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Synthesis and characterization of $[MCl_2(^nPr\text{-}N(Ph_2P)_2]$ (M = Pt, Pd) complexes and hydroformylation of 1-octene using $[PtCl_2(R\text{-}N(Ph_2P)_2)]$ (R = benzyl, 2-picolyl, ^{n}Pr) complexes

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Abstract The synthesis and characterization of platinum(II) and palladium(II) complexes of the type $[PtX_2(^nPr\text{-}N(Ph_2P)_2)]$ (X = Cl, I) and $[PdCl_2(R\text{-}N(Ph_2P)_2)]$ {R = ^{n}Pr, *p*-OMe(C_6H_4)} containing aminodiphosphine *P,P*-bidentate ligands is described. Complexes of the type $[PtCl_2(R\text{-}N(Ph_2P)_2)]$ (where R = benzyl, 2-picolyl and ^{n}Pr) catalyzed the hydroformylation of 1-octene, albeit at low activities and slightly elevated regioselectivities toward the linear aldehyde, when compared with analogous compounds containing small bite angles.

Introduction

Hydroformylation reactions are based mainly on four transition metal catalysts, namely Rh, Co, Pt and Ru. Rh and Co catalysts have been extensively studied, and much of their mechanistic detail has been uncovered [1, 2]. Pt and Ru catalysts have been studied mainly for academic interest, while Co and Rh have been used industrially for many years [3]. Platinum(II)-catalyzed hydroformylation in the presence of a $SnCl_2$ cocatalyst has been thoroughly investigated, particularly in asymmetric reactions where high stereoselectivity is prevalent [4]. Specifically, platinum(II) catalysts containing bidentate diphosphine ligands have demonstrated good activities and selectivities toward the linear aldehyde [5, 6].

The natural bite angle has been reported to have a decisive effect on activity, stability and selectivity achieved by catalysts in hydroformylation reactions [7, 8]. Many examples, especially in Pt/Sn systems utilizing diphosphine ligands, show that catalytic efficiency is directly related to bite angle [9, 10]. Herein, we report the synthesis and characterization of new platinum(II) and palladium(II) complexes containing small bite angle bidentate diphosphine ligands as well as the catalytic activity of the platinum(II) complexes in the hydroformylation of 1-octene.

Experimental

All reactions were conducted under nitrogen using a dual high-vacuum/nitrogen line to carry out standard Schlenk techniques unless otherwise stated. Solvents used were all of analytical grade and were further purified by distillation under a nitrogen atmosphere and dried over the appropriate drying agents. K_2PtCl_4 and $PdCl_2$ were obtained from Johnson Matthey. All other reagents were purchased from Sigma–Aldrich and used as received. The complexes $[PtCl_2(cod)]$, $[PdCl_2(cod)]$, $[PtCl_2(dppp)]$ as well as complexes **7** and **8** were prepared following reported literature procedures [11–14].

NMR spectra were recorded on a Varian Mercury-XR300 spectrometer. Microanalyses were performed using a Fisons EA 1108 CHNS Elemental Analysis apparatus. Melting points were obtained using a Kofler hot stage microscope (Riechert Thermovar). FT-IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrophotometer. GC analyses of the hydroformylation reaction mixtures were performed using a Varian 3900 gas

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chromatograph equipped with a packed DB-WAX column (25 m × 320 μm (internal diameter) × 1.20 μm film thickness). The carrier gas was nitrogen with a constant flow of 25 mL/min.

Synthesis of the complexes

*Synthesis of [$PdCl_2$(^{n}Pr–N(Ph_2P)$_2$)] (**3**)*

The ligand ^{n}Pr–N(Ph_2P)$_2$ (**1**) (0.073 g, 0.175 mmol) was added to a solution of [$PdCl_2$(cod)] (0.050 g, 0.175 mmol) in freshly distilled CH_2Cl_2 (10 mL). The reaction mixture was stirred for 3 h after which time the reaction volume was reduced to approximately 2 mL in vacuo. Thereafter, diethyl ether (20 mL) was added, and the resulting yellow precipitate was filtered off and dried for 3 h in vacuo to give a solid yellow product (**3**). Yield: 68% (0.072 g). M.p: 288–290 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.54–7.89 (m, 20H, ArH), 2.95 (m, 2H), 1.20 (m, 2H), 0.52 (t, 3H, ^2J(H–H) = 7.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ (ppm): 31.3 (s). Selected IR (KBr, ν/cm^{-1}): 829 (P–N). Elemental Anal. Found: C, 53.8; H, 4.4; N, 2.1%. Calcd. for $C_{27}H_{27}NP_2PdCl_2$: C, 53.6; H, 4.5; N, 2.3%.

*Synthesis of [$PdCl_2$(p-OMe(C_6H_4)-N(Ph_2P)$_2$)] (**4**)*

Complex **4** was prepared in the same way as outlined for complex **3** using the ligand *p*-OMe(C_6H_4)-N(Ph_2P)$_2$ (**2**) (0.086 g, 0.175 mmol) and [$PdCl_2$(cod)] (0.050 g, 0.175 mmol). The product was isolated as a yellow solid. Yield: 72% (0.084 g). M.p: does not melt below 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 6.51–7.96 (m, 24 H, ArH), 4.26 (s, 3H, O-CH_3). ^{31}P NMR (121 MHz, $CDCl_3$) δ (ppm): 70.1 (s). Selected IR (KBr, ν/cm^{-1}): 828 (P–N). Elemental Anal. Found: C, 55.4; H, 4.1; N, 2.1%. Calcd. for $C_{31}H_{27}NOP_2PdCl_2$: C, 55.7; H, 4.1; N, 2.1%.

*Synthesis of [$PtCl_2$(^{n}Pr–N(Ph_2P)$_2$)] (**5**)*

The ligand ^{n}Pr–N(Ph_2P)$_2$ (**1**) (0.036 g, 0.086 mmol) was added to a solution of [$PtCl_2$(cod)] (0.032 g, 0.086 mmol) in freshly distilled CH_2Cl_2 (10 mL). The reaction mixture was stirred for 3 h after which time the reaction volume was reduced to approximately 2 mL in vacuo. Thereafter, diethyl ether (20 mL) was added, and the resulting white precipitate was filtered off and dried for 3 h in vacuo to give a solid white product (**5**). Yield: 67% (0.040 g). M.p: does not melt below 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.26–7.87 (m, 20H, ArH), 2.94 (m, 2H), 1.15 (m, 2H), 0.51 (t, 3H, ^2J(H–H) = 7.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ (ppm): 17.3 (s, ^{1}J(Pt–P) = 3,300 Hz). Selected IR (KBr, ν/cm^{-1}): 826 (P–N). Anal. Found: C, 46.5; H, 4.0; N, 1.9%. Calcd. for $C_{27}H_{27}NP_2PtCl_2$: C, 46.8; H, 3.9; N, 2.0%. EI-MS: 657.5 [M-Cl]$^+$.

*Synthesis of [PtI_2(^{n}Pr–N(Ph_2P)$_2$)] (**6**)*

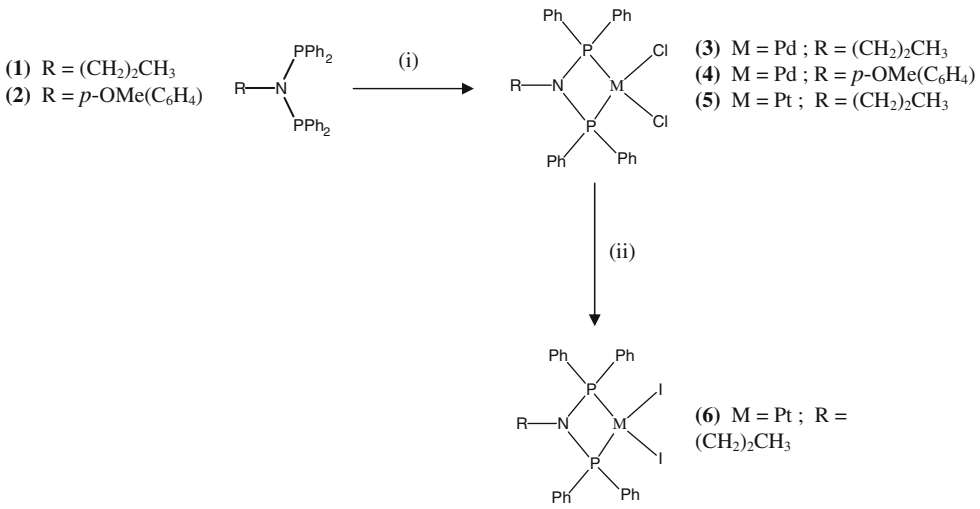
Complex **6** was prepared by adding complex **5** (0.12 g, 0.173 mmol) to a solution of NaI (0.052 g, 0.346 mmol) in acetone (50 mL). The reaction mixture was stirred for 45 min after which time the solvent was removed under high vacuum. Distilled water (2 × 10 mL) was used to wash the excess salt, and the product was extracted using CH_2Cl_2. The yellow product (**6**) was recrystallized using a CH_2Cl_2/hexane solution (10 mL/10 mL) to give a pale yellow solid. Yield: 65% (0.098 g). M.p: does not melt below 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.18–7.49 (m, 20H, ArH), 2.75 (m, 2H), 1.05 (m, 2H), 0.44 (t, 3H, ^2J(H–H) = 7.3 Hz). ^{31}P NMR (121 MHz, $CDCl_3$) δ (ppm): 13.3 (s, ^1J(Pt–P) = 3,019 Hz). Selected IR (KBr, ν/cm^{-1}): 834 (P–N). Elemental Anal. Found: C, 37.2; H, 3.4; N, 1.4%. Calcd. for $C_{27}H_{27}NP_2PtI_2$: C, 37.0; H, 3.1; N, 1.6%.

General procedure for 1-octene hydroformylation reactions

In a typical experiment, the platinum(II) complex (0.029 mmol) and anhydrous $SnCl_2$ (5 mg, 0.029 mmol) were added to a solution of dry toluene (11 mL) and 1-octene (8.9 mL, 0.06 mmol) in a stainless steel pipe reactor. The reactor was initially pressurized to 50-bar total pressure ($CO:H_2$ = 1:1) and placed in an oil bath at 100 °C for 15 min with stirring of 600 rpm being accomplished by means of a magnetic follower. The total pressure was then increased to 80 bar, and syngas was supplied on demand to maintain the reaction pressure at 80 bar throughout the reaction period. After the desired reaction time was reached, the syngas supply was shut down and the reactor was cooled in an ice bath. The excess pressure was then vented from the cooled reactor, and a sample of the resulting pale yellow solution was taken for GC analysis. The yield of aldehyde was calculated by using the mass of the toluene solvent as an internal reference.

Results and discussion

The aminodiphosphine ligands **1** and **2** were prepared according to the reported literature procedures [15, 16]. The platinum(II) and palladium(II) complexes (**3–5**) were prepared following straightforward synthetic routes, by the reaction of the ligands **1** and **2** with either $PtCl_2$(cod) or $PdCl_2$(cod) in CH_2Cl_2 (Scheme 1). The complexes are



Scheme 1 Syntheses of complexes **3**–**6**. Reagents and conditions: (i) (a) MCl_2(cod) (M = Pt, Pd); (b) CH_2Cl_2, RT, 3 h (ii) (a) NaI; (b) $(CH_3)_2CO$, RT, 45 min

isolated as either white or yellow solids in moderate to good yields and are air stable as solids and in solution. Complex **6** was prepared *via* a halide exchange reaction using **5** and NaI in acetone, followed by recrystallization from a CH_2Cl_2/hexane solution to afford a pale yellow solid in 65% yield. The complexes were unambiguously characterized using ^{1}H, ^{31}P NMR spectroscopy, IR spectroscopy and elemental analysis.

Palladium(II) complexes **3** and **4** displayed sharp singlets in their ^{31}P NMR spectra, with complex **4** showing an anomalous ^{31}P chemical shift at 70.1 ppm, attributed to the electron-withdrawing inductive effect of the aromatic ring. Platinum(II) complexes **5** and **6** displayed singlets flanked by characteristic platinum satellites, attesting to the purity of the synthesized complexes. Complexes **5** and **6** differ only in the coordinating halide groups. The only significant variation observed in the ^{1}H NMR spectrum was a downfield shift for the peak corresponding to the methyl group of the (alkyl)aminodiphosphine ligand which appeared at δ 0.51 ppm for **5** and δ 0.44 ppm for **6**. The coupling constants of the dichloride complex **5** were 3,300 Hz (^{1}J(Pt–P)), while the diiodo complex **6** displayed a significantly smaller coupling constant of 3,019 Hz (^{1}J(Pt–P)). Similar reductions in coupling constants upon exchange of Cl with I ions in similar platinum complexes have been reported [17]. IR spectra display absorption bands around 880 cm^{-1}, assigned to the P–N bond.

Hydroformylation of 1-octene

The platinum complexes (**5**, **7**, **8**) were evaluated as catalyst precursors for the hydroformylation of 1-octene. In the present work, complex **5** and its analogues of the type [$PtCl_2$(R-N($Ph_2P)_2$)] {R = benzyl (**7**), 2-picolyl (**8**)} gave active platinum catalysts, although demonstrating low activity in the hydroformylation of 1-octene in the presence of the cocatalyst $SnCl_2$ (Table 1). All the experiments were performed in triplicate, and the mean values were taken as the final results. The activity of these complexes was compared to that of [$PtCl_2$(dppp)] which has previously shown good activity and selectivity toward the linear aldehyde in the hydroformylation reaction [9]. Under our conditions, the complex [$PtCl_2$(dppp)] also consistently gave high activities (Table 1).

Table 1 Hydroformylation of 1-octene using complexes **5**, **7** and **8** in the presence of $SnCl_2$

Complex	Time (h)	Conversion[a] (%)	Hydrogenation[b] (%)	Yield[c] (%)	n:i[d]	TOF[e] (h^{-1})
[$PtCl_2$(dppp)]	20	100	20	58	1.7	626
[$PtCl_2$(^{n}Pr-N($Ph_2P)_2$)] (**5**)	20	5	19	22	6	28
[$PtCl_2$(benzyl-N($Ph_2P)_2$)] (**7**)	20	4	19	26	6	23
[$PtCl_2$(2-picolyl-N($Ph_2P)_2$)] (**8**)	20	2	23	23	3	10

Reaction conditions: 80-bar syngas ($CO:H_2$ = 1:1), 100 °C, 600-rpm stirring, Pt:Sn = 1:1

[a] % Conversion = 100 − (n(1 − octene)out/n(1 − octene)in) × 100

[b] % Hydrogenation = n(octane)/n(1 − octene converted) × 100

[c] % Yield Nonanal = n(nonanal)/n(1 − octene converted) × 100

[d] n:i = normal:iso ratio representing the linear-to-branched selectivity

[e] TOF = n(1 − octene converted)/{n(Pt) × h}

Complexes **5**, **7** and **8** represent platinum complexes containing a chelating, bidentate diphosphine small bite angle ligand, with the added effect of an amino group coordinated to both phosphorus atoms. These ligands are no doubt not the best ligands in platinum-catalyzed hydroformylation. However, they are still worth investigating for posterity. The complexes are air-stable solids and thermally stable, which did not melt nor decompose below 300 °C, due to strong coordination to the metal center provided by the phosphorus atoms.

The complexes (**5**, **7**, **8**) exhibited low activities in 1-octene hydroformylation when subjected to 80 bar syngas at 100 °C for short periods of 3–4 h, and the conversion obtained was less than 1% for all three complexes. When the reaction time was lengthened to 20 h, the conversion increased to 5, 4 and 2% for **5**, **7** and **8** respectively (Table 1). Increasing the length of reaction time did not greatly increase the conversion. This suggests that the complexes were retarding the catalytic reaction, and either a structural or electronic effect was causing the low activity rather than an induction period required for the catalysis to commence. Alternatively, catalyst decomposition may have resulted in the catalyst system deactivating.

The hydrogenation observed for complexes **5** and **7** (19%) was similar to that observed using [$PtCl_2$(dppp)] (20%), while it was slightly higher for complex **8** (23%). This is an interesting observation since the only structural difference between complexes **7** and **8** is the presence of a pyridyl group on the ligand backbone of **8**, suggesting that this functional group is increasing the hydrogenating ability of the complex.

The yield of nonanal was considerably lower than that observed for [$PtCl_2$(dppp)] at 22, 26 and 23% for **5**, **7** and **8** respectively. The n:i ratios revealed that a large proportion of the products formed were linear aldehydes. This was considerably higher than the linearity achieved when using [$PtCl_2$(dppp)], providing evidence that these catalysts impose a greater steric effect resulting in more linear products. Hayashi et al. found that $PtCl_2$-diphosphine-$SnCl_2$ systems with diphosphine ligands containing rigid ring skeletons show remarkable linearity in the platinum-catalyzed hydroformylation of 1-pentene [9].

Basic amines such as Et_3N have been reported to obstruct the Pt/Sn-catalyzed hydroformylation of styrene completely [18]. Abstraction of $HSnCl_3$ by an amine from the [PtH(diphosphine)($SnCl_3$)] intermediate renders the catalyst inactive [19]. Thus, the interference of the nitrogen atoms of the ligands used in our study with intermediates in the hydroformylation cycle cannot be ruled out as a possible cause of low activity.

It is well-known that the bite angle has a considerable influence on the rate in platinum-catalyzed hydroformylation. For example, the catalytic activity of complexes of the type [$PtCl_2(Ph_2P(CH_2)_nPh_2P)$] ($n = 1$–4) were found to depend strongly on the length of the bridging group in the hydroformylation of 1-pentene [9]. The complex, [$PtCl_2$-($Ph_2P(CH_2)Ph_2P$)], containing a methylene bridge, showed the lowest hydroformylation activity and was almost ineffective as a hydroformylation catalyst precursor. The complexes in the present work contain small bite angles similar to that of [$PtCl_2(Ph_2P(CH_2)Ph_2P)$] and the same trend in low hydroformylation activity is observed. Thus, it would appear that the bite angle is a decisive factor in activity and selectivity of the hydroformylation catalyst [7, 8].

Conclusion

Two platinum(II) and two palladium(II) complexes containing aminodiphosphine ligands were synthesized and characterized using spectroscopic and analytical techniques. The catalytic potential of three platinum(II) complexes was evaluated in the hydroformylation of 1-octene. The complexes exhibit low catalytic activity in the hydroformylation of 1-octene in the presence of cocatalyst $SnCl_2$. Variation of functional groups on the aminodiphosphine ligand results in only slight differences in the overall activity. Under identical reaction conditions (80 bar, 100 °C), the catalyst containing a larger bite angle, [$PtCl_2$(dppp)], exhibited significantly higher conversion and yield of aldehydes but achieved considerably lower linearity of products.

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