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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.