The complexation of nickel(II) and palladium(II) by heterotridentate ligands with [P,N,O] donor sets

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Abstract

Phosphorus-containing heterotridentate ligands prepared by the condensation of 2-(diphenylphosphino)aniline with 5-chlorosalicylaldehyde (HL^1), 5-nitrosalicylaldehyde (HL^2), 5-bromosalicylaldehyde (HL^3), 5-methoxysalicylaldehyde (HL^4) or 3-methoxysalicylaldehyde (HL^5) react directly with $NiCl_2 \cdot 6H_2O$ or $[(cod)PdCl_2]$ to form complexes of general formula $[\eta^3(L)M(II)Cl]$. These are characterised by spectroscopic, microanalytical and crystallographic methods. The crystal structures of $[\eta^3(L^3)Ni(II)Cl]$ (**3**) and $[\eta^3(L^2)Pd(II)Cl]$ (**6**) confirm tridentate [P,N,O] coordination of the deprotonated ligands to the metal centres, forming both five- and six-membered rings. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Nickel complexes; Palladium complexes; Tridentate ligand complexes

1. Introduction

Bidentate ligands, which comprise mixed hard/soft donor sets, continue to attract the attention of coordination chemists. In particular, those ligands, which can be described as functionalised phosphines, are frequently used to form complexes with middle and late transition metals [1].

A number of groups have expanded upon this premise and have prepared mixed tridentate ligands with [P,N,E] donor sets (E = O, S or N′) and explored their complexation behaviour. In the cases where E = O, the ligands are either monobasic, with ionisable protons, [2–8] or neutral, where the oxygen donor is part of an ether function [9–12]. From amongst the former we have previously reported the ligand prepared from the Schiff base condensation of 2-(diphenylphosphino)aniline with salicylaldehyde and its complexes with Group 10 metals [7] and ruthenium [8]. To extend the study of these ligands, we report the preparation of a range of complexes of general formula $[\eta^3(L)M(II)-Cl]$, where (L) is a monobasic ligand prepared by the condensation of 2-(diphenylphosphino)-aniline with substituted salicylaldehydes, Fig. 1.

2. Experimental

2.1. Materials

Complexation reactions were performed under an atmosphere of oxygen-free nitrogen; diethyl ether and dichloromethane were distilled under nitrogen from sodium–benzophenone ketyl and calcium hydride respectively; all other solvents were analytical grade and used without further purification. The compounds $[(cod)Pd(II)Cl_2]$ (cod = cycloocta-1,5-diene) [13] and 2-(diphenylphosphino)aniline [14] were prepared by liter-
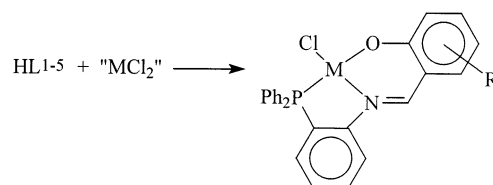
$MCl_2 = Ni(II)Cl_2 \cdot 6H_2O$, **1-5**; $MCl_2 = [(cod)Pd(II)Cl_2]$, **6-10**.

Fig. 1. The preparation of **1–10**.

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Table 1
Crystal data and structure determination parameters for **3** and **6**·CHCl$_3$

Compound	**3**	**6**·CHCl$_3$
Empirical formula	C$_{25}$H$_{18}$BrClNNiOP	C$_{25}$H$_{18}$Cl$_2$NOPPd·CHCl$_3$
M	553.44	676.04
Temperature (K)	293(2)	293(2)
Crystal size (mm)	$0.08 \times 0.1 \times 0.2$	$0.1 \times 0.1 \times 0.2$
Crystal system	monoclinic	triclinic
Space group	$P21/n$	$P\bar{1}$
Unit cell dimensions		
a (Å)	12.3042(4)	9.6740(4)
b (Å)	12.3559(4)	10.5463(4)
c (Å)	14.9487(5)	13.2275(5)
α (°)	90	87.3610(10)
β (°)	100.395(1)	77.5690(10)
γ (°)	90	88.7600(10)
U (Å^3)	2235.34(13)	1316.40(9)
Z	4	2
$F000$	1112	672
D_{calc}	1.645	1.706
μ (mm^{-1})	2.865	1.295
Total data	9580	6739
Unique data	3218	3109
R_{int}	0.0337	0.0198
R_1, wR_2	0.0274, 0.0566	0.0281, 0.0617
Residual electron density	0.426, −0.483	0.395, −0.364
Absorption correction	SADABS	SADABS

ature methods; ligands HL$^{1-5}$ were prepared according to a published method [8]; nickel chloride hexahydrate and the substituted salicylaldehydes were obtained commercially (Aldrich) and used as received.

2.2. Instrumentation

Infrared spectra were recorded as KBr pellets over the range 4000–200 cm^{-1} using a Perkin–Elmer system 2000 FT spectrometer. The ^{1}H NMR spectra were recorded on a Bruker AC250 FT spectrometer (250 MHz) with chemical shifts (δ) reported relative to external TMS. The ^{31}P{^{1}H} NMR spectra were recorded on a Jeol FX90Q spectrometer (36.2 MHz) with chemical shifts (δ) reported relative to external 85% H$_3$PO$_4$; NMR spectra for **6**–**10** were recorded in CDCl$_3$ solutions. Elemental analyses were performed using a Perkin–Elmer 2400 CHN Elemental Analyser by the Loughborough University Microanalytical Service within the Department of Chemistry.

2.2.1. X-ray crystallography

X-ray crystallographic studies were performed on **3** and **6**·CHCl$_3$ at ambient temperatures using a Siemens SMART diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and ω scans. The crystal data, a summary of the data collections and the structure refinements for these compounds are given in Table 1, selected bond lengths and angles are collected in Table 2. All structures were solved by direct methods

and all of the non-hydrogen atoms refined with anisotropic displacement parameters. Refinement was by full-matrix least-squares methods on F^2, calculations were performed using the program SHELXTL-PC [15].

2.3. Preparation of complexes

2.3.1. [η^3(L^1)Ni(II)Cl] (**1**)

To a solution of NiCl$_2$·6H$_2$O (0.057 g, 0.24 mmol) in 95% ethanol (5 ml) was added solid [HL^1] (0.10 g, 0.24 mmol). The solution was stirred at room temperature

Table 2
Selected bond lengths (Å) and angles (°) for **3** and **6** [a]

	3	**6**
Bond lengths		
M–P	2.1487(9)	2.1908(9)
M–N	1.887(2)	2.020(2)
M–O	1.881(2)	2.034(2)
M–Cl	2.1857(8)	2.3006(9)
C=N	1.304(3)	1.307(4)
C–O	1.295(3)	1.292(4)
Bond angles		
N–M–O	93.40(9)	93.91(10)
N–M–P	86.35(7)	85.88(8)
O–M–Cl	90.70(6)	89.26(7)
P–M–Cl	89.53(7)	91.10(3)
O–M–P	179.11(7)	175.73(8)
N–M–Cl(1)	175.59(7)	176.32(8)

[a] Estimated S.D. in parentheses.

for 30 min and then warmed to reflux for 5 min. The deep-red solution was cooled to room temperature and the solvent was removed under reduced pressure. The red–brown residue was extracted into 2 ml of $CHCl_3$ from which the product was obtained as red crystals after addition of 10 ml of diethyl ether. The product **1** was collected by suction filtration and dried in vacuo. Yield: 0.076 g of red–brown crystals, 72%. Complexes **2–5** were prepared by the same route and on the same scale. Complex **2**. Yield: 0.090 g of brown crystals, 68%. Complex **3**. Yield: 0.082 g of deep-red crystals, 66%. Complex **4**. Yield: 0.080 g of brown crystals, 72%. Complex **5**. Yield: 0.088 g of brown crystals, 78%.

2.3.2. $[\eta^3(L^1)Pd(II)Cl]$ (**6**)

To a solution of $[(cod)PdCl_2]$ (0.068 g, 0.24 mmol) in 10 ml of CH_2Cl_2 was added solid $[HL^1]$ (0.10 g, 0.24 mmol). The solution was stirred at room temperature for 30 min and then warmed to reflux for 5 min. The orange solution was cooled to room temperature and the solvent was removed under reduced pressure. After addition of 10 ml of diethyl ether the orange residue was extracted into 2 ml of $CHCl_3$ from which the product was obtained as yellow crystals. The product **6** was collected by suction filtration and dried in vacuo. Yield: 0.104 g of yellow–orange crystals, 88%. Com-

plexes **7–10** were prepared by the same route and on the same scale. Complex **7**. Yield: 0.104 g of yellow–orange crystals, 79%. Complex **8**. Yield: 0.111 g of yellow–orange crystals, 81%. Complex **9**. Yield: 0.089 g of scarlet crystals, 71%. Complex **10**. Yield: 0.111 g of brick red crystals, 88%.

3. Results and discussion

The stoichiometric reaction of HL^{1-5} with either $NiCl_2 \cdot 6H_2O$ in ethanol or $[(cod)Pd(II)Cl_2]$ in dichloromethane gives the complexes $[\eta^3(L^{1-5})M(II)Cl]$ **1–10** in moderate to high yields. This formulation is supported by elemental analysis, spectroscopic data and in two cases by crystallographic investigations.

3.1. IR spectroscopy

Selected IR data for the complexes **1–10** and the ligands HL^{1-5} are presented in Table 3. The bands due to $v(C=N)$ are readily identified in both the complexes and in the free ligands and serve as a useful indication that complexation has occurred. There is a distinct bathochromic shift on complexation typical for imines on coordination to transition metal centres. In the

Table 3
Microanalytical and selected IR data for **1–10**

Complex	Microanalysis (calc.) (%)			M.p. (°C)	IR (cm^{-1})	
	C	H	N		$v(C=N)$	$v(M–Cl)$
1	58.5 (59.0)	3.4 (3.4)	2.8 (2.5)	>340	1608	393
2	55.7 (55.9) [a]	3.5 (3.7) [a]	5.2 (5.2) [a]	196 (d)	1608	393
3	52.9 (52.8)	3.4 (3.2)	2.6 (2.5)	296–297	1601	390
4	62.0 (61.9)	4.4 (4.2)	2.8 (2.8)	282–283	1590	383
5	61.5 (61.9)	4.0 (4.2)	2.5 (2.8)	312–313	1588	394
6	53.7 (53.9)	3.3 (3.3)	2.3 (2.5)	316–317	1606	347
7	52.7 (52.9)	3.1 (3.2)	4.6 (4.9)	194–195	1606	347
8	49.7 (50.0)	3.2 (3.0)	2.2 (2.3)	202 (d)	1600	345
9	58.2 (57.6)	3.9 (3.9)	2.5 (2.6)	274–275	1591	341
10	58.2 (57.8)	3.7 (4.0)	2.9 (2.6)	306–307	1588	346

[a] As monohydrate.

Table 4
NMR data for **6–10** (free ligand values included for comparison)

Complex	$^{31}P\{^1H\}$ (ligand) [a]	H–C=N (ligand) [b]	Aromatic (ligand) [b]	$–OCH_3$ (ligand) [b]
6	47.8 (−14.6)	8.95 (8.19)	8.22–6.89 (7.50–6.75)	
7	46.9 (−14.6)	8.59 (8.27)	8.01–6.82 (7.49–6.75)	
8	46.9 (−14.5)	8.78 (8.27)	7.82–6.47 (7.70–6.47)	
9	49.1 (−14.9)	8.56 (8.33)	8.00–6.45 (7.70–6.60)	3.75 (3.84)
10	49.4 (−15.4)	8.70 (8.36)	8.10–6.73 (7.44–6.39)	3.77 (3.71)

[a] δ in ppm relative to external 85% phosphoric acid.
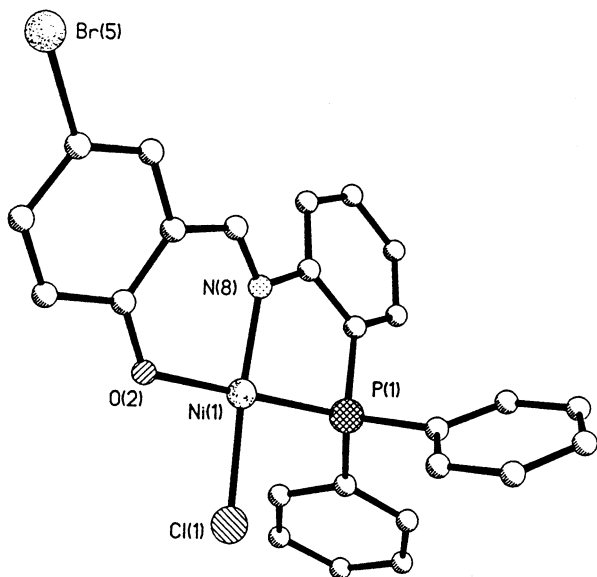[b] δ in ppm relative to external TMS.

Fig. 2. Crystal structure of [η^3(L^3)Ni(II)Cl] (**3**) (hydrogen atoms omitted for clarity).
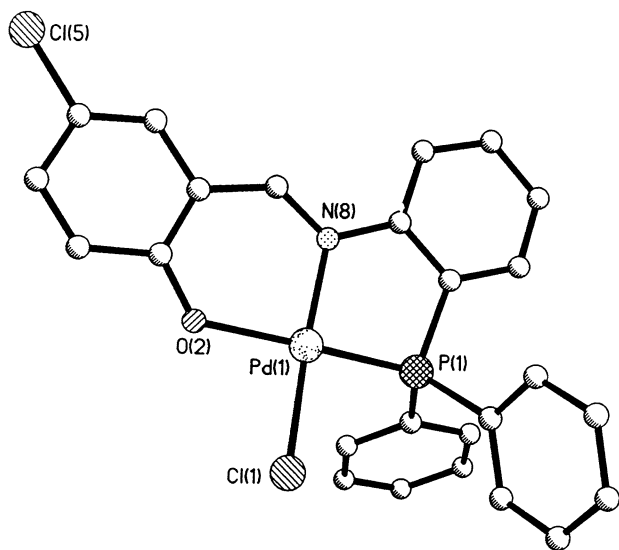

Fig. 3. Crystal structure of [η^3(L^2)Pd(II)Cl] (**6**) (hydrogen atoms omitted for clarity).

protonated free ligand, there is a strong intramolecular hydrogen-bonding interaction between the phenolic proton and the basic imine nitrogen, forming a pseudo six-membered ring. This can be observed in the solid state structures of such ligands and in their IR spectra [16]. When coordination to a metal centre displaces this proton, there is a change in the (C=N) stretching frequency, which depends upon the acidity of the proton in the free ligand and the Lewis acidity of the coordinated metal. In all the complexes **1**–**10** there is a shift to lower wavenumber with respect to the free ligand, suggesting an increase in the length of the (C=N) bond

brought about by an increased donation of electron density from the imine nitrogen to the nickel or palladium centres.

3.2. NMR spectroscopy

Selected NMR data (^{31}P{^{1}H}, ^{1}H) for **6**–**10** are collected in Table 4. For the complexes of Ni(II) **1**–**5** there were no NMR spectra observed, indicating that in solution these samples are paramagnetic. Since complexes of Ni(II), which have a square planar geometry are expected to be diamagnetic, this observation implies that these complexes are distorted from idealised geometry in solution. Inspection of the complex **3** in the solid state also indicates a somewhat distorted structure, which is in agreement with this observation.

The ^{31}P{^{1}H} NMR spectra show singlets for the Pd(II) complexes with a downfield shift of between 61.4 and 64.8 ppm on coordination. The values of ^{31}P chemical shift, both in the free ligands and in their complexes, are quite similar indicating that the substitution on the aldehyde fragment has little effect on the chemical shift. In the ^{1}H NMR spectra of the Pd(II) complexes, the azomethine proton is shifted downfield by between 0.23 and 0.76 ppm with respect to the free ligand value, and no intramolecular coupling of the imine proton with the ^{31}P nuclei was observed. The aromatic protons also show a similar shift on complexation, entirely consistent with expectations.

3.3. Single-crystal X-ray diffraction studies

The crystal structures of complexes **3** and **6** (Figs. 2 and 3; selected bond lengths and angles are presented in Table 2) reveal in general a square planar geometry at the metal atom with tridentate [P,N,O] coordination of the ligand, where the remaining bound chloride ligand is obligatorily disposed *trans* to N(1). The complexes **1**–**10** are neutral owing to the deprotonation of the oxygen atom of the tridentate ligand upon complexation.

Crystal structures **3** and **6** both exhibit distortions from idealised square planar geometry at the metal, probably due to the bulk of the phosphine group and to the bite angle of the P,N chelate. The *trans* O–M–P [179.11(7)–175.73(8)°] and *trans* N–M–Cl [175.59(7)–176.32(8)°] axes are less than 180° in both complexes, and the *cis* P–M–N and *cis* N–M–O angles are also principally dependent upon the sizes of the N,O and P,N chelate rings, so that *cis* N–M–O for **3** and **6**, which both comprise a six-membered N,O ring, are 93.40(9) and 93.91(10)°, respectively, both greater than 90°. The five-membered P,N chelate rings have concomitantly smaller P–M–N angles of 86.35(7) and 85.88(8)° and are indicative of the reduced bite presented by this smaller ring size.

4. Conclusions

Tridentate ligands derived from the condensation of 2-(diphenylphosphino)aniline and substituted salicyl-aldehydes are readily prepared and form stable complexes with Group 10 metals. From the number of Schiff-base ligands already known, it seems that there may be a great number of similar ligands which could be prepared using the approach outlined here, and a correspondingly large number of complexes with a range of properties available.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre as nos. CCDC 136356 (**3**) and CCDC 136357 (**6**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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