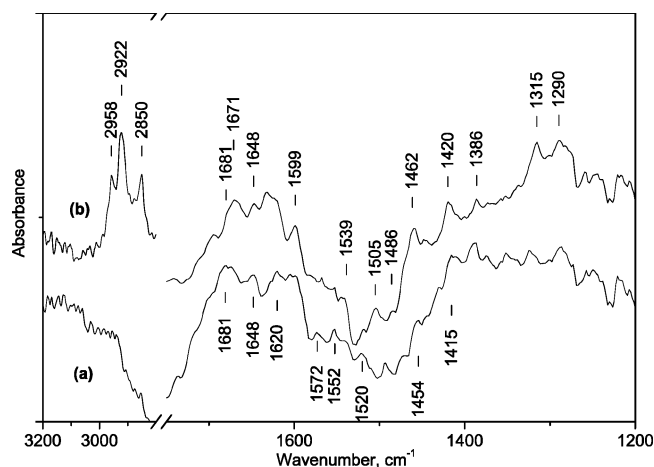

Figure 7. DRIFTS spectra of Pt/Al₂O₃ catalyst pre-modified with cinchonidine after treatment of the reaction mixture (50 mM solution of PPD in dichloromethane) with hydrogen pressure of 10 bar: (a) 1 min; (b) 45 min.

at 1315 and 1290 cm⁻¹ are present in the spectra after hydrogenation reaction together with the carbonyl bands. The IR bands corresponding to hydroxyl C−O vibration modes of the hydroxyketones and diols are weak but clearly visible after 1 min of catalyst exposure to hydrogen pressure. The development of these peaks is obvious. The bands at 1315 and 1290 cm⁻¹ are among the most prominent peaks in the spectrum obtained on the catalysts after 45 min of reaction. A water band appears at 1620 cm⁻¹ in the spectra of the catalytic samples. It can be attributed to the reaction between the hydrogen and surface oxygen. It is worth mentioning that carbonaceous impurities observed in the 1590−1530 cm⁻¹ region of the spectrum of CD and PPD co-adsorbed on Pt/Al₂O₃ are not detected in the spectra of the catalytic samples. Evolution of methane has been reported based on TPD analysis of the catalytic samples.[61] Therefore, we assume that under the high hydrogen pressure conditions, solvent decomposition products are effectively removed from the catalyst surface.

Computational Studies. The adsorption of 1-phenyl-1,2-propanedione with platinum has been studied in detail by density functional theory (DFT). Several adsorption modes which were not considered previously[59] due to their low stability, are presented here and discussed in the light of the spectroscopic results. Illustrations of the structure of PPD adsorbed on Pt
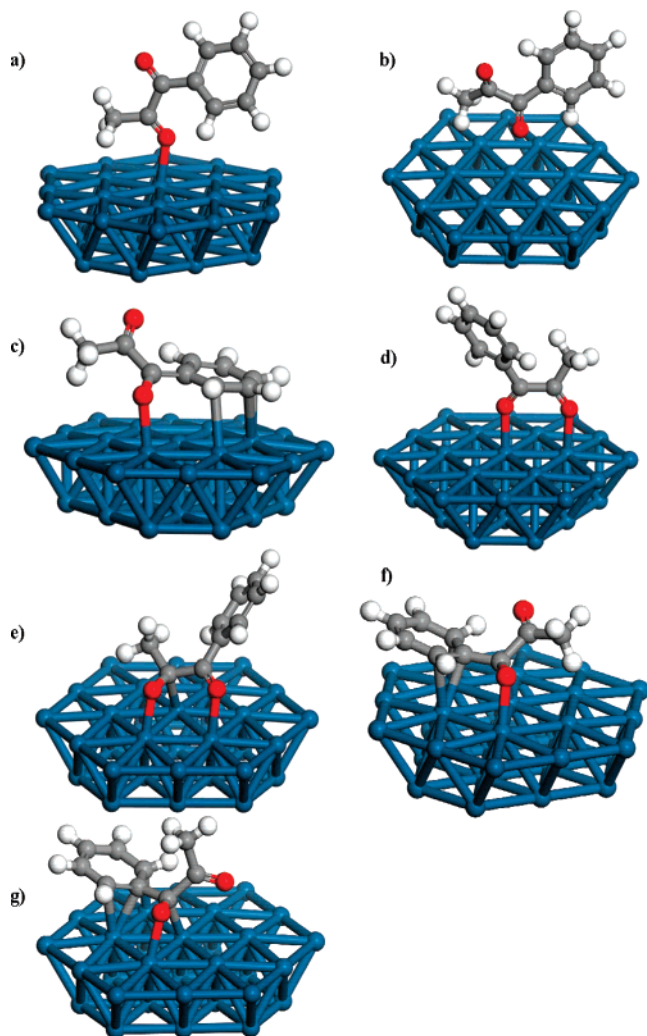
Figure 8. Adsorption configurations of PPD on Pt: (a) η^1(O2); (b) η^1(O1); (c) pseudo-η^1(O1); (d) di-η^1(O1,O2); (e) η^2(C2,O2); (f) η^2-(C1,O1); (g) η^3(C1,O1,O2).

TABLE 4: Adsorption Energies for Different Adsorption Modes of 1-Phenyl-1,2-propanedione

adsorption configuration	ΔE (kJ mol^{-1})
η^1(O1)	-19^a
η^1(O2)	-36
pseudo-η^1(O1)	-55
di-η^1(O1, O2)	-3^a
η^2(C1, O1)	-88^b
η^2(C2, O2)	-38^a
η^3(C1, O1, O2)	-59

^{a} Taken from ref 59. ^{b} Phenyl ring only partly adsorbed

cluster with different configuration modes are represented in Figure 8. The adsorption energies are given in Table 4. η^1-Adsorption modes were considered first. Of the η^1 structures, η^1(O2) was found as the most stable with adsorption energy of -36 kJ mol^{-1}. In contrast, the end-on adsorption of PPD by O-lone pair of the carbonyl group adjacent to the phenyl ring is clearly less stable having the adsorption energy of -19 kJ mol^{-1}. We also attempted to find a stable η^1(O1) adsorption mode in which the phenyl ring is parallel to the surface but not adsorbed. This, however, leads to a configuration of PPD on a platinum cluster labeled as pseudo-η^1(O1), in which the aromatic carbon atoms contribute to the adsorption energy. The optimization history curvature indicates that pseudo-η^1(O1) is rather an intermediate that leads to a structure in which the phenyl ring

is chemisorbed on the surface. A stable η^1(O1) adsorption mode, in which phenyl ring is parallel to the surface, was not found.

Previously, it has been reported that the adsorption energy of -169 kJ mol^{-1} for η^2 having a phenyl ring co-adsorbed with C1=O1 and the O=C−C=O system in an *s*-trans conformation is the most stable adsorption configuration.[59] These results, however, refer to low-pressure conditions. Under the high reactant concentration conditions, as routinely employed for the catalytic experiments, one of the adsorption states with lower adsorption energy can be favored due to a phenyl−phenyl lateral repulsive interaction. This encouraged us to investigate η^2-configurations in which the phenyl ring is not co-adsorbed together with the carbonyl group. The adsorption energy for such η^2(C1, O1) is decreased to -88 kJ mol^{-1}. However, it is notable that the carbon atoms in the phenyl ring do contribute to the adsorption and the structure of the phenyl ring is slightly distorted.

The η^3-structure is a variation of η^2, where the second oxygen atom interacts with the surface by its O-lone pair. The additional interaction of the non-adsorbed carbonyl group with the surface leads to a decrease in adsorption energy of -59 kJ mol^{-1}.

The results of the DFT calculations are well in agreement with the experimental data. Only η^1 adsorption via oxygen O2 was detected on the surface of the Pt/Al$_2$O$_3$ catalyst whereas the other η^1 adsorptions were not observed.

Discussion

Adsorption of the modifier. In the present work, we were particularly interested in assigning the adsorption modes by IR spectroscopy. One of the first attempts to correlate the IR spectra of adsorbed cinchonidine with its geometry on the surface was performed by Zaera and Kubota.[13] They used signals at 1217, 1255, and 1385 cm^{-1} to assign the flat adsorption mode and the signals at 1510, 1574, and 1591 cm^{-1} as a fingerprint of the N-lone-pair-bonded adsorption mode. Three distinct adsorption regimes were identified by exposure of a platinum surface to cinchonidine solutions in carbon tetrachloride at different saturation levels. The intensity of the 1217 cm^{-1} IR peak reaches a maximum when the cinchonidine-to-platinum molar ratio is 1:10. This then was correlated with the maximum enantio-selectivity of ethyl pyruvate hydrogenation in acetic acid. Later, a detailed vibrational band assignment for cinchonidine was carried out by the Zaera and Williams groups.[15] In the latter study, the peaks at 1217 and 1255 cm^{-1} were assigned to the carbon tetrachloride solvent. The band at 1385 cm^{-1} is due to the quinoline ring stretch and the quinoline in-plane C−H bend. According to the surface selection rule,[74] these vibrations should not be observed when the quinoline plane is parallel to the surface. However, it is also mentioned that the C8−C9 stretch, having no restrictions for detection of this mode, is characterized by an IR peak at 1390 cm^{-1}. A low concentration cinchonidine solution (0.5 mM in CCl$_4$) was used for saturation of the platinum surface with cinchonidine-to-platinum molar ratio of approximately 1:30. The corresponding IR spectrum consisted of peaks at 1217, 1255, 1390, 1464, and 1550 cm^{-1}. The latter band was not considered due to the potential carbon tetrachloride interference. The peak at 1464 cm^{-1} associated with the quinuclidine CH$_2$ scissoring vibration is indicative of a parallel adsorption mode but only in the absence of any of the intense peaks in the 1500−1600 cm^{-1} region due to the conformational flexibility of the quinuclidine part of the molecule.[75]

Ferri and Bürgi have made significant contributions to characterizing the cinchonidine adsorption on platinum.[18,19] They assigned the signals at 1567 and 1530 cm^{-1} with a strongly

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adsorbed species while the signals at 1590 and 1511 cm^{-1} were assigned to weakly adsorbed species. The band at 1530 cm^{-1} was associated with α-H-abstracted quinolyl species (labeled c in Figure 1), while the band at 1567 cm^{-1} was assigned to the strongly adsorbed species most populated at the low concentration (coverage).

In the present work, we have utilized the quinoline ring in-plane vibrations in the 1500−1600 cm^{-1} region as the only reliable source for assignment of cinchonidine adsorption modes which are tilted with respect to the platinum surface. The analysis of the spectra of cinchonidine adsorbed on the actual catalyst from the solution of different concentrations here reveals a new signal at 1550 cm^{-1}, which is present in the spectrum of cinchonidine on Pt/Al$_2$O$_3$ with coverage reproducing the catalytic conditions. Clearly, this band can be assigned to the quinoline-in-plane vibrations only, since in the present investigation the solvent cannot perturb this region as carefully examined by the analysis of the spectrum of the catalyst treated with dichloromethane overnight. For the adsorption of cinchonidine via its π-system, but with some degree of tilting with respect to the platinum surface (labeled (b) in Figure 1), the fundamental vibrations of cinchonidine quinoline ring are expected to be altered. Taking into account the presence of a maximum in the enantioselectivity−modifier concentration dependence for PPD hydrogenation, the sufficient stability of the tilted π-bonded adsorption species as calculated by Vargas[50] and finally, the results obtained here, we assume that the signal at 1550 cm^{-1} can be identified as a tilted π-bonded cinchonidine. Moreover, the participation of a tilted π-bonded cinchonidine in the enantiodifferentiation mechanism of PPD hydrogenation is not inconceivable. More detailed studies are, however, necessary to clarify its role. Previously, DFT calculations of acetone adsorption on Pt(111) allowed Jeffery and co-workers[76] to propose that the modifier is interacting with an end-on adsorbed ketone group to tilt the plane of the molecule toward the surface.

Adsorption of PPD. The C═O bonds are inclined with respect to the metal surface making possible the observation of C−O stretch by IR. Contrary to the case of butane-2,3-dione,[57] PPD has two distinguishable and chemically unequivalent carbonyl groups. The IR spectra of PPD adsorbed on Pt demonstrated the selective η^1-adsorption of PPD via oxygen O2. The reason for this preference originates from the structure of PPD. The carbonyl adjacent to the phenyl ring (C1═O1) has a sterically bulkier substituent which eventually results in hindered adsorption. This is especially conceivable under the high PPD coverage conditions applied during a typical catalytic experiment. As can be seen in Figure 8, η^1(O2) has a very similar adsorption mode to that of η^1 of acetone that is known to have a rather high adsorption energy of around 50 kJ mol^{-1}.[76]

The fact that the δ_{as}(CH$_3$) band (1415 cm^{-1}) is more intensive than the δ_s(CH$_3$) band (1346 cm^{-1}) is consistent with an η^1-(O2) adsorption geometry in which the C−CH$_3$ bond is roughly parallel to the surface. Notably, in η^1(O2)-configuration the interacting C−O bond is inclined to the surface at an angle of close to 60° as suggested for the interaction of the carbonyl lone-pair electrons with metals.[77] This angle can nevertheless be altered by steric effect of the substituents.

Very interesting results were obtained when PPD was co-adsorbed together with cinchonidine on the catalyst (Figure 6, spectrum b). The shift in the vibrational frequency of the C2═O2 stretch from 1710 cm^{-1} for PPD on clean platinum surface to 1671 cm^{-1} for PPD on platinum pre-modified with cinchoni-

dine was observed. The other carbonyl group in the Pt/CD/PPD sample is represented in the spectrum by two bands, one having the ν(C1O1) identical to the band in "PPD on clean platinum" spectrum, whereas the band is red-shifted by 30 cm^{-1}. This indicates that surface induced hydrogen bonding occurs between the adsorbed species of cinchonidine and PPD,[78] where C2═O2 carbonyl is always hydrogen-bonded while the C1═O1 simultaneously exists as a hydrogen-bonded and free entity.

The red shift of carbonyl bands of 30 cm^{-1} in the spent catalyst collected after the reaction cannot be assigned to the presence on the platinum surface of PPD hydrogenation products. The IR frequencies of carbonyls in 1-hydroxy-1-phenyl-2-propanone (1715 cm^{-1})[79] and 2-hydroxy-1-phenyl-1-propanone (1680 cm^{-1})[80] are similar to that of in PPD.

Our conclusions are well in line with the results in the literature. Adsorption of methyl pyruvate (MePy) on platinum was studied by McBreen and co-workers.[22] It was demonstrated that a di-η^1-configuration of MePy, characterized as surface enediolate state, is the most stable configuration on clean Pt (111) surface. As the coverage of MePy is increased, the η^1-configuration starts to populate the surface. The surface pre-coverage with (1-naphtyl)ethylamine inhibits the formation of enediolate species of co-adsorbed MePy and stabilizes the η^1-state as a result of H-bonding between the carbonyl group of MePy and the NH$_2$ group of the modifier. The H-bonding is detected by shift of the carbonyl band from 1737 cm^{-1} for the free carbonyl in η^1-configuration to 1700 cm^{-1} for the hydrogen-bonded carbonyl.

A red shifted broad band of ketopantolactone carbonyl group was observed at 1725 cm^{-1} by in situ ATR and modulation spectroscopy experiments when ketopantolactone is co-adsorbed on the Pt/Al$_2$O$_3$ thin film with cinchonidine.[20] Interestingly, that the shift was not observed when N-methyl cinchonidinium chloride was used instead of the parent alkaloid. It clearly indicates that quinuclidine-N is directly involved in the formation of the hydrogen bond between cinchonidine and the reactant. In the same study, the N−H stretching vibration was detected as a broad band at 2580 cm^{-1} when cinchonidine was co-adsorbed with ketopantolactone. Unfortunately, appearance of the N−H band was not detected in the current investigation, probably because of the broad featuring of this band and the low signal intensities, whereas the red shift of the carbonyl bands in the present study is in good agreement with the results of Baiker.[20]

In the present paper, the 5% Pt/Al$_2$O$_3$ catalysts with adsorbed modifiers and PPD were analyzed by ex situ DRIFTS method. The main advantage of this method is that the actual catalyst can be directly analyzed in a powder form without preliminary sample preparation. The disadvantage of the DRIFTS method is a result of its merit, as the spent catalyst should be separated from the reaction mixture and can be studied ex situ only. Obviously, in situ ATR-IR approach offers significant benefits for studying the solid−liquid interface. One limitation, however, has been the nature of the thin metal film directly deposited on the internal reflection element. The properties of the film have a pronounced effect on the band shape and frequency of the adsorbate due to anomalous dispersion.[81] Yet, it was demonstrated that hydrogen treatment leads to sintering of Pt islands[82] changing the properties of the film. Moreover, the examples of utilization of the real catalyst films are scarce up to date.[83] The vast majority of the studies performed with the model catalyst[18,19,67] have no direct relevance with the enantioselective heterogeneous hydrogenation.

Ideally a combination of ex situ studies of the real catalysts and in situ analysis of the model catalyst films may be utilized to obtain the most relevant information on the adsorption and interactions of reactant and the chiral modifier on the catalyst surface. The data on the adsorption of cinchonidine on Pt obtained in the present study is in agreement with the earlier observations by others verifying the reliability of the ex situ measurement technique applied here. The adsorption of PPD on the platinum catalyst is studied here for the first time by IR. Interactions between the modifier and substrate are in line with the earlier reports of McBreen[22] and Baiker.[20]

It should be specifically mentioned, that according to the surface selection rule,[74] species parallel to the surface, such as those described in[59] and thought to be relevant in the hydrogenation step, cannot be detected by IR methods. Therefore, the observed interaction of PPD and cinchonidine on the catalyst surface does not necessarily contribute to the enantioselective hydrogenation. At present it is not possible to distinguish between the spectator and active species. An extensive theoretical investigation is required in order to elucidate the role of the η^1(O1)-PPD species observed on the platinum catalyst surface and the involvement of the complex formed from the O-lone pair adsorbed PPD and CD formed complex in the enantio-differentiation mechanism.

Conclusions

Adsorption of 1-phenyl-1,2-propanedione and cinchonidine on a 5% Pt/Al$_2$O$_3$ under the high reactant concentration profile utilized in catalysis was studied using ex situ DRIFTS. The η^1-(O2) configuration of 1-phenyl-1,2-propanedione was detected. DFT calculations demonstrated that η^1(O2) configuration is the most stable end-on adsorption mode of PPD. Tilted π-bonded adsorption mode of cinchonidine was revealed on the platinum catalyst at higher concentration of CD than commonly utilized for enantioselective hydrogenation of keto-esters. Since the enantioselective hydrogenation of PPD is carried out at high CD concentrations, a tilted π-bonded adsorption mode of cinchonidine may have a role in the enantiodifferentiation. A red shift in the C=O vibrations of PPD was observed in the spectra of co-adsorbed PPD and CD indicating a hydrogen-bonding interaction between PPD and cinchonidine.

Supporting Information Available: The crystal structure of 11-TES-10,11-DHCD in the electronic Crystallographic Information File (CIF) format, description of catalytic hydrogenation experiments, details of X-ray structure determination, and computational methodology. This material is available free of charge via the Internet at http://pubs.acs.org.

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