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

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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].

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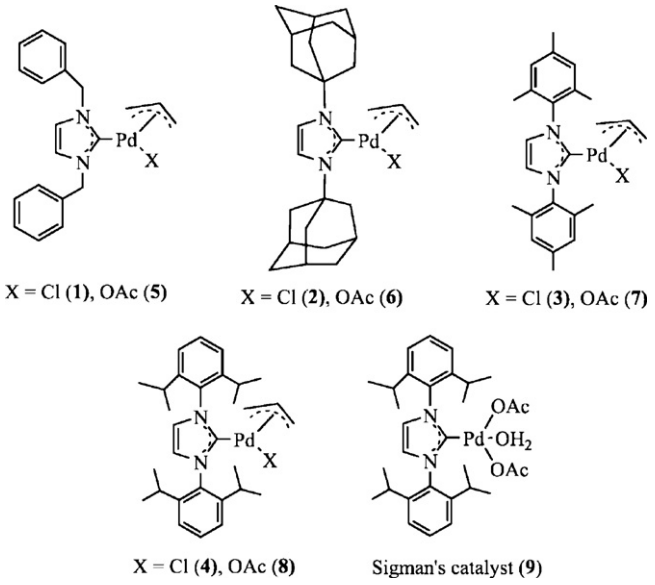
Herein we report the synthesis of neutral Pd(II) complexes of the type Pd(X)(η^3-allyl)(NHC) (X = Cl, OAc) (Scheme 1) bearing the NHC ligands *N*,*N*′-bis(benzyl)-imidazol-2-ylidene (L_1) (**1**, **5**), *N*,*N*′-bis(adamantyl)-imidazol-2-ylidene (L_2) (**2**, **6**), *N*,*N*′-bis(mesityl)-imidazol-2-ylidene (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).

*2.2.3. Preparation of Pd(κ^1-O-OAc)(η^3-allyl)(κ^1-C-L_2) (**6**)*

Compound **2** (120.0 mg, 0.231 mmol) was dissolved in CH_2Cl_2 (10 mL). To this solution was added AgOAc (38.6 mg, 0.231 mmol) under vigorous stirring at room temperature. The suspension was allowed to stir at the latter temperature for 1.5 h. The suspension was then passed through a plug of celite and the obtained clear solution was concentrated to a small volume (2 mL). Then diethyl ether (10 mL) was added to the solution, causing the precipitation of the product as yellow semi-crystalline powder that was separated by filtration and dried in a stream of nitrogen. Yield: 87.7 mg (75%). Anal. calcd. for $C_{28}H_{40}N_2O_2Pd$: C, 61.97; H, 7.37; N, 5.16. Found: C, 62.14; H, 7.51; N, 5.23. ^{1}H NMR (δ, 400.13 MHz, CD_2Cl_2, 21 °C) 1.79 (brs, 10H, adamantyl-H), 1.84 (s, 3H, CH_3), 1.99 (d, $^3J_{HH}$ = 15.6 Hz, 1H, allyl-H), 2.26 (brs, 8H, adamantyl-H), 2.43 (m, 6H, adamantyl-H), 2.55 (m, 6H, adamantyl-H), 2.82 (brs, 1H, allyl-H), 3.45 (d, $^3J_{HH}$ = 13.2 Hz, 1H, allyl-H), 4.33 (d, $^3J_{HH}$ = 7.6 Hz, 1H, allyl-H), 5.31 (quintet, $^3J_{HH}$ = 6.0 Hz, 1H, allyl-H), 7.30 (s, 2H, imi-H). ^{13}C{^{1}H} NMR (δ, 100.62 MHz, CD_2Cl_2, 21 °C) 23.94 (s, CH_3), 30.16 (s, adamantyl-C), 35.91 (s, adamantyl-C), 43.63 (s, adamantyl-C), 46.73 (s, allyl-C), 58.96 (s, adamantyl-C), 67.88 (s, allyl-C), 111.17 (s, allyl-C), 116.73 (s, imi-C), 175.56 (s, *C*OCH$_3$), 176.37 (s, NCN). ^{1}H NMR (δ, 400.13 MHz, CD_2Cl_2, −60 °C) 1.70 (m, 10H, adamantyl-H), 1.84 (s, 3H, CH_3), 2.19 (m, 11H, adamantyl-H), 2.42 (m, 6H, adamantyl-H), 2.53 (m, 3H, adamantyl-H), 3.20 (d, $^3J_{HH}$ = 5.2 Hz, 1H, allyl-H), 3.42 (d, $^3J_{HH}$ = 13.2 Hz, 1H, allyl-H), 4.21 (d, $^3J_{HH}$ = 6.8 Hz, 1H, allyl-H), 5.29 (m, 1H, allyl-H), 7.22 (s, 1H, imi-H), 7.27 (s, 1H, imi-H). ^{13}C{^{1}H} NMR (δ, 100.62 MHz, CD_2Cl_2, −60 °C) 24.37 (s, CH_3), 29.79 (s, adamantyl-C), 29.84 (s, adamantyl-C), 29.92 (s, adamantyl-C), 35.62 (s, adamantyl-C), 43.10 (s, adamantyl-C), 43.51 (s, adamantyl-C), 44.29 (s, adamantyl-C), 47.95 (s, allyl-C), 57.85 (s, adamantyl-C), 58.81 (s, adamantyl-C), 67.52 (s, allyl-C), 111.28 (s, allyl-C), 116.65 (s, imi-C), 117.39 (s, imi-C), 175.52 (s, *C*OCH$_3$), 176.08 (s, NCN).

*2.2.4. Preparation of Pd(κ^1-O-OAc)(η^3-allyl)(κ^1-C-L_3) (**7**)*

To a solution of **3** (140.0 mg, 0.287 mmol) in CH_2Cl_2 (10 mL) was added AgOAc (47.9 mg, 0.287 mmol) under vigorous stirring at room temperature. After a reaction time of 1 h, the suspension was passed through a plug of celite and the obtained clear solution was concentrated to a small volume (3 mL). Then diethyl ether (15 mL), was added, causing the precipitation of the product as a brownish micro-crystalline powder that was separated by filtration and dried in a stream of nitrogen. Yield: 95.3 mg (65%). Anal. calcd. for $C_{26}H_{32}N_2O_2Pd$: C, 61.15; H, 6.27; N, 5.48. Found: C, 61.23; H, 6.32; N, 5.53. ^{1}H NMR (δ, 400.13 MHz, CD_2Cl_2, 21 °C) 1.74 (brs, 3H, COCH$_3$), 1.95 (brs, 1H, allyl-H), 2.17 (s, 12H, Ar-*o*-CH$_3$), 2.39 (s, 6H, Ar-*p*-CH$_3$), 2.85 (br d, 1H, allyl-H), 2.99 (d, $^3J_{HH}$ = 13.6 Hz, 1H, allyl-H), 3.95 (d, $^3J_{HH}$ = 7.6 Hz, 1H, allyl-H), 4.86 (m, 1H, allyl-H), 7.04 (s, 4H, Ar), 7.13 (s, 2H, imi-H). ^{13}C{^{1}H} NMR (δ, 100.62 MHz, CD_2Cl_2, 21 °C) 15.10 (s, Ar-*o*-CH$_3$), 20.87 (s, Ar-*p*-CH$_3$), 23.20 (s, CO*C*H$_3$), 43.65 (s, allyl-C), 70.09 (s, allyl-C), 113.57 (s, allyl-C), 122.84 (s, imi-C), 128.80 (s, Ar), 135.53 (s, Ar), 135.99 (s, Ar), 138.85 (s, Ar), 169.42 (s, COCH$_3$), 182.87 (s, NCN). ^{1}H NMR (δ, 400.13 MHz, CD_2Cl_2, −60 °C) 1.54 (br d, $^3J_{HH}$ = 12.0 Hz, 1H, allyl-H), 1.72 (s, 3H, COCH$_3$), 2.10 + 2.11 (s, 12H, Ar-*o*-CH$_3$), 2.34 (s, 6H, Ar-*p*-CH$_3$), 2.95 (m, 2H, allyl-H), 3.87 (d, $^3J_{HH}$ = 6.4 Hz, 1H, allyl-H), 4.89 (m, 1H, allyl-H), 7.01 + 7.02 (s, 4H, Ar), 7.14 (s, 2H, imi-H). ^{13}C{^{1}H} NMR (δ, 100.62 MHz, CD_2Cl_2, −60 °C) 17.82 (s, Ar-*o*-*C*H$_3$), 21.21 (s, Ar-*p*-CH$_3$), 23.70 (s, CO*C*H$_3$), 44.35 (s, allyl-C), 69.47 (s, allyl-C), 114.05 (s, allyl-C), 122.93 (s, imi-C), 128.84 (s, Ar), 135.62 (s, Ar), 135.64 (s, Ar), 138.93 (s, Ar), 176.32 (s, COCH$_3$), 181.29 (s, NCN).

*2.2.5. Preparation of Pd(κ^1-O-OAc)(η^3-allyl)(κ^1-C-L_4) (**8**)*

To a solution of **4** (170.0 mg, 0.298 mmol) in CH_2Cl_2 (15 mL) was added AgOAc (49.7 mg, 0.298 mmol) under vigorous stirring at room temperature. After a reaction time of 1 h, the suspension was passed through a plug of celite and the obtained clear solution was concentrated to a small volume (2 mL), followed by the addition of diethyl ether (10 mL), which caused the precipitation of the product as an off-white micro-crystalline powder that was separated by filtration and dried in a stream of nitrogen. Yield: 124.1 mg (70%). Anal. calcd. for $C_{32}H_{44}N_2O_2Pd$: C, 64.62; H, 7.40; N, 4.71. Found: C, 64.74; H, 7.53; N, 4.82. ^{1}H NMR (δ, 400.13 MHz, CD_2Cl_2, 21 °C) 1.52 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.36 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.73 (s, 3H, COC*H*$_3$), 2.21 (brs, 2H, allyl-H), 2.89 (septet, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 3.10 (d, $^3J_{HH}$ = 13.6 Hz, 1H, allyl-H), 4.08 (d, $^3J_{HH}$ = 7.6 Hz, 1H, allyl-H), 4.87 (quintet, $^3J_{HH}$ = 6.0 Hz, 1H, allyl-H), 7.21 (s, 2H, imi-H), 7.35 (d, $^3J_{HH}$ = 7.6 Hz, 4H, Ar-*m*-H), 7.52 (t, $^3J_{HH}$ = 7.6 Hz, 2H, Ar-*p*-*H*). ^{13}C{^{1}H} NMR (δ, 100.62 MHz, CD_2Cl_2, 21 °C) 22.35 (s, CH(*C*H$_3$)$_2$), 23.53 (brs, CO*C*H$_3$), 25.61 (s, CH(*C*H$_3$)$_2$), 28.49 (s, *C*H(CH$_3$)$_2$), 44.21 (s, allyl-C), 71.82 (s, allyl-C), 113.38 (s, allyl-C), 123.79 (s, Ar-*m*-C), 124.44 (s, imi-C), 129.87 (s, Ar-*p*-C), 135.88 (s, Ar-*ipso*-C), 145.99 (s, Ar-*o*-C), 175.90 (s, *C*OCH$_3$), 185.26 (NCN). ^{1}H NMR (δ, 400.13 MHz, CD_2Cl_2, −60 °C) 1.04 (d, $^3J_{HH}$ = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 1.13 (d, $^3J_{HH}$ = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 1.25 (d, $^3J_{HH}$ = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 1.32 (d, $^3J_{HH}$ = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 1.76 (s, 3H, COC*H*$_3$), 1.78 (allyl-H, overlapped signal), 2.64 (septet, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 2.81 (septet, $^3J_{HH}$ = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 2.91 (d, $^3J_{HH}$ = 5.2 Hz, 1H, allyl-H), 3.15 (d, $^3J_{HH}$ = 13.2 Hz, 1H, allyl-H), 3.86 (d, $^3J_{HH}$ = 7.2 Hz, 1H, allyl-H), 4.92 (quintet, $^3J_{HH}$ = 6.0 Hz, 1H, allyl-H), 7.22 (s, 2H, imi-H), 7.35 (d, $^3J_{HH}$ = 7.6 Hz, 4H, Ar-*m*-*H*), 7.54 (t, $^3J_{HH}$ = 7.6 Hz, 2H, Ar-*p*-H). ^{13}C{^{1}H} NMR (δ, 100.62 MHz, CD_2Cl_2, −60 °C) 21.92 (s, CH(*C*H$_3$)$_2$), 22.43 (s, CH(*C*H$_3$)$_2$), 23.90 (s, CO*C*H$_3$), 25.64 (s, CH(*C*H$_3$)$_2$), 26.35 (s, CH(*C*H$_3$)$_2$), 28.54 (s, *C*H(CH$_3$)$_2$), 28.65 (s, *C*H(CH$_3$)$_2$), 45.02 (s, allyl-C), 70.99 (s, allyl-C), 113.87 (s, allyl-C), 123.92 (s, imi-C), 124.05 (s, imi-C), 124.86 (s, Ar-*m*-C), 130.10 (s, Ar-*p*-C), 135.62 (s, Ar-*ipso*-C), 145.91 (s, Ar-*o*-C), 145.98 (s, Ar-*o*-C), 176.66 (s, *C*OCH$_3$), 184.17 (NCN).

*2.2.6. Preparation of trans-[$PdCl_2$(κ^1-C-L_1)$_2$] (**10**)*

The imidazolium salt (HL_1)BF_4 (100.0 mg, 0.300 mmol) was reacted with K^{t}OBu (40.0 mg, 0.300 mmol) and $PdCl_2$(η^4-COD) (40.0 mg, 0.150 mmol) in dry CH_3CN (15 mL) under a nitrogen atmosphere at room temperature for 12 h. Afterwards, the solvent was removed completely under vacuum. To the resulting residue was added water (20 mL) and CH_2Cl_2 (20 mL). The organic layer was separated and dried over $MgSO_4$. The inorganic salt was removed from the solution by filtration and the resulting solution was concentrated to dryness, obtaining a solid that was suspended in THF, filtered off, washed with THF (3× 15 mL) and then dried under vacuum. Yield: 54.6 mg (27%). Anal. calcd. for $C_{34}H_{32}Cl_2N_4Pd$: C, 60.59; H, 4.79; N, 8.31. Found: C, 60.33; H, 4.79; N, 7.89. ^{1}H NMR (δ, 400.13 MHz, DMF-d_7, 21 °C) δ 5.86 (s, 4H, CH_2), 7.31 (m, 8H, CH_2 + Ar), 7.70 (m, 4H, imi-H), 8.02 (m, 20H, Ar). Due to the low solubility of **10** in all common organic solvents including DMF-d_7, we failed in acquiring a reliable ^{13}C{^{1}H} NMR spectrum.

*2.2.7. Selected NMR data for [Pd(μ-OH)(κ^1-O-OAc)(κ^1-C-L_2)]$_2$ (**11**)*

To a solution of **6** (46.5 mg, 0.085 mmol) in wet THF (4 mL) was added K-^{t}OBu (10.1 mg, 0.09 mmol) at room temperature. The obtained suspension was allowed to stir for 1 h. Afterwards, the solvent was completely removed by vacuum and the remaining solid was suspended in CH_2Cl_2 (4 mL). The latter suspension was filtered through a plug of celite and the obtained yellow solution was concentrated to half of its original volume (2 mL). Diethyl ether was then slowly added in order to obtain a yellowish powder, that was dried under nitrogen. The ^{1}H NMR spectrum of the obtained powder acquired in CD_2Cl_2 revealed that the isolated powder was a mixture of compounds, containing **11** in a low amount (15%). Several attempts to obtain **11** as a pure compound failed due to

the similar solubility property of all compounds present in the isolated mixture. As a consequence, only selected ^{1}H and ^{13}C{^{1}H} NMR chemical shifts for **11** are reported.

^{1}H NMR (δ, 400.13 MHz, CD_2Cl_2, 21 °C) −4.01 (s, 2H, OH), 1.40 (s, 6H, $COCH_3$), 7.26 ($^3J_{HH}$ = 2.4 Hz, 2H, imi-H), 7.30 ($^3J_{HH}$ = 2.4 Hz, 2H, imi-H). ^{13}C{^{1}H} NMR (δ, 100.62 MHz, CD_2Cl_2, 21 °C) 22.96 (s, $COCH_3$), 116.75 (s, imi-C), 117.29 (imi-C), 175.66 (s, $COCH_3$), 185.61 (s, NCN).

2.3. Variable-temperature ^{1}H HPNMR experiments with **2**

A solution of **2** (0.015 mmol) in toluene-d_8 (2 mL) was transferred into a 10 mm sapphire tube followed by the acquisition of a ^{1}H NMR spectrum at room temperature. Afterwards the NMR tube was removed from the NMR probe and successively charged with a 1:1 mixture of meso/rac-2,4-pentanediol (82.0 μL, 0.75 mmol) and air (20 bar). The sapphire tube was then placed again into the NMR probe, followed by the acquisition of a ^{1}H NMR spectrum at room temperature. The NMR probe was then gradually heated from room temperature to 80 °C in a temperature interval of 10 °C. At each temperature a ^{1}H NMR spectrum was acquired. The sapphire tube was then heated for 2 h at 80 °C, acquiring ^{1}H NMR spectra in a time interval of half an hour. Afterwards the NMR probe was cooled to room temperature and a final ^{1}H NMR spectrum was acquired. The gas pressure was then released and the NMR solution was subjected to a GC/MS analysis.

2.4. Crystallography

Single crystals of **1**, **8**, **10** and **11**·$2C_7H_8$ suitable for a single crystal X-ray structure analysis have been obtained by diffusion of a toluene-layered dichloromethane solution of the corresponding compounds at room temperature. Typically, a suitable crystal was mounted on a glass fiber with silicon grease and placed in the cold nitrogen stream. Diffraction data for **1** and **10** were collected on a Bruker APEX II diffractometer, while diffraction data for **8** and **11**·$2C_7H_8$ were collected on an Oxford Diffraction CCD diffractometer, using Mo Kα radiation (λ = 0.71069 Å) with both diffractometers. The diffraction data were corrected for Lorentz and polarization effects and an absorption correction was performed using the SADABS program [31a]. All structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares methods against F^2 using either the SHELXTL [31b] or WINGX [31c] software package. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were added at calculated positions and refined applying a riding model with isotropic U values depending on the U_{eq} of the adjacent carbon atom. Crystallographic data (excluding structure factors) were deposited with the Cambridge Crystallographic Data Centre. CCDC-742450 (**1**); CCDC-742449 (**8**); CCDC-742448 (**10**); CCDC-742447 (**11**·$2C_7H_8$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223/336033; e-mail: deposit@ccdc.cam.uk).

2.4.1. Catalytic oxidation reactions

Typically, the amount of precursor (0.01 mmol) was added at room temperature to a round bottom-flask that contained a 19:1 (v:v) solvent mixture of toluene and DMSO (20 mL). To the latter solution was added the substrate (1.00 mmol) and the obtained clear solution was transferred into a 65 mL stainless steel autoclave equipped with a home-made temperature and pressure controller and a magnetic stirrer. The autoclave was then heated to 80 °C by means of an oil bath. Once the desired temperature had been reached the autoclave was pressurized with 20 bar of air and stirring of the catalytic solutions was started. After the desired reaction time the autoclave was successively removed from oil bath, cooled to 10 °C by means of a water-ice bath, followed by the release of the air pressure from the autoclave. Afterwards, the catalytic solution was subjected to GC and GC/MS analyses.

2.4.2. Blank reaction

A 19:1 (v:v) solvent mixture of toluene and DMSO (20 mL) was heated in a 65 mL stainless steel autoclave equipped with a home-made temperature and pressure controller and a magnetic stirrer at 80 °C in the presence of 20 bar of air for 2 h. Afterwards the autoclave was cooled to room temperature, the air pressure released and the solution was analyzed by GC and GC/MS.

3. Results and discussion

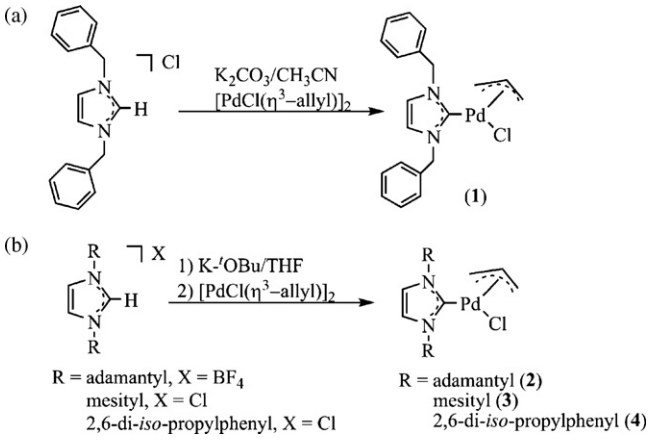
3.1. Synthesis of complexes

Compound **1** has been obtained by the reaction of *N*,*N*′-bis(benzyl)-imidazolium chloride with K_2CO_3 and [Pd(η^3-allyl)Cl]$_2$ in acetonitrile in 47% yield (Scheme 2a), while the known related complexes **2**–**4** (Scheme 2b) have been synthesized following a synthetic procedure reported by Nolan and co-workers [28]. The synthetic protocol for the latter compounds comprises the deprotonation of the corresponding imidazolium salt with K-^{t}OBu in THF at room temperature (**2**) or at 50 °C (**3** and **4**), followed by the reaction of the "in situ" generated imidazol-2-ylidene ligand with [PdCl(η^3-allyl)]$_2$ in the same solvent at room temperature (Scheme 2b).

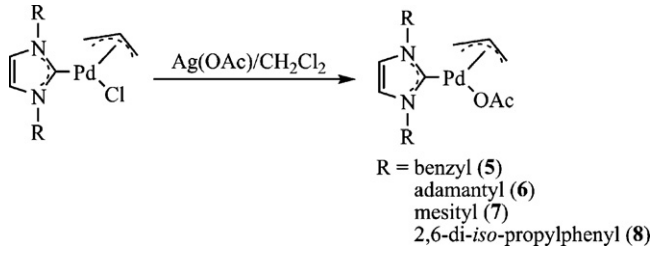
Unlike complexes **2**–**4** that are stable compounds even when stored in the presence of air and moisture, **1** is converted by moisture into the palladium bis-carbene complex *trans*-$PdCl_2(\kappa^1$-*C*-$L_1)_2$ (**10**). This compound has been also obtained by an independent synthesis in relatively low yield (27%), which involves the reaction of $PdCl_2$(η^4-COD) with the corresponding "in situ" synthesized carbene in acetonitrile. The low yield of **10** is due to the concomitant formation of **10** and its *cis*-isomer along with not yet identified compounds. Due to its low solubility, complex **10** has been characterized in solution only by ^{1}H NMR spectroscopy, and in the solid state by elemental analysis and a single crystal X-ray structure analysis (*vide infra*).

The chloride complexes **1**–**4** have been converted into the corresponding acetate complexes **5**–**8** by reaction of the former with silver acetate in dichloromethane at room temperature as shown in Scheme 3.

All acetate complexes have been isolated as micro-crystalline compounds in good yield (65–80%). The crystal structure of **8**, the synthesis of which has been recently reported by Pregosin and co-workers [32] confirms unambiguously the κ^1-*O* coordination of the acetate group to palladium (*vide infra*).



Scheme 2.



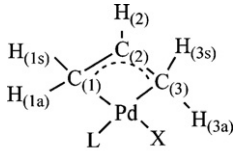
Scheme 3.

An attempt of crystallizing **6** from a (1:1) solvent mixture of toluene and CH_2Cl_2 in air at room temperature led to the formation of a small amount of both crystals (i.e. 5%) and a powdered material that ^{1}H NMR spectroscopy showed to be the corresponding imidazolium salt and **6**. A single crystal X-ray structure analysis of the crystalline material proved it to be the binuclear OH-bridged palladium carbene complex [Pd(μ-OH)(κ^1-*O*-OAc)(κ^1-*C*-L_2)]$_2$ (**11**) (*vide infra*). Consistently, the ^{1}H NMR spectrum of the latter compound exhibits a singlet centred at −4.01 ppm that is characteristic for the [Pd-(μ-OH)]$_2$ core in **11** [33]. In addition, the presence of two ^{1}H doublets centred at 7.26 and 7.30 ppm ($^3J_{HH}$ = 2.4 Hz) for the imidazol-2-ylidene hydrogen atoms shows their chemical inequivalence due to the hinged structure of **11**. An attempt to synthesize **11** by an independent synthesis from **6** and K-^{t}OBu in wet THF gave a mixture of compounds that contained **11** in only 15% yield. K-^{t}OBu yields in the presence of traces of water hydroxide ions and *t*-BuOH. The latter alcohol may be involved in the protonation reaction of the coordinated allyl unit yielding free propene. The major side reaction is the nucleophilic attack of K-^{t}OBu on the coordinated allyl moiety, giving allyl *t*-butyl ether and a non-identified Pd(0) carbene compound, that decomposes in part to palladium black. Any attempt to increase the yield of **11** and to isolate it as a pure compound failed so far.

3.2. NMR characterization of complexes

Solutions of the new synthesized Pd(η^3-allyl) complexes in CD_2Cl_2 have been characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. The NMR signal assignment was based on HMQC experiments. The ^{1}H NMR spectra of the isolated compounds acquired at room temperature are in accordance with a fluxional behaviour of the metal coordinating allyl unit do to a rapid η^3–η^1–η^3 allyl rearrangement [32,34]. As a consequence, the ^{1}H NMR signals of $H_{(1a)}$ and $H_{(1s)}$ (a = *anti*, s = *syn* with respect to $H_{(2)}$) (Scheme 4) are not resolved at room temperature, while analogous ^{1}H spectra acquired at −60 °C in CD_2Cl_2 exhibited for $H_{(1a)}$ and $H_{(1s)}$ doublets with a $^3J_{HH}$ of around 13 and 7 Hz, respectively. The ^{1}H NMR signals assigned to $H_{(3a)}$ and $H_{(3s)}$ (Scheme 4) are well resolved doublets even at room temperature.

The ^{13}C{^{1}H} NMR spectra of the Pd(η^3-allyl) compounds studied herein showed for the allyl-carbon atoms $C_{(1)}$, $C_{(2)}$ and $C_{(3)}$ (Scheme 4) at room temperature as well as singlets at −60 °C in the typical chemical shift range as observed for related Pd(η^3-allyl) complexes [32,34].



Scheme 4.

3.3. Crystal structure determination of *1*, *8*, *10* and *11*·2C_7H_8

Crystals, suitable for a single crystals structure analysis have been obtained by slow diffusion of toluene into a CH_2Cl_2 solution of the corresponding compound at room temperature. Crystallographic data for **1**, **8**, **10** and **11**·2C_7H_8 are summarized in Table 1, while selected bond distances and angles are reported in the caption of the ORTEP plot of each crystal structure.

The crystal structure of **1** (Fig. 1) shows one molecule of **1** in the asymmetric unit.

The palladium atom, that exhibits a square planar coordination geometry in **1**, deviates from the best coordination plane defined by C(1), C(18), C(20) and Cl(1) of 0.0593(25) Å in direction of C(13). The Pd–C(1) bond length of 2.035(4) Å is comparable with that found for related Pd(η^3-allyl)(NHC)-complexes [28,32,34]. The reason for the slightly different Pd(1)–C(18), Pd(1)–C(20) and Pd(1)–Cl(1) bonding distances when compared to those of the related structure bearing *N*,*N*′-bis(1-S,S-phenylethylimidazol)-2-ylidene is mainly steric in nature [28]. Both, the *N*,*N*′-di-substituted imidazol-2-ylidene unit and the η^3-allyl group are tilted with respect to the coordination plane by 72.38(21)° and 60.90(53)°, respectively.

The crystal structure of **8** (Fig. 2) exhibits one molecule of the latter compound in the asymmetric unit.

The palladium atom is coordinated by the carbene carbon atom C(1), a η^3-allyl group and a monodentate-coordinating acetate anion which is disordered over two equally occupied positions sharing the carboxylate carbon atom C(31). The acetate oxygen atom O(2a) shows a small intra-molecular distance to the allyl-hydrogen atom H(28b) of 2.793 Å.

The palladium atom in **8** deviates form the best coordination plane defined by the atoms C(1), C(28), C(30), O(1a), O(1b)

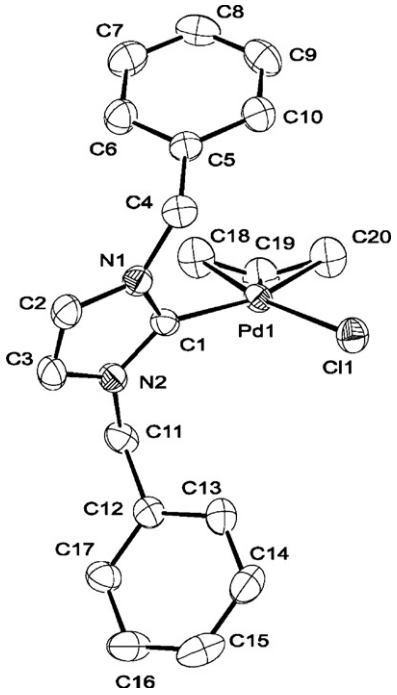


Fig. 1. ORTEP plot of **1**. Thermal ellipsoids are drawn at the 30% probability level and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Pd(1)–Cl(1) 2.4028(14), Pd(1)–C(1) 2.035(4), Pd(1)–C(18) 2.084(5), Pd(1)–C(19) 2.124(6), Pd(1)–C(20) 2.222(5), C(18)–C(19) 1.346(8), C(19)–C(20) 1.367(8), Cl(1)–Pd(1)–C(1) 95.30(12), C(1)–Pd(1)–C(20) 162.38(19), Cl(1)–Pd(1)–C(18) 170.06(16).

Table 1
Crystallographic data for **1**, **8**, **10** and **11**·2C_7H_8.

	1	**8**	**10**	**11**·2C_7H_8
Empirical formula	$C_{20}H_{21}ClN_2Pd$	$C_{32}H_{44}N_2O_2Pd$	$C_{34}H_{32}Cl_2N_4Pd$	$C_{64}H_{88}N_4O_6Pd_2$
Formula weight	431.24	595.09	673.94	1222.18
Crystal color, shape	Yellow, plate	Yellow, plate	Yellow, prism	Yellow, plate
Crystal size (mm)	0.24 × 0.15 × 0.11	0.30 × 0.20 × 0.10	0.25 × 0.20 × 0.10	0.20 × 0.20 × 0.10
Temperature (K)	150(2)	170(2)	150(2)	170(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	*C*2/*c*	$P2_1$	$P2_1/n$	*P*-1
a (Å)	23.983(8)	9.1960(2)	10.966(7)	12.2299(4)
b (Å)	11.764(4)	17.5190(3)	12.534(9)	13.9907(3)
c (Å)	13.788(4)	9.9456(2)	11.432(8)	16.7472(4)
α (°)				82.052(2)
β (°)	98.99(2)	109.266(2)	106.174(13)	85.085(2)
γ (°)				84.234(2)
Volume (Å^3)	3842(2)	1512.55(5)	1509.1(18)	2816.14(13)
Z	8	2	2	2
F(000)	1744	624	688	1280
ρ_{calc} (g cm^{-3})	1.491	1.307	1.483	1.441
μ (Mo Kα) (mm^{-1})	1.108	0.643	0.822	0.695
θ range (°)	1.72–26.75	3.86–37.39	2.28–28.99	3.69–32.48
Index range	$-29 \le h \le 30$, $-14 \le k \le 14$, $-17 \le l \le 17$	$-15 \le h \le 15$, $-29 \le k \le 27$, $-16 \le l \le 16$	$-13 \le h \le 14$, $-16 \le k \le 16$, $-15 \le l \le 15$	$-17 \le h \le 17$, $-20 \le k \le 21$, $0 \le l \le 24$
Reflections collected	22614	20713	16253	17879
Independent reflections	4068	12372	3950	17879
Refined parameters	205	364	187	689
Goodness-of-fit on F^2	0.918	1.035	1.043	0.814
R_1 ($2\sigma(I)$)	0.0422	0.0284	0.0370	0.0574
R_1 (all data), *wR*2 (all data)	0.0646, 0.1222	0.0348, 0.0719	0.0602, 0.0980	0.1488, 0.1157
Largest diff peak and hole (eÅ^{-3})	1.627, −0.836	1.017, −0.526	0.654, −0.781	1.412, −0.812

of 0.1197(29) Å in direction of C(25). The Pd–C(1) bonding distance of 2.0399(12) Å and the almost perpendicular orientation of the imidazol-2-ylidene unit with respect to the best coordination plane defined by the atoms C(1), Pd(1), C(29), O(1a) and O(1b) of 85.96(0.24)° is comparable to analogous structural parameters found for the related chloride [28] and iodide [32] structure. The 2,6-di-*iso*-propylphenyl moieties show a torsion angle of 81.70(0.36)° and 83.76(0.19)° with respect to the imidazol-2-ylidene plane, defined by the atoms C(1), N(1) and N(2). The coordinating allyl moiety is tilted with respect to the best coordination plane of 52.03(0.25)°, which is in agreement with analogous torsion anglers found for related neutral and cationic Pd(η^3-ally)(NHC) complexes [32]. Due to the significantly different *trans* influence of the carbene carbon atom C(1) and the acetate oxygen atoms O1(1a) and O(1b), two different Pd-allyl-carbon atom distances of 2.2195(13) Å (Pd(1)–C(28)) and of 2.065(18) Å (Pd(1)–C(30)) have been observed.

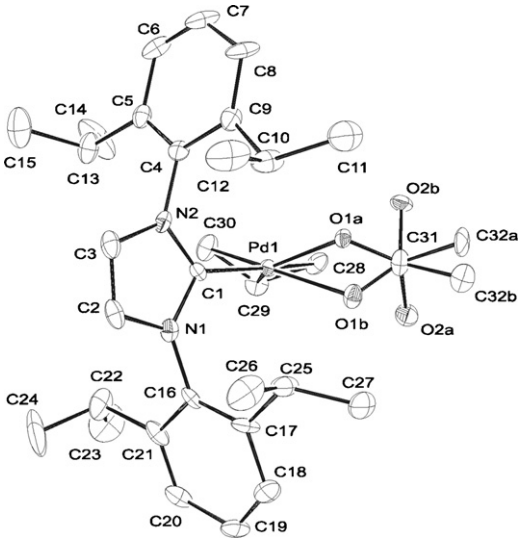


Fig. 2. ORTEP plot of **8**. Thermal ellipsoids are drawn at the 30% probability level and hydrogen atoms are omitted for clarity. The indices a and b are referred to the two equally occupied acetate positions. Selected bond distances (Å) and angles (°): Pd(1)–C(1) 2.0399(12), Pd(1)–C(28) 2.2195(13), Pd(1)–C(29) 2.1403(17), Pd(1)–C(30) 2.0651(18), Pd(1)–O(1a) 2.108(6), Pd(1)–O(1b) 2.132(7), C(28)–C(29) 1.370(3), C(29)–C(30) 1.419(3), C(1)–Pd(1)–C(28) 165.09(6), C(1)–Pd(1)–C(29) 129.19(8), C(1)–Pd(1)–C(30) 96.79(8), C(1)–Pd(1)–O(1a) 91.87(16), C(1)–Pd(1)–O(1b) 98.66(17), C(28)–C(29)–C(30) 120.1(3).

The crystal structure of **10** (Fig. 3) confirms the *trans* arrangement of both chloride and NHC ligands with respect to the palladium atom. The palladium atom is square planar coordinated, occupying a centre of inversion. As a consequence, half of the molecule (i.e. labeled part of Fig. 3) constitutes the asymmetric unit.

The imidazol-2-ylidene units coordinated to palladium are tilted with respect to the palladium coordination plane defined by Pd(1), Cl(1) and C(1) of 71.05(0.12)°. Both the Pd(1)–C(1) and Pd(1)–Cl(1) distances of 2.036(3) and 2.3204(16) Å, respectively, are comparable with analogous distances found in related Pd-bis(carbene) structures [35].

The crystal structure of **11**·2C_7H_8 (Fig. 4) exhibits compound **11** and two molecules of toluene in the asymmetric unit.

Both palladium atoms in the dimeric structure of **11**·2C_7H_8 are bridged by two OH-groups. As a consequence, the central [Pd(μ-OH)]$_2$ core is folded showing an intra-planar angle between both Pd-coordination planes of 21.44(6)°. The different Pd-bridging oxygen distances [33] clearly reflect the higher *trans* influence of the carbene carbon atom when compared to the monodentate-coordinating acetate group. Both *trans*-coordinating NHC ligands are almost perpendicular (85.06(0.16)°) with respect to the corresponding palladium coordination plane. The palladium–carbene–carbon bonding distances of 1.977(3) Å (Pd(1)–C(1)) and 1.979(4) Å (Pd(2)–C(24)) are in agreement with related distances found in other NHC-modified palladium complexes [32,34].

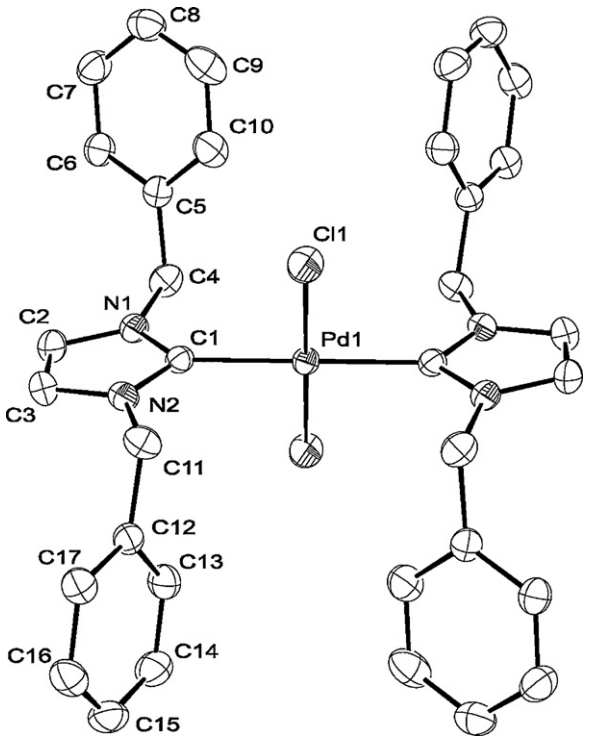
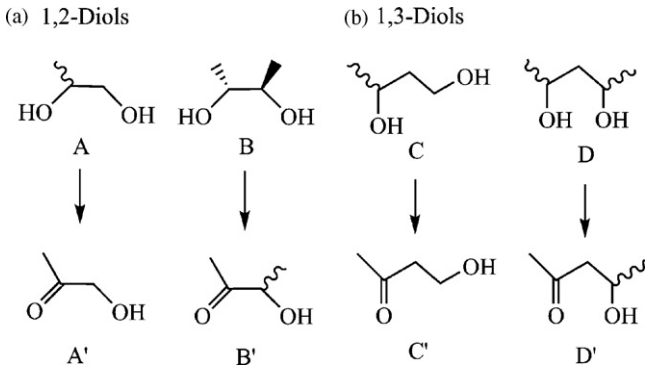


Fig. 3. ORTEP plot of **10**. Thermal ellipsoids are drawn at the 30% probability level and hydrogen atoms are omitted for clarity. Only non-hydrogen atoms belonging to the asymmetric unit have been labeled. Selected bond distances (Å) and angles (°): Pd(1)–Cl(1) 2.3204(16), Pd(1)–C(1) 2.036(3), Cl(1)–Pd(1)–C(1) 91.26(8).

3.4. Catalytic study

3.4.1. Catalytic aerobic oxidation of diols

Compounds **1**–**8** were applied as precursors for the selective aerobic oxidation of unprotected 1,2-diols (i.e. (±) 1,2-propanediol (A) and 2R, 3R-butanediol (B)) and 1,3-diols (i.e. (±) 1,3-butanediol (C) and a 1:1 mixture of meso/rac-2,4-pentanediol (D)) as shown in Scheme 5.



Scheme 5.

The catalytic reactions were carried out in a 19:1 (v:v) solvent mixture of toluene and DMSO, in order to fully dissolve the substrates, and in the presence of 20 bar of air. The catalytic activity as well as the chemoselectivity provided by **1**–**8** have been compared with that of the reference precursor **9** (Scheme 1) by carrying out catalytic reactions under identical experimental conditions.

It is important to mention at this stage that the air pressure (i.e. 20 bar) and the reaction temperature (i.e. 80 °C) are optimized reaction parameters. The results of this comparative catalytic study are summarized in Table 2.

Irrespective of the precursor employed, hydroxy ketones (A′–D′, Scheme 5) have been chemoselectively obtained, confirming the preference of Pd(II)-based catalysts to dehydrogenate sec-

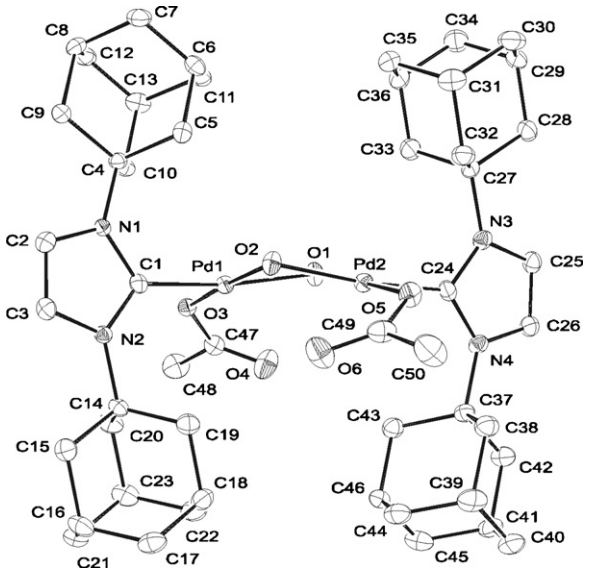


Fig. 4. ORTEP plot of **11**·2C_7H_8. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond distances (Å) and angles (°): Pd(1)–C(1) 1.977(3), Pd(1)–O(1) 2.058(2), Pd(1)–O(2) 2.013(3), Pd(1)–O(3) 2.004(3), Pd(2)–C(24) 1.979(4), Pd(2)–O(1) 2.010(3), Pd(2)–O(2) 2.054(2), Pd(2)–O(5) 2.028(3), C(1)–Pd(1)–O(3) 92.80(13), O(1)–Pd(1)–O(2) 82.06(10), O(1)–Pd(1)–C(1) 171.02(12), O(2)–Pd(1)–O(3) 175.94(10), C(24)–Pd(2)–O(5) 90.85(14), O(1)–Pd(2)–O(2) 82.24(10), O(1)–Pd(2)–O(5) 175.41(10), O(2)–Pd(2)–C(24) 172.70(13).

Table 2
Aerobic oxidation of unprotected 1,2- and 1,3-diols with complexes **1**–**9**.[a].

Entry	Precursor	Substrate	Conv. (%)[b]	
			1 h	2 h (3 h) (5 h)
1	**1**	A	24	26
2	**2**	A	30	56 (60) (74)
3[c]	**2**	A		14
4[d]	**2**	A		24
5[e]	**2**	A	5	8
6	**3**	A	9	18
7	**5**	A	20	22
8	**6**	A	10	18
9	**7**	A	16	22
10	**8**	A	23	26
11[f]	**8**	A	29	32
12[g]	**8**	A	25	26
13	**9**	A	24	24
14	**2**	B	27	50 (60) (73)
15	**8**	B	29	34
16[f]	**8**	B	50	60
17	**9**	B	32	33
18	**2**	C	11	22 (24)
19	**8**	C	33	38
20[f]	**8**	C	31	34
21	**9**	C	32	36
22	**2**	D	14	26 (36)
23	**8**	D	44	52
24[f]	**8**	D	40	50
25	**9**	D	47	52

[a] Catalytic conditions: precursor 0.01 mmol, 19:1 (v:v) toluene/DMSO 20 mL, substrate 1.00 mmol, p(air) 20 bar, *T* 80 °C.
[b] Conversion given as average value of 3 catalytic runs.
[c] Addition of Cs_2CO_3 0.02 mmol.
[d] Addition of H_2O_2 (35% water solution) 20 μL.
[e] Addition of hydroxyacetone 1.00 mmol.
[f] Addition of NaOAc 0.02 mmol.
[g] Addition of acetic acid (HOAc) 0.02 mmol.

ondary over primary alcohol functional groups [12]. Indeed, 1,3-propanediol and 1,2-ethanediol were not oxidized under the catalytic conditions employed in this study. The selective oxidation of a primary alcohol group in the presence of a secondary alcohol within the same molecule is feasible only by a synthetic protocol that comprises a protecting–deprotecting synthetic strategy of the secondary alcohol group [20b].

A comparison of the catalytic performance of the precursors by employing 1,2-propanediol (i.e. A, Scheme 5) as substrate, showed that **2** is the most efficient catalyst precursor, outperforming even the reference system **9** in terms of catalytic activity and stability with time (Table 2, entry 2 vs. 13). An attempt of increasing further the catalytic efficiency of **2** by adding a base such as Cs_2CO_3 in order to foster the Pd-alkoxide formation failed (Table 2, entry 3 vs. 2) most likely due to coordination of carbonate to the palladium centre, which would hinder the access of the substrate to palladium. Precursor **4** was under identical catalytic conditions completely inactive, which is ascribed to the lacking activation of the precursor and not to its decomposition to palladium black. In fact, **4** was recovered unchanged after the catalytic reaction. Precursor **1** showed a rapid deactivation in the second hour of reaction due to the formation of **10** in the course of the catalytic reaction. A parallel catalytic batch reaction with the latter compound in the presence of 1,2-propanediol gave no substrate conversion, confirming the requirement of coordinating only one carbene to the metal centre.

Within the series of the palladium-acetate precursors **5**–**8**, complex **8** was the most promising one, showing a catalytic activity that resembles that of the reference system (Table 2, entry 10 vs. 13). Importantly, the catalytic activity of **8** increased by adding 2 mol equivalents of NaOAc to the reaction solution when 1,2-diols (i.e. substrates A and B) were employed (Table 2, entries 11/16 vs. 10/15). In contrast, analogous catalytic reactions carried out with 1,3-diols in the presence of NaOAc showed no beneficial effect of the latter base (Table 2, entries 20/24 vs. 19/23). The same applies to catalytic reactions carried out with **8** in the presence of 2 mol equivalent of HOAc (entry 12 vs. 10). Both NaOAc and HOAc are known to have a stabilizing effect on palladium in the course of the catalytic cycle [22]. The experimental fact, that this observation applies for the oxidation of 1,2-diols and not 1,3-diols may be due to the difference in palladium coordination property of the latter substrates, which may be higher for 1,3-diols. All catalytic reactions carried out in the presence of the palladium-acetate precursors showed, regardless of the substrate employed, the formation of a significant amount of palladium black in the course of the catalytic reaction. As a consequence, the catalytic activity dropped significantly in the second hour of reaction (Table 2), whereas **2** always gave a transparent yellow solution with only a trace amount of palladium black after catalysis. Nevertheless, **2** showed a drop of the catalytic activity with substrates A and B during the third hour of reaction (Table 2, entries 2 and 14). In order to rationalize this experimental result, a catalytic reaction with **2** in the presence of a 1:1 molar mixture of 1,2-propanediol and hydroxyacetone (i.e. reaction product) was carried out. As a result, the catalytic activity of **2** dropped significantly when compared to that obtained by carrying out the analogous reaction in the absence of added hydroxyacetone (Table 2, entry 5 vs. 2). From this experimental result, we can thus infer that the oxidation product (i.e. hydroxy ketone) formed in the course of the catalytic reaction competes with the substrate for the coordination to palladium, slowing down thus the kinetics of catalytic cycle.

3.4.2. Mechanistic considerations

In order to shed light on the mechanism operative in the catalytic oxidation reaction catalyzed by the precursors studied herein, variable-temperature ^{1}H HPNMR studies with **2** in toluene-d_8 were carried out in the presence of substrate D (Scheme 5) and 20 bar of air. Fig. 5 shows a sequence of selected ^{1}H NMR spectra acquired in the course of the NMR study carried out with **2**.

The ^{1}H NMR spectrum of a solution of **2** and substrate D in toluene-d_8 in the presence of air (20 bar) shows unambiguously the presence of signals stemming from the coordinating allyl-unit (Fig. 5, trace a). By heating the latter NMR solution to 80 °C, corresponding to the reaction temperature employed in the catalytic batch reactions, the characteristic signals of the coordinating allyl unit disappeared (Fig. 5, trace b) and new NMR signals appeared due to the starting catalytic conversion of the substrate. After a reaction time of 2 h, the ^{1}H NMR spectrum, acquired at 80 °C, showed a NMR singlet of low intensity at around 9.50 ppm, that was assigned to the 2-imidazolium-hydrogen atom. The GC/MS analysis of the NMR solution revealed a substrate conversion of 32% into D′ and the presence of propene in solution.

It is important to mention that a non-deareated solution of **2** in dry or wet toluene-d_8 is stable (i.e. no propene release) even on heating it at 80 °C for 10 min, whereas an analogous solution of **8**, leads under identical experimental conditions to the concomitant formation of palladium black and allyl acetate, the presence of which in solution has been proved by GC/MS analysis. The absence of activation of **4** under the present catalytic conditions is most likely due to a strong chloride coordination to palladium. Accordingly, the crystal structures of **4** exhibits a Pd–Cl bond length of (2.370(5) Å) which is significantly shorter when compared to that of **2** (2.391(14) Å) [28].

It is thus reasonable to assume that anion dissociation (i.e. Cl, OAc) from palladium is important for the propene release from precursor A (Scheme 6). In consequence of the anion dissociation, the substrate may form the palladium-hydrido-allyl species C [36], that releases propene by a reductive elimination reaction forming the Pd(0) species D (Scheme 6) [22a].

The latter species undergoes either decomposition to palladium black and carbene or enters the catalytic cycle upon reversible coordination of oxygen, yielding intermediate E (Scheme 6), which is most likely protonated by the free acid to yield the palladium-hydroperoxide species (F) [37]. The latter intermediate is then transformed into the neutral palladium–alkoxide species (G) (Scheme 6) with concomitant release of H_2O_2. The formation of H_2O_2 in the course of the catalytic reactions is in line with the oxygen consumption (i.e. measured by a flow meter) and with the formation of trace amounts of dimethyl sulfone, that has been detected after the catalytic reactions. In fact, a blank reaction carried out with the solvent mixture proved a H_2O_2-mediated

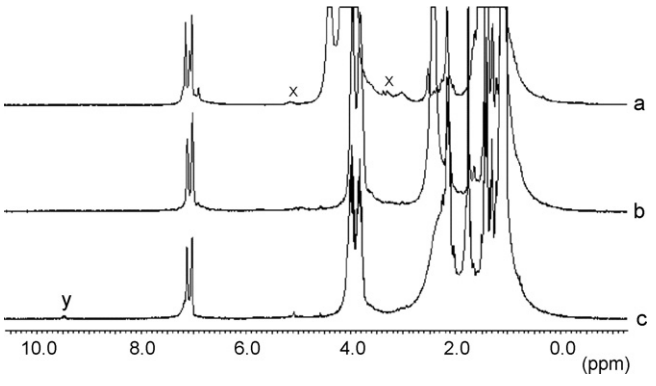
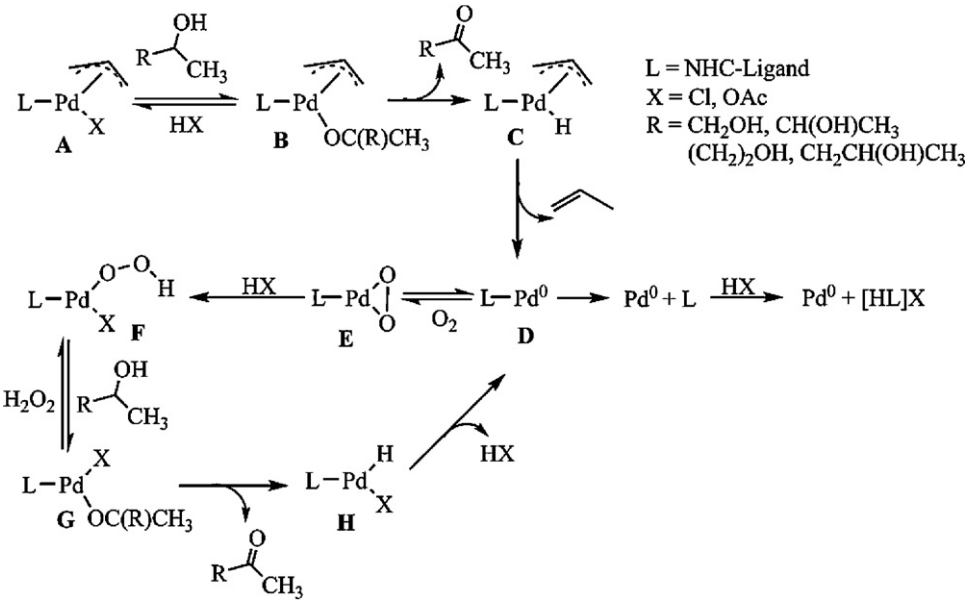


Fig. 5. Selected ^{1}H NMR spectra of the variable-temperature HPNMR study (sapphire tube, toluene-d_8, 200.13 MHz) of the aerobic oxidation of substrate D with **2**: (a) solution of **2** in toluene-d_8 in the presence of substrate D and air (20 bar) at room temperature (x = ^{1}H NMR signal assigned to the coordinating allyl moiety); (b) after heating the NMR solution to 80 °C; (c) after heating the latter solution for 2 h at 80 °C (y = ^{1}H NMR signal assigned to the 2-imidazolium-hydrogen atom).



Scheme 6. Proposed catalytic cycle.

oxidation of DMSO to dimethyl sulfone (i.e. 3% of dimethyl sulfone was formed at a reaction time of 2 h at 80 °C) [38]. Since H_2O_2 is a stronger Broensted acid as compared to the diols employed (p*K*a 11.6 vs. 15.0), the equilibrium between intermediates F and G (Scheme 6) would be shifted towards the former in the presence of H_2O_2 [15b]. Accordingly, a catalytic reaction of substrate A with **2** in the presence of added H_2O_2 (35% water solution) showed a significant drop of the catalytic activity of **2** as compared to that observed without added H_2O_2 (Table 2, entry 4 vs. 2). The catalytic cycle proceeds then by the β-hydride elimination reaction of intermediate G forming the palladium-hydride H with concomitant release of the oxidized substrate. The reductive elimination of the acid (HX) from the latter intermediate generates the palladium (0) intermediate (D), closing thus the catalytic cycle (Scheme 6).

The formation of palladium black in the course of the catalytic batch reactions is mainly ascribed to the carbene dissociation form Pd(0)–carbene intermediate D (Scheme 6).

4. Conclusions

Neutral Pd(X)(η^3-allyl) complexes (X = Cl and OAc) bearing monodentate NHC ligands have been synthesized, characterized and utilized as catalyst precursors for the aerobic oxidation of unprotected 1,2 and 1,3-diols in a 1:1 (v:v) solvent mixture of toluene and DMSO. Irrespective of the precursor employed, hydroxy ketones have been chemoselectively obtained. A comparative catalytic study has shown that **2** generates the most active and most stable catalytic system for the oxidation of unprotected 1,2-diols, outperforming the reference precursor **9**.

A variable-temperature ^{1}H HPNMR studies carried out with **2** under catalytic conditions proved that propene is released from the palladium centre in the course of the precursor activation step most likely through a reductive elimination reaction of a palladium-allyl-hydride intermediate.

Acknowledgments

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