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Chemoselective aerobic oxidation of unprotected diols catalyzed by Pd–(NHC) (NHC = N-heterocyclic carbene) complexes

Lorenzo Bettucci[a], Claudio Bianchini[a], Werner Oberhauser[a,*], Tsun-Hung Hsiao[b], Hon Man Lee[b,**]

[a] Istituto di Chimica dei Composti Organometallici (ICCOM - CNR), Area di Ricerca CNR di Firenze, via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy
[b] Department of Chemistry, National Changhua University of Education, 50058 Changhua, Taiwan

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ABSTRACT

Neutral Pd(X)(η^3-allyl) (X = Cl, OAc (acetate)) complexes bearing mono-coordinating NHC ligands have been synthesized, characterized and employed to catalyze the aerobic oxidation of unprotected 1,2- and 1,3-diols selectively to hydroxy ketones. A comparison of the catalytic performance of these precursors with a reference system has shown that the precursor with the ligands *N*,*N*′-bis(adamantyl)imidazol-2-ylidene and chloride is the most efficient for the chemoselective oxidation of 1,2-diols is concerned. High-pressure ^{1}H NMR (HPNMR) experiments in combination with catalytic batch reactions have provided valuable information on the activation of the precursor as well as on the stability of the catalysts.

1. Introduction

The oxidation of alcohols to carbonyl compounds is an important functional group transformation in organic synthesis. Among the synthetic protocols developed so far, the Omura and Swern [1a] and the Dess–Martin [1b] oxidation have been extensively used to convert primary and secondary alcohol functional groups into the corresponding aldehyde or ketone. These methods, however, are often scarcely selective, and therefore alternative synthetic protocols have been developed to obtain a higher selectivity for the oxidation of secondary alcohols [2a], using stoichiometric amounts of chemical oxidizing reagents [2b–d]. An attractive and more sustainable oxidant is molecular oxygen because it is readily available, inexpensive and can produces either H_2O and/or H_2O_2 as by-products of the oxidation reactions. The most applied metals for the aerobic oxidation of alcohols are Mn [3], Fe [4], Ru [5], Co [6], Cu [7], Pt [8], Zn [9], V [10], Ni [11] and Pd [12]. In particular, palladium-based oxidation catalysts have been extensively used for aerobic alcohol oxidations since Blackburn and Schwartz [13] reported the homogeneous oxidation of secondary alcohols to ketones by molecular oxygen under mild reaction conditions. Since then, increasing research efforts have been made in an attempt of developing new Pd-based catalysts for the aerobic alcohol oxidation. In this respect, the most significant catalytic systems applied up to now for the aerobic oxidation of alcohols are: (i) the $Pd(OAc)_2$/DMSO system [14] developed by Peterson and Larock, (ii) the Uemura $Pd(OAc)_2$/pyridine system [15] and its NEt_3-modified version introduced by Sigman [16], (iii) the Sheldon $Pd(OAc)_2$/modified-phenanthroline system [17], (iv) the Pd–sparteine system [18], (v) the neutral cyclopalladate complexes [19] applied by Moberg and (vi) the Sigman Pd–NHC complex of the formula $Pd(OAc)_2(H_2O)L$ with L being 1,3-di-(2,6-*iso*-propyl)phenyl-imidazol-2-ylidene [20]. The latter complex represents the first example of a Pd–NHC complex utilized for the aerobic oxidation of alcohols under rather mild reaction conditions [20b] exploiting the exceptional stability towards air and moisture of the NHC ligands [21].

From several mechanistic studies of aerobic oxidation reactions of alcohols catalyzed by ligand-stabilized palladium complexes has clearly emerged the requirement of: (i) a monodentate ligand that stabilizes palladium and lowers significantly the energy barrier for the β-hydride elimination reaction of the palladium alkoxide species (rate-determining step of the catalytic oxidation cycle) [22]; (ii) a base to convert the alcohol into the corresponding alkoxide, that subsequently undergoes a β-hydride elimination reaction to give a Pd-hydride species and the oxidized substrate.

Alternatively to the Sigman complex, aerobic alcohol oxidation reactions can be promoted by neutral Pd(η^3-allyl)(NHC) complexes, largely employed in C–C and C–N coupling reactions such as the Suzuki–Miyaura coupling [23], the Buchwald–Hartwig amination [23a,b], the allylic alkylation reaction [24] the telomerization reaction of 1,3-butadienes with alcohol [25] and the chemoselctive anaerobic oxidation of secondary alcohols [26].

* Corresponding author. Tel.: +39 055 5225384; fax: +39 055 5225203.
** Co-corresponding author. Tel.: +886 4 7232105 3523; fax: +886 4 7211190.
E-mail addresses: werner.oberhauser@iccom.cnr.it (W. Oberhauser), leehm@cc.ncue.edu.tw (H.M. Lee).

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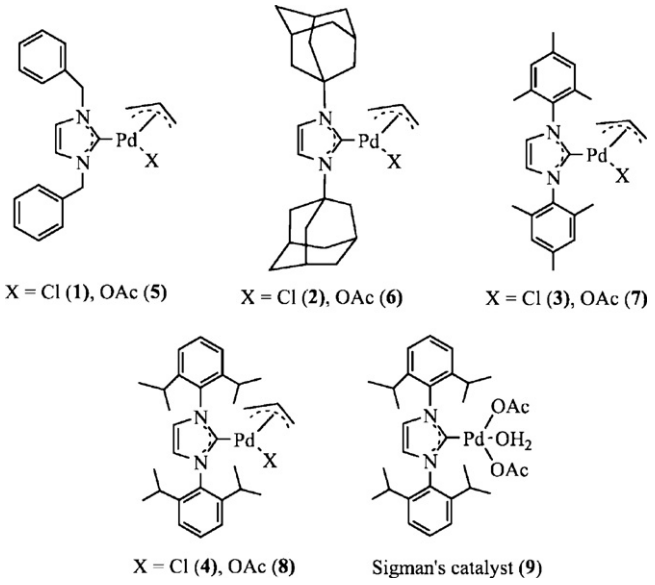
Herein we report the synthesis of neutral Pd(II) complexes of the type Pd(X)(η^3-allyl)(NHC) (X = Cl, OAc) (Scheme 1) bearing the NHC ligands *N*,*N*′-bis(benzyl)-imidazol-2-ylidene (L_1) (**1**, **5**), *N*,*N*′-bis(adamantyl)-imidazol-2-ylidene (L_2) (**2**, **6**), *N*,*N*′-bis(mesityl)-imidazol-2-ylidene (L_3) (**3**, **7**) and *N*,*N*′-bis(di(2,6-*iso*-propyl)phenyl)-imidazol-2-ylidene (L_4) (**4**, **8**) and their application in the aerobic oxidation of unprotected 1,2- and 1,3-diols in a solvent mixture of toluene and DMSO.

2. Experimental

2.1. Materials and equipments

All synthetic reactions and manipulations were carried out under a nitrogen atmosphere by using standard Schlenk techniques. Solvents were either distilled or passed through columns containing dehydrating agents. Reagents were used as received from Aldrich, unless stated otherwise. Compounds $PdCl_2(\eta^4$-COD) (COD = 1, 5-cyclooctadiene) [27a], $[PdCl(\eta^3$-allyl)$]_2$ [27b], $PdCl(\eta^3$-allyl)$(\kappa^1$-*C*-$L_2)$ (**2**) [28], $PdCl(\eta^3$-allyl)$(\kappa^1$-*C*-$L_3)$ (**3**) [28], $PdCl(\eta^3$-allyl)$(\kappa^1$-*C*-$L_4)$ (**4**) [28] and $Pd(\kappa^1$-*O*-OAc$)_2(H_2O)(\kappa^1$-*C*-$L_4)$ (**9**) [22a] and $(HL_1)Cl$ [29] were prepared according to literature methods. Deuterated solvents for routine NMR measurements were dried with activated molecular sieves. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained with a Bruker Avance DRX-400 spectrometer (400.13 and 100.62 MHz, respectively). HMQC spectra were acquired with the same NMR spectrometer. Chemical shifts are reported in ppm (δ) with reference to either TMS as an internal standard (^1H and $^{13}C\{^1H\}$ NMR spectra). ^1H HPNMR experiments were carried out on a Bruker Avance II-200 spectrometer equipped with a 10 mm BB probe using a 10 mm sapphire tube (Sahikon, Milford, NH), equipped with a titanium high-pressure charging head constructed at ICCOM-CNR [30]. Microanalyses were performed using a Carlo-Erba Model 1106 elemental analyzer. Oxidation reactions were performed with 65 mL stainless steel autoclaves, constructed at ICCOM-CNR, equipped with magnetic stirring, oil bath heating and a temperature and pressure controller. GC analyses were performed on a Shimadzu 2010 gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μm film thickness) VF-WAXms capillary column. GC/MS analyses were performed on a Shimadzu QP 5000 apparatus equipped with 30 m (0.32 mm i.d., 0.50 μm film thickness) CP-WAX 52 CB WCOT-fused silica column.



Scheme 1.

2.2. Syntheses

2.2.1. Preparation of $PdCl(\eta^3$-allyl$)(\kappa^1$-*C*-$L_1)$ (**1**)

The imidazolium salt (200.0 mg, 0.705 mmol) was reacted with K_2CO_3 (100.0 mg, 0.724 mmol) and $[Pd(\eta^3$-allyl)Cl$]_2$ (130.0 mg, 0.350 mmol) in dry CH_3CN (15 mL) under a nitrogen atmosphere at room temperature for 1 day. The solvent was then completely removed under vacuum, followed by the addition of water (20 mL) and dichloromethane (20 mL). After vigorous stirring of the emulsion, the organic layer was separated, dried with $MgSO_4$, filtered and the remaining solution was concentrated to dryness. The residue was washed with dry hexane (3× 15 mL). The pale yellow product was dried under vacuum. Yield: 142.8 mg (47%). Anal. calcd. for $C_{20}H_{21}Cl_1N_2Pd$: C, 55.72; H, 4.87; N, 6.49. Found: C, 55.03; H, 4.67; N, 6.30. ^1H NMR (δ, 400.13 MHz, CD_2Cl_2, 21 °C) 2.02 (d, $^3J_{HH}$ = 12.0 Hz, 1H, allyl-H), 3.13 (m, 2H, allyl-H), 4.16 (d, $^3J_{HH}$ = 7.2 Hz, 1H, allyl-H), 5.18 (m, 1H, allyl-H), 5.42 (d, $^2J_{HH}$ = 13.6 Hz, 2H, Ar*C*H_aH_b), 5.50 (d, $^2J_{HH}$ = 13.6 Hz, 2H, ArCH$_a$*H*$_b$), 6.99 (s, 2H, imi-H), 7.32–7.41 (m, 10H, Ar). $^{13}C\{^1H\}$ NMR (δ, 100.62 MHz, CD_2Cl_2, 21 °C) 48.76 (s, allyl-C), 54.68 (s, Ar*C*H$_a$H$_b$), 71.62 (s, allyl-C), 114.87 (s, allyl-C), 121.60 (s, imi-C), 127.95 (s, Ar), 128.02 (s, Ar), 128.71 (s, Ar), 136.85 (s, Ar), 181.51 (s, NCN). ^1H NMR (δ, 400.13 MHz, CD_2Cl_2, −60 °C) 1.90 (d, $^3J_{HH}$ = 12.4 Hz, 1H, allyl-H), 3.07 (d, $^3J_{HH}$ = 13.6 Hz, 1H, allyl-H), 3.12 (d, $^3J_{HH}$ = 6.4 Hz, 1H, allyl-H), 4.13 (d, $^3J_{HH}$ = 7.6 Hz, 1H, allyl-H), 5.19 + 5.35 (m, 4H, allyl-H + ArCH$_a$H$_b$), 5.68 (d, $^3J_{HH}$ = 14.8 Hz, 1H, ArCH$_a$H$_b$), 6.97 (s, 1H, imi-H), 7.02 (s, 1H, imi-H), 7.27–7.37 (m, 10H, Ar). $^{13}C\{^1H\}$ NMR (δ, 100.62 MHz, CD_2Cl_2, −60 °C) 49.48 (s, allyl-C), (ArCH$_a$H$_b$, overlapped signal), 71.65 (s, allyl-C), 115.34 (s, allyl-C), 121.69 (s, imi-C), 122.26 (s, imi-C), 127.81 (s, Ar), 128.13 (s, Ar), 128.86 (s, Ar), 136.93 (s, Ar), 180.41 (s, NCN).

2.2.2. Preparation of $Pd(\kappa^1$-*O*-OAc$)(\eta^3$-allyl$)(\kappa^1$-*C*-$L_1)$ (**5**)

Compound **1** (150.0 mg, 0.348 mmol) was dissolved in CH_2Cl_2 (15 mL). To this solution was added AgOAc (58.1 mg, 0.348 mmol) under vigorous stirring at room temperature. The suspension was allowed to stir at the latter temperature for 1 h. Afterwards the suspension was passed through a plug of celite and the clear solution was concentrated to a small volume (2 mL). On addition of diethyl ether (10 mL) the product precipitated as yellow micro-crystalline compound, which was separated by filtration and dried in a stream of nitrogen. Yield: 126.6 mg (80%). Anal. calcd. for $C_{22}H_{24}N_2O_2Pd$: C, 58.12; H, 5.28; N, 6.16. Found: C, 58.22; H, 5.52; N, 6.30. ^1H NMR (δ, 400.13 MHz, CD_2Cl_2, 21 °C) 1.91 (s, 3H, CH_3), 2.12 (brs, 1H, allyl-H), 2.38 (brs, 1H, allyl-H), 3.34 (d, $^3J_{HH}$ = 13.6 Hz, 1H, allyl-H), 4.17 (d, $^3J_{HH}$ = 7.6 Hz, 1H, allyl-H), 5.24 (quintet, $^3J_{HH}$ = 6.8 Hz, 1H, allyl-H), 5.50 (s, 2H, ArCH_2), 6.96 (s, 4H, imi-H), 7.32–7.40 (m, 10H, Ar). $^{13}C\{^1H\}$ NMR (δ, 100.62 MHz, CD_2Cl_2, 21 °C) 23.46 (s, CH_3), 43.08 (s, allyl-C), 54.55 (s, ArCH_2), 70.41 (s, allyl-C), 114.76 (s, allyl-C), 121.38 (s, imi-C), 128.02 (s, Ar), 128.10 (s, Ar), 128.60 (s, Ar), 137.03 (s, Ar), 176.31 (s, *C*OCH_3), 181.60 (s, NCN). ^1H NMR (δ, 400.13 MHz, CD_2Cl_2, −60° C) 1.88 (s, 3H, CH_3), 1.94 (d, $^3J_{HH}$ = 12.0 Hz, 1H, allyl-H), 2.87 (d, $^3J_{HH}$ = 6.0 Hz, 1H, allyl-H), 3.32 (d, $^3J_{HH}$ = 13.6 Hz, 1H, allyl-H), 4.11 (d, $^3J_{HH}$ = 7.2 Hz, 1H, allyl-H), 5.27 (quintet, $^3J_{HH}$ = 6.0 Hz, 1H, allyl-H), 5.40 (s, 2H, ArCH_2), 5.44 (s, 2H, ArCH_2), 6.97 (s, 2H, imi-H), 7.27–7.39 (m, 10H, Ar). $^{13}C\{^1H\}$ NMR (δ, 100.62 MHz, CD_2Cl_2, −60 °C) 23.95 (s, CH_3), 43.98 (s, allyl-C), (ArCH_2, overlapped signal), 70.34 (s, allyl-C), 115.20 (s, allyl-C), 121.80 (s, imi-C), 127.80 (s, Ar), 128.08 (s, Ar), 128.87 (s, Ar), 137.14 (s, Ar), 176.92 (s, *C*OCH_3), 180.44 (s, NCN).