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Catalyst poisoning in catalyzed imine hydrogenation: A novel zwitterionic Rh(I)/*o*-hydroxy-substituted imine complex

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Dedicated to Professor Bogdan Marciniec on the occasion of his 65th birthday, and to acknowledge his contributions to organometallic chemistry and catalysis.

Abstract

During investigation of the homogeneous H_2-hydrogenation of the ketimine $(o\text{-}HOC_6H_4)C(Me)=NCH_2Ph$ catalyzed by the $[Rh(COD)(PPh_3)_2]PF_6$ precursor in MeOH at ambient conditions, we have isolated $[Rh\{\eta^4\text{-}(C_6H_4O)^{(-)}C(Me)=N^{(+)}(H)CH_2Ph\}(PPh_3)_2]PF_6$ (**3**), an unusual zwitterionic Rh complex in which the imine is coordinated via the C_4 part of the *o*-hydroxy-arene moiety in a quinoid form; this tautomer is generated via proton transfer from the O-atom to the N-atom within the molecular, benzenoid form. Precipitation of **3** from the MeOH solution, even under H_2, causes sequestration of the Rh and complete suppression of the catalytic activity. (In a previously studied system with the corresponding, non-hydroxy-substituted ketimine, $PhC(Me)=NCH_2Ph$, the Rh was sequestered as an inactive *o*-metalated species). The solid state structure of **3** is retained in CH_2Cl_2 solution, but in MeOH and Me_2CO reversible loss of the ketimine generates the *cis*-$[Rh(PPh_3)_2(solvent)_2]PF_6$ species.

Keywords: Catalysis; Hydrogenation; Imine complex; Rhodium complex; Phosphine ligand; Zwitterion

1. Introduction

Homogeneous hydrogenation of imines catalyzed by metal complexes is an area of intense current interest, particularly with regard to mechanistic aspects of the process and their implications for the design and use of improved catalysts for generation of chiral amines [1].

Our investigations on the H_2-hydrogenation of imines catalyzed by the $[Rh(COD)(PPh_3)_2]PF_6$ precursor have revealed that, depending on the electronic and steric properties of the substrates and their hydrogenation products (amines), the reactivity patterns and/or coordination modes of the imines and amines can be very different under identical conditions; we have established cyclometalation [2] and hydrolysis [3] of the imine, π-arene coordination of an amine formed by hydrogenation [4], and N-coordination of an amine formed via the hydrolysis [3]. The H_2-hydrogenation of $PhC(Me)=NCH_2Ph$ in MeOH at room temperature and 1 atm H_2 catalyzed by 10^{-3} M $[Rh(COD)(PPh_3)_2]PF_6$ precursor (which in situ generates *cis*,*trans*,*cis*-$[Rh(H)_2(PPh_3)_2(MeOH)_2]PF_6$) is slow, with 40% conversion after 24 h at substrate: Rh = 100 [2]. This is because the Rh, while bonded in the usual η^1-N fashion, is sequestered as a catalytically inactive *o*-metalated species [2], the orthometalation involving the *o*-hydrogen of the Ph substituent on the imine C-atom. It was thus of interest to eliminate this orthometalation reaction by incorporating *o*-substituents, and initially $(o\text{-}HOC_6H_4)C(Me)=NCH_2Ph$ was chosen. This ketimine was found not to be hydrogenated at all under ambient conditions, because the Rh is now converted to a very different, and apparently unique, type of complex, namely $[Rh\{\eta^4\text{-}(C_6H_4O)^{(-)}C(Me)=N^{(+)}(H)CH_2Ph\}(PPh_3)_2]PF_6$; this paper reports on the full characterization of this compound.

2. Experimental

2.1. General

Synthetic procedures were performed at room temperature (~20 °C) using standard Schlenk techniques under an atmo-

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sphere of dry Ar. The solid imine (o-HOC_6H_4)C(Me) = NCH_2Ph was synthesized in this laboratory previously by Dr. D.E. Fogg [5]. The $[Rh(COD)(PPh_3)_2]PF_6$ complex, and the readily derived *cis*,*trans*,*cis*-$[Rh(H)_2(PPh_3)_2(solv)_2]PF_6$ (**1**) and *cis*-$[Rh(PPh_3)_2(solv)_2]PF_6$ (**2**) species (solv = MeOH, Me_2CO), were prepared according to literature procedures [6,7]. Other reagents were purchased from commercial sources and used as supplied. Solvents were dried over the appropriate agents and distilled under N_2 prior to use. NMR spectra were recorded on Bruker AV 300 (300 MHz for ^1H, 121 MHz for $^{31}P\{^1H\}$, 75 MHz for ^{13}C) and Bruker AV 400 (400 MHz for ^1H, 162 MHz for $^{31}P\{^1H\}$, 100 MHz for ^{13}C) spectrometers; residual solvent protons (^1H, relative to external $SiMe_4$), and 85% aq. H_3PO_4 ($^{31}P\{^1H\}$), were used as references. All J values are given in Hz. The infrared spectrum was recorded on an ATLI Mattson Genesis Series FTIR spectrophotometer, and IR bands (KBr pellet) are reported in cm^{-1}. Elemental analysis was performed by Mr. M. Lakha of this department on a Carlo Erba 1108 analyzer.

2.2. Synthesis of $[Rh\{\eta^4\text{-}(C_6H_4O)^{(-)}C(Me) = N^{(+)}(H)CH_2Ph\}(PPh_3)_2]PF_6$ (3)

A red solution of *cis*-$[Rh(PPh_3)_2(MeOH)_2]PF_6$ (**2**, 0.09 mmol) in MeOH (5 mL) was treated with (o-HOC_6H_4)C(Me) = NCH_2Ph (0.041 g, 0.181 mmol) under Ar, and the mixture stirred at room temperature for 2 h. The dark-red solid that slowly precipitated over this period was collected by filtration, washed with Et_2O (3× 4 mL) and dried in vacuo. Yield: 0.045 g (50%). Anal. calcd. for $C_{51}H_{45}F_6NOP_3Rh$: C, 61.39; H, 4.55; N, 1.40. Found: C, 61.42; H, 4.79; N, 1.60. ^1H NMR (400 MHz, CD_2Cl_2): δ 2.11 (s, 3 H, CH_3), 4.23 (d, 1 H, m'-$\eta^4(C_6H_4O)$, $^3J_{HH} = 7$), 4.73 (d, 1 H, o-$\eta^4(C_6H_4O)$, $^3J_{HH} = 6$), 4.85 (ABX multiplet, 2 H, CH_2, $J_{AB} = 17$, $J_{AX} = J_{BX} = 6$), 5.04 (t, 1 H, m-$\eta^4(C_6H_4O)$, $^3J_{HH} = 5$), 7.10 (t, 1 H, p-$\eta^4(C_6H_4O)$, $^3J_{HH} = 6$), 6.97–7.70 (m, 35 H, Ar), 14.96 (s, 1 H, N···H···O). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 14.82 (s, CH_3), 50.2 (s, CH_2), 84.5 (s, m-η^4-C_6H_4O), 89.1 (s, m'-η^4-C_6H_4O), 100.8 (s, o-η^4-C_6H_4O), 105.1 (s, p-η^4-C_6H_4O), 106.1 (s, *ipso*-η^4-C_6H_4O), 128.2–135.2 (m, C–Ar), 171.2 (s, C=O), 171.5 (s, C=N). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ 39.5 (d, $J_{RhP} = 203$). IR (KBr pellet): $\nu = 1581$ (C=N), 1966 (C=O), 3055, 3447 (N···H···O).

2.3. Crystal structure determination

Measurements were made at 173(1) K on a Rigaku/ADSC CCD area detector diffractometer with graphite monochromated Mo Kα radiation (0.71073 Å). Some crystallographic data for **3** are shown in Table 1. Data for **3** were collected using the d*TREK [8] software package and processed using TwinSolve [9]. Data were corrected for absorption effects using a multi-scan technique (TwinSolve), with normalized minimum and maximum transmission coefficients of 0.778 and 0.962, respectively. The structure was solved by direct methods [10]. All non-hydrogen atoms were refined anisotropically. The N···H···O hydrogen atom was located in a difference map and refined isotropically, while all other H-atoms were included in calculated positions but not refined. The final cycle of full-matrix least-squares refinement on F^2 was based on 8096 reflections and 589 variable parameters (least squares function minimized $\Sigma w(F_o^2 - F_c^2)^2$, where $w = 1/[\sigma^2(F_o^2) + (0.0381P)^2 + 1.1685P]$ and $P = (F_o^2 + 2F_c^2)/3$), and converged to $R_1 = 0.043$, $wR_2 = 0.074$, GOF = 1.03. Neutral atom scattering factors were taken from Cromer and Waber [11] and anomalous dispersion effects were included in F_{calc} [12], the values of $\Delta f'$ and $\Delta f''$ being those of Creagh and McAuley [13]. Values for the mass attenuation coefficients are those of Creagh and Hubbell [14], and all calculations were performed using SHELXL-97 [15].

Table 1
Crystallographic data for $[Rh\{\eta^4\text{-}(C_6H_4O)^{(-)}C(Me) = N^{(+)}(H)CH_2Ph\}(PPh_3)_2]PF_6$ (**3**)

Data	**3**
Formula	$C_{51}H_{45}F_6NOP_3Rh$
Formula weight	997.70
Crystal system	Triclinic
Crystal size (mm)	0.40 × 0.20 × 0.07
Space group	P-1 (#2)
a (Å)	12.120(1)
b (Å)	13.004(1)
c (Å)	15.354(1)
β (°)	78.891(5)
Volume (Å^3)	1864.2(4)
Z	2
Absorption coefficient (mm^{-1})	0.549
Total reflections	18856
Unique reflections	8096
R_{int}	0.028
No. of variables	589
R_1 ($I > 2\sigma(I)$)	0.030 (6778 obs. refl.)
wR_2[a]	0.074 (all data)
gof	1.03 (all data)

[a] $w = 1/[\sigma^2(F_o^2) + (0.0381P)^2 + 1.1685P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Complete crystallographic material for complex **3** has been deposited with the Cambridge Crystallographic Data Centre; copies of the data (CCDC: 296071) can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

Reaction of either *cis*,*trans*,*cis*-$[Rh(H)_2(PPh_3)_2(MeOH)_2]PF_6$ (**1**) [6] or *cis*-$[Rh(PPh_3)_2(MeOH)_2]PF_6$ (**2**) [7] in MeOH at room temperature under Ar with two equivalents of the ketimine (o-HOC_6H_4)C(Me) = NCH_2Ph for 2 h results in the slow, spontaneous precipitation of the dark-red solid $[Rh\{\eta^4\text{-}(C_6H_4O)^{(-)}C(Me) = N^{(+)}(H)CH_2Ph\}(PPh_3)_2]PF_6$ (**3**) that was isolated and fully characterized (Fig. 1). X-ray quality needle crystals of **3** were obtained by slow evaporation of a CH_2Cl_2 solution of the complex layered with hexanes. The structure of the cation is shown in Fig. 2 and selected bond lengths and angles are listed in Table 2.

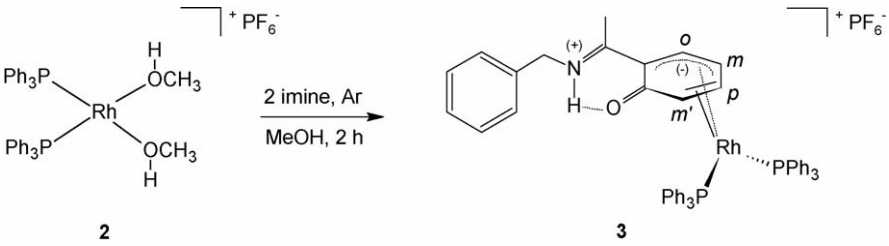

Fig. 1. Formation of complex **3**.

Salient structural features of **3** are: (i) the carbon–nitrogen bond length that is typical of a C=N double bond [16], (ii) a carbon-oxygen bond length at the *ortho* position that corresponds to C=O [17], showing that the ring is in a keto form (see also the ^{13}C NMR data discussed below), (iii) N–H and O–H bond lengths that support H-transfer to the N-atom from the *o*-hydroxy group; typical values for N–H and O–H bond lengths within quinoid or benzenoid forms of *o*-hydroxy Schiff bases fall in the 0.90–1.10 Å range [18,19], (iv) the three angles of 124.5°, 119.2° and 110.4° and the near co-planarity at the N-atom that are consistent with an sp^2-hybridized N-atom (the H-atom is 0.4 Å out of the C(45)–N–C(43) plane), (v) the atoms: C(45), N, C(43), and C(37) through to C(41), are essentially (within 0.08 Å) in a plane, while C(42) is 0.13 Å out of this plane, these data presumably relating to delocalization of an electron into the quinone ring (see below), (vi) the C–C bond lengths of the coordinated ring display values that are intermediate between single and double bonds, with the C(38)–C(39), C(39)–C(40) and C(40)–C(41) bonds shorter (1.399(4), 1.398(4) and 1.399(4) Å, respectively), and thus bearing more unsaturated character, than C(41)–C(42), C(42)–C(37) and C(37)–C(38) (1.451(4), 1.459(4) and 1.424(4) Å, respectively), and (vii) the distances between the ring C-atoms and the Rh, in particular the especially long Rh(1)–C(42) of 2.692 Å, are consistent with the C(38)–C(39) and C(40)–C(41) being the coordinating bonds in an overall η^4-interaction (Table 2).

The IR data show medium-intensity $\nu_{C=N}$ and $\nu_{C=O}$ bands at 1581 and 1966 cm^{-1}, respectively, and two broad absorptions at 3055 and ~3450 cm^{-1}, that correspond to the N···H···O hydrogen-bonding network.

The solid state data point to the zwitterionic structure shown schematically in Fig. 1. To the best of our knowledge, the structure is of a completely new type: this particular imine and other similar *o*-hydroxy substituted imines have been reported to generate only complexes with the imine coordinated as a N,O-bidentate ligand [20].

The novel, η^4-bonding of the imine arises because Schiff bases formed from *ortho*-hydroxy substituted acetophenones can exist in tautomeric forms due to intramolecular H-bonding between the hydroxyl H-atom and the N-atom [18,21]. Depending on the extent of the interaction, complete transfer of the proton from the –OH to the N-atom may occur, giving con-

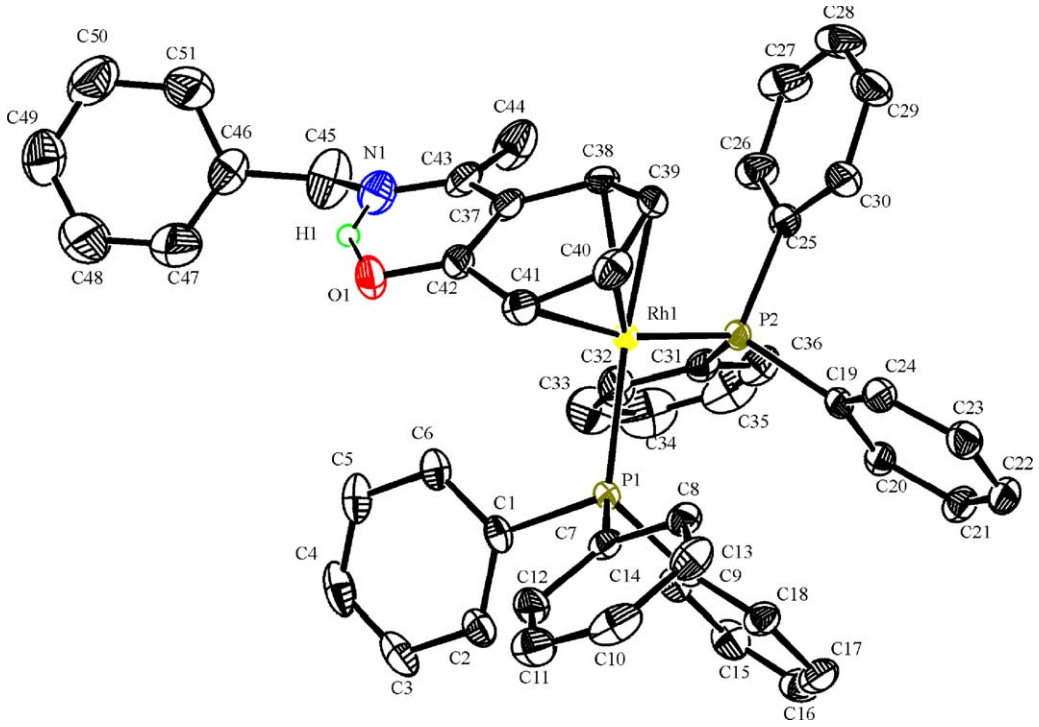

Fig. 2. ORTEP representation of the cation [Rh{η^4-$(C_6H_4O)^{(-)}C(Me)=N^{(+)}(H)CH_2Ph$}-$(PPh_3)_2$]$^+$ of complex **3**, with 50% probability thermal ellipsoids.

Table 2
Selected bond distances and angles for complex **3**, with estimated standard deviations in parentheses

Bond	Length (Å)	Bond	Angle (°)
Rh(1)–P(1)	2.2720(6)	P(1)–Rh(1)–P(2)	95.90(2)
Rh(1)–P(2)	2.2644(7)	C(37)–Rh(1)–C(38)	33.76(9)
C(42)–O(1)	1.252(3)	C(38)–Rh(1)–C(39)	36.27(10)
C(37)–C(43)	1.433(4)	C(39)–Rh(1)–C(40)	36.48(10)
C(43)–C(44)	1.495(4)	C(40)–Rh(1)–C(41)	36.15(9)
C(43)–N(1)	1.297(4)	C(37)–C(42)–O(1)	123.1(2)
N(1)–C(45)	1.483(4)	C(41)–C(42)–O(1)	122.3(2)
N(1)–H(1)	0.91(2)	C(37)–C(42)–C(41)	114.4(2)
O(1)–H(1)	1.93(2)	C(37)–C(43)–N(1)	118.5(3)
C(37)–Rh(1)	2.550(2)	C(44)–C(43)–N(1)	119.3(3)
C(38)–Rh(1)	2.258(2)	C(43)–N(1)–C(45)	124.5(3)
C(39)–Rh(1)	2.237(2)	C(43)–N(1)–H(1)	119.2(15)
C(40)–Rh(1)	2.231(3)	C(45)–N(1)–H(1)	110.4(15)
C(41)–Rh(1)	2.276(3)	N(1)–C(45)–C(46)	112.0(3)
O(1)···N(1)	2.607(3)	N(1)–H(1)–O(1)	130(2)
C(38)–C(39)	1.399(4)		
C(39)–C(40)	1.398(4)		
C(40)–C(41)	1.399(4)		
C(41)–C(42)	1.451(4)		
C(42)–C(37)	1.459(4)		
C(37)–C(38)	1.424(4)		

version of the molecular form (benzenoid, enol-type) into the quinoid, keto-type tautomer. Zwitterionic species characterized by an intramolecular charge-separation are possible intermediates in the tautomerization process [18,21] (Fig. 3). The imine (o-HOC_6H_4)C(Me) = NCH_2Ph molecule is reported to be stable at standard conditions (i.e. showing no proton transfer), although the O–H···N intramolecular H-bond, with an O···N distance of 2.497(3) Å, is among the shortest known [21b]. The observed imine tautomerization is likely metal-assisted.

Complete hydrogen transfer from the –OH to the N-atom would, in fact, involve formation of a C=C bond between the *ipso*-C of the ring and the azomethine C-atom (Fig. 3), and consequently a C–N single bond. The X-ray structural data (and supporting NMR data, see below), however, show retention of the C=N moiety, implying that the coordinated imine features a positive charge at the N-atom, and a negative charge formally at the *ipso*-C but presumably being partially delocalized within the coordinated ring.

The NMR data show that the solid state structure of **3** is maintained in CH_2Cl_2 solution. The $^{31}P\{^1H\}$ NMR spectrum shows an expected doublet at δ 39.5 with a J_{RhP} value of 208 Hz indicative of *cis*-phosphines within Rh^I-π-bound arene complexes [4,22]. The ^1H NMR spectrum is informative in that upfield-shifted resonances are seen for three protons of the coordinated ring, while the fourth resonance remains within the aromatic region; such data are consistent with η^4-binding with the initial arene moiety [23]. The resonance for the CH_2 protons (a singlet at δ 4.80 in the free ligand) appears as an ABX multiplet due to coupling to the N···H···O proton, as revealed by a ^1H–^1H COSY NMR experiment, which also aided in the assignment of the ring proton resonances. The CH_2 resonance is well simulated using J_{AB} = 17 Hz, $J_{AX} = J_{BX}$ = 6 Hz (Fig. 4); the resonance for the N···H···O proton, however, does not show the coupling and appears as a broad singlet at $\delta \sim 15$, shifted 1 ppm upfield from the sharp singlet for the free imine. The singlet Me resonance (δ 2.11) is also upfield-shifted of that of the free ligand (δ 2.50). The ^{13}C NMR spectrum confirms the structural features, displaying five typically upfield-shifted resonances for the C-atoms of the coordinated ring [22], as well as a δ 171.2 resonance for the carbonyl group, not seen for the free imine, where the C–OH resonance is observed at δ 160.0; the data are consistent with a tautomeric rearrangement of the imine into the pseudo-ketonic form. The resonance of the azomethine C-atom (δ 171.5) is shifted from the corresponding one of the free ligand (δ 178.0). A ^1H–^{13}C HMQC NMR experiment shows direct correlation between the ABX multiplet (^1H NMR) and the ^{13}C resonance of the CH_2 group, as well as between the upfield-shifted ^1H resonances and the corresponding ones in the ^{13}C spectrum. This helped in the assignments of the various resonances, which were further aided by the display of long-range correlations in a ^1H–^{13}C HMBC NMR spectrum.

Complex **3** is air-stable in non- or weakly-coordinating solvents such as CH_2Cl_2, and shows no reactivity toward 1 atm H_2. However, in more strongly coordinating media (MeOH, Me_2CO), a slow equilibrium ($t_{1/2} \sim 1$ h) is established at room temperature between **3** and *cis*-$[Rh(PPh_3)_2(solv)_2]PF_6$ (**2**), in which the solvent displaces the imine; this is essentially the reverse of the synthetic procedure for **3** (cf. Fig. 1), the suc-

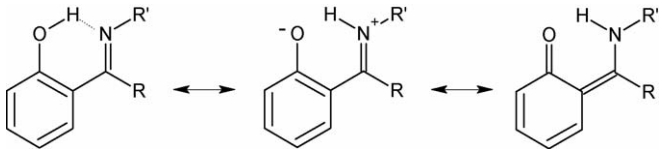

Fig. 3. Tautomerism of *o*-hydroxy-substituted Schiff bases.

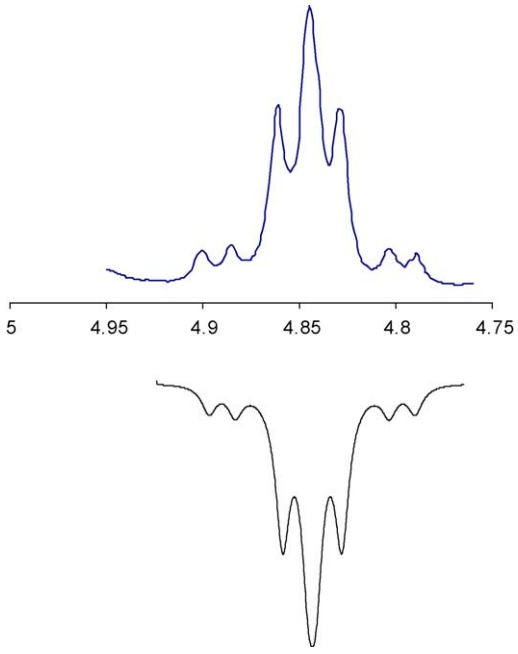

Fig. 4. Experimental (top) and simulated (bottom) ABX multiplet pattern for the CH_2 ^1H NMR resonance of complex **3** (simulated using J_{AB} = 17 Hz, $J_{AX} = J_{BX}$ = 6 Hz).

cess of which depends on the limited solubility of **3** in MeOH, while the complex is readily soluble in Me_2CO. Room temperature NMR data for solutions of **3** in both solvents reveal a **3**:**2** ratio of ~5:1. As mentioned above, the dihydride *cis*,*trans*,*cis*-$[Rh(H)_2(PPh_3)_2(MeOH)_2]PF_6$ (**1**) can also be used as precursor for the synthesis of **3**; an equilibrium mixture with the imine is again slowly established (in the NMR tube) in MeOH and in Me_2CO, accompanied by loss of the hydrides as H_2 (see at δ ~4.5 in these solvents). Use of higher imine concentrations for the synthesis of **3** did not improve significantly the 50% isolated yields obtained when imine: Rh = 2. Exposure of the equilibrium mixtures to 1 atm H_2 resulted in complete, rapid conversion to the dihydride **1**, and liberation of the imine; no hydrogenation to amine was detected.

Of interest, the dinuclear $[(Ph_3P)Rh(\mu\text{-}PhPPh_2)]_2[PF_6]_2$ complex [**7b**] also reacts in CD_2Cl_2 with two equivalents of imine to give solely complex **3**, implying that the coordinating ability of the imine quinonid-type arene ring is stronger than that of the bridging phenyl groups of PPh_3 in the precursor complex.

4. Conclusions

Our studies on homogeneous H_2-hydrogenation of imines catalyzed by the $[Rh(COD)(PPh_3)_2]PF_6$ precursor in MeOH solution were extended to the imine $(o\text{-}HOC_6H_4)C(Me)=NCH_2Ph$. Such Schiff bases of *ortho*-hydroxy-substituted acetophenones display (via hydrogen transfer) tautomerism involving a benzenoid form and a quinoid form. This behavior determines a unique coordination chemistry of the imine to the Rh, and isolation under hydrogenation conditions of the catalytically inactive, zwitterionic complex $[Rh\{\eta^4\text{-}(C_6H_4O)^{(-)}C(Me)=N^{(+)}(H)CH_2Ph\}(PPh_3)_2]PF_6$ containing an η^4-arene coordination mode of the original *o*-hydroxy(arene) moiety. This structure is maintained in CH_2Cl_2 solution but, in MeOH and Me_2CO, reversible loss of the ketimine generates *cis*-$[Rh(PPh_3)_2(solvent)_2]PF_6$ species.

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