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Nickel(II), Palladium(II) and Platinum(II) Dichloro Complexes Containing Optically Active Diphosphines

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The preparation of new square-planar nickel(II), palladium(II) and platinum(II) dichloro complexes containing (R)-1,2-bis(diphenylphosphino)propane (R-prophos) (2S,3S)2,3-bis(diphenylphosphino)butane (S,S-chiraphos) and (R)-1,2-bis(diphenylphosphino)-1-phenylethane (R-phephos) is reported. The complexes have been characterized by elemental analysis, electronic, CD, infrared and ^{1}H- and ^{31}P-NMR spectral measurements.

Introduction

Rhodium complexes containing optically active diphosphines have been extensively investigated in view of their efficiency in asymmetric hydrogenation [1–9]. Similar chiral complexes of other transition metals, however, have been much less studied despite their increasing importance in other examples of catalytic homogeneous asymmetric reactions [10, 11]. In the line of our investigations in asymmetric hydroformylation catalyzed by rhodium and platinum [12] and in asymmetric cross-coupling reactions catalyzed by nickel and palladium [13–15] using chiral homologs of 1,2-bis(diphenylphosphino)ethane as the asymmetric ligands, we report on the synthesis and characterization of complexes of the type $MCl_2(\overset{\frown}{L\,L})$, where M is nickel(II), palladium(II) and platinum(II) and $\overset{\frown}{L\,L}$ is (R)-1,2-bis(diphenylphosphino)propane (R-prophos) [16], (2S,3S)2,3-bis(diphenylphosphino)butane (S,S-chiraphos) [17] and (R)-1,2-bis(diphenylphosphino)-1-phenylethane (R-phephos) [18].

Results and Discussion

The complexes I–IX were prepared with a slight modification of the method previously described in the literature [19].

The complexes are indefinitely stable both in solution and in the solid state and behave as non-electrolytes at 25 °C in dichloromethane solution ($C \cong 10^{-3}$ *M*).

Moreover, the molecular weight measurements are in reasonable agreement with the formation of a monomer. The poor solubilities of the complexes II, V and VII rule out the determination of molecular weight.

The stretching vibrations due to ν(M–Cl) were found in the region between 360 and 280 cm^{-1} depending on the metal used. These values are typical of monomeric square-planar *cis*-dichloro complexes of nickel(II), palladium(II) and platinum(II) containing diphosphine ligands [19, 20].

The ^{1}H-NMR data of the nine complexes are similar to those of the free ligands (see experimental section).

However, the low field ^{1}H-NMR spectra of the complexes show a common, peculiar pattern, two protons of the phenyl groups experiencing an anisotropic deshielding compared to the others. For example, the ^{1}H-NMR spectrum of the free diphosphine (R)-prophos shows the aromatic protons as a complex multiplet centered at 2.8 τ (20 H), while the resonance pattern of the phenyl protons of the complex I consists of two complex multiplets centered at 1.9 τ (2 H) and 2.6 τ (18 H).

The complexes III, VI and IX containing the (R)-phephos diphosphine show a further peculiarity, arising from the upfield shielding of two other aromatic protons. It is reasonable to presume that this upfield resonance can be due to two protons of the phenyl group being bound to the backbone.

These observed patterns are similar to those reported for analogous complexes of iridium(III), rhodium(I) and platinum(II) [4, 21–23]. The ^{31}P-NMR data are shown in Table I.

It is well known that the phosphorus atoms belonging to a five-membered chelate ring exhibit an 'anomalously' large coordination chemical shift, Δ_{obs}, which can be considered as being made up of the expected chemical shift calculated from the relation $\Delta = A\delta + B$ [24] together with a 'ring contribu-

TABLE I. ^{31}P-NMR Data for Diphosphines and their Complexes with Ni(II), Pd(II) and Pt(II).[a]

		P_A				P_B				
		δ	Δ_{obs}	Δ_R	J_{Pt-P}	δ	Δ_{obs}	Δ_R	J_{Pt-P}	J_{PP}
	$Ph_2P_ACH(CH_3)CH_2P_BPh_2$	0.2	–	–	–	–22.0	–	–		20.1
	$Ph_2P_ACH(CH_3)CH(CH_3)P_BPh_2$	–10.7	–	–	–	–10.7	–	–		–
	$Ph_2P_ACH(Ph)CH_2P_BPh_2$	1.6	–	–	–	–23.0	–	–		16.4
I	$NiCl_2[Ph_2P_ACH(CH_3)CH_2P_BPh_2]$	62.1	61.9	40.5	–	44.0	66.0	37.3		76.9
II	$NiCl_2[Ph_2P_ACH(CH_3)CH(CH_3)P_BPh_2]$	57.7	68.4	43.4	–	57.7	68.4	43.4		–
III	$NiCl_2[Ph_2P_ACH(Ph)CH_2P_BPh_2]$	66.3	64.7	43.5	–	38.0	61.0	32.0		82.4
IV	$PdCl_2[Ph_2P_ACH(CH_3)CH_2P_BPh_2]$	70.6	70.4	32.4	–	52.2	74.2	29.2		5.5
V	$PdCl_2[Ph_2P_ACH(CH_3)CH(CH_3)P_BPh_2]$	64.5	75.2	33.7	–	64.5	75.2	33.7		–
VI	$PdCl_2[Ph_2P_ACH(Ph)CH_2P_BPh_2]$	73.0	71.4	33.8	–	42.5	65.5	20.2		4.5
VII	$PtCl_2[Ph_2P_ACH(CH_3)CH_2P_BPh_2]$	47.4	47.2	28.1	3603	30.2	52.2	26.2	3567	7.3
VIII	$PtCl_2[Ph_2P_ACH(CH_3)CH(CH_3)P_BPh_2]$	40.6	51.3	29.0	3527	40.6	51.3	29.0	3527	–
IX	$PtCl_2[Ph_2P_ACH(Ph)CH_2P_BPh_2]$	49.2	47.6	29.3	3581	21.4	44.4	18.1	3538	11.0

[a] In CD_2Cl_2 solution.

tion' ΔR, *i.e.* $\Delta_{obs} = \Delta + \Delta_R$ [25]. We have used for A and B the values recently reported for analogous nickel(II), palladium(II) and platinum(II) complexes containing unsymmetrical *cis*-diphosphino alkenes [26].

The assignment of the resonance for the free (R)-prophos and for the complexes containing it was made through selective ^{1}H decoupling of the ^{31}P-NMR spectra.

The assignment for (R)-phephos has already been reported [18]. From an inspection of the data of Table I, it can be observed that the Δ_R values decrease on going from nickel, to palladium and finally to platinum complexes. This behaviour agrees with a general trend observed for analogous types of complexes [26]. Furthermore, for a given metal, the Δ_R values for the P_A atoms of the coordinated diphosphines are rather similar, whereas those for the P_B atoms differ much more from each other, the largest difference being observed for each metal when (R)-phephos is the chelate ligand.

The observed J_{PP} coupling constants in the complexes containing the (R)-prophos and (R)-phephos agree well with the general trend previously observed for analogous complexes containing saturated diphosphines or unsymmetrical *cis*-diphosphino alkenes [26, 27].

The UV-visible and CD spectral data are reported in Table II. It seems to be generally agreed that spin-allowed d–d metal transition are responsible for the low energy bands observable in the spectra of I–IX complexes [28]. The higher energy bands could be attributed to a ligand-to-metal charge-transfer transition, but until now there appears to have been little or no attempt to assign them [29].

For nickel-complexes (I–III), in the range between 390 and 680 nm, in correspondence with a broader absorption band, it is possible to observe in CD spectra three bands, which have signs that seem to be connected to chirality of the ligands.

In I and III complexes, where the absolute configuration of the chiral centre of the ligand is R, upon going to higher energy, the first (520–530 nm) and third (390–400 nm) bands are positive and the second one (458–463 nm) is negative. In contrast, in the complex II, where two optically active carbon atoms of S,S absolute configuration are present, an opposite trend was recorded*. Also in palladium and platinum complexes (IV–IX) it is possible to observe the same correlation between the sign of the CD bands due to d–d metal transition and the absolute configuration of the chiral centres in the ligand.

This observation may be useful for assigning absolute configuration of chiral carbon atoms in analogous types of ligands.

The overreported full characterization of optically active diphosphine complexes of nickel(II), palladium(II) and platinum(II), could give in our opinion useful information in the identification of chiral organometallic intermediates which might be isolated in asymmetric reactions.

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*It is to note that in the case of the $NiCl_2$(norphos)[norphos=bicyclo [2,2,1] hept-5-ene-2,3-diylbis(diphenylphosphine)] [30] having two optically carbon atoms of R,R absolute configuration, the CD spectra bands have the same signs of those of complexes I and III, in which only one centre of R absolute configuration is present [31].

TABLE II. Absorption and CD Spectral Data for the Complexes $MCl_2(\widehat{LL})$.[a]

M $\widehat{LL}$	(R)-prophos		(S,S)-chiraphos		(R)-phephos	
	UV-visible λ_{max}, nm (ϵ/mol^{-1} dm^3 cm^{-1})	CD λ_{max}, nm ($\Delta\epsilon$/mol^{-1} dm^3 cm^{-1})	UV-visible λ_{max}, nm (ϵ/mol^{-1} dm^3 cm^{-1})	CD λ_{max}, nm ($\Delta\epsilon$/mol^{-1} dm^3 cm^{-1})	UV-visible λ_{max}, nm (ϵ/mol^{-1}, dm^3 cm^{-1})	CD λ_{max}, nm ($\Delta\epsilon$/mol^{-1} dm^3 cm^{-1})
Ni		530 (+0.91)		528 (−1.39)		520 (+0.99)
	465 (1600)	463 (−2.08)	460 (1550)	460 (+2.61)	460 (1570)	458 (−1.63)
		398sh (+0.10)		390sh (−0.22)		400 (+0.18)
	320sh (–)	327 (+5.40)	315sh (–)	327 (−7.56)	320sh (–)	326 (+5.64)
		302sh (−5.61)		302sh (+9.00)	290 (20500)	295 (+10.72)
	285 (8100)	280 −(22.53)	285 (8900)	280 (+30.15)		277 (−9.30)
		250 (+15.81)		248 (−17.10)		258 (+16.36)
						239 (−5.36)
Pd	340 (7200)	355 (+1.31)	335 (7250)	355 (−2.33)	335 (7250)	345 (+4.84)
		317 (−3.02)		315 (+4.98)		315 (−0.50)
		295 (+3.29)		294 (−6.85)		294 (+8.77)
	265 (27000)	275 (−15.78)	265 (26500)	273 (+29.92)	265 (22000)	255 (+23.20)
				262sh (+8.10)		
Pt		345 (+0.11)		346 (−0.29)		340 (+0.14)
	305 (2900)	315 (−0.72)	305 (3100)	315 (+1.66)	300sh (3100)	315 (−0.45)
		285 (+0.45)		285 (−0.99)		285sh (+2.72)
	275sh (–)	278 (−0.23)	275sh (–)	278 (+1.69)	275sh (–)	274 (+5.98)
	268sh (–)	271 (−1.15)	268sh (–)	270 (+3.18)	268sh (–)	266 (+6.33)
	255 (21500)	255 (+5.76)	255 (20000)	255 (−18.22)	252sh (19000)	255 (+10.52)
		238 (−13.01)		238 (+19.10)		230 (+21.20)

[a] In CH_2Cl_2 solution.

Experimental

The solvents used were 'puriss' grade quality and were dried and degassed before use. Melting points were determined on a Tottoli-apparatus and are uncorrected. Molecular weights were measured in CH_2Cl_2 solution with a Mechrolab vapor-phase Osmometer Model 301B. IR spectra were recorded on a 457 Perkin Elmer spectrometer using Nujol mulls on CsI plates.

Absorption and CD spectra were obtained using a Cary 14 spectrophotometer and a JASCO J-40AS dichrograph respectively. ^1H-NMR spectra were recorded at 60 MHz with an FT-WP 60 Brucker spectrometer in CD_2Cl_2 solution using TMS as internal standard. ^{31}P-NMR spectra were registered at 24.28 MHz in CH_2Cl_2/CD_2Cl_2 solutions with ^1H complete decoupling: 85% H_3PO_4 was used as external standard, with the convention that increasing frequency is positive. $PdCl_2(C_6H_5CN)_2$ and $PtCl_2(C_6H_2CN)_2$ were prepared by literature method [32].

All reactions were carried out under dry nitrogen.

Preparation of Optically Active Diphosphines

The diphosphines were prepared according to the published methods.

(R)-1,2-bis(diphenylphosphino)propane (R-prophos) [16]

^1H-NMR: 2.73–2.85 τ (m., 20H, C_6H_5); 7.53–8.40 τ (complex m., 3H, CH + CH_2); 8.79 τ (d.d., 3H, CH_3; J_{HH} = 6.4 Hz, J_{PH} = 15.6 Hz).

(2S,3S)2,3-bis(diphenylphosphino)butane (S,S-chiraphos) [17]

^1H-NMR: 2.8 τ (m, 20H, C_6H_5); 7.30–7.94 τ (m, 2H, CH); 8.94 τ (d.d., 6H, CH_3; J_{HH} = 6.8 Hz. J_{PH} = 13.7 Hz).

(R)-1,2-bis(diphenylphosphino)-1-phenylethane (R-phephos) [18]

^1H-NMR: 2.70–2.94 τ (complex m., 25H, C_6H_5); 6.58–6.99 τ (complex m., 1H, CH); 7.41–7.68 τ (complex m., 2H, CH_2).

Preparation of the Complexes

$NiCl_2[Ph_2PCH(CH_3)CH_2PPh_2]$, I

A solution of (R)prophos (1.7 g, 4.2 mmol) in dichloromethane (10 ml) was added to a stirred solution of 1.0 g (4.2 mmol) of $NiCl_2 \cdot 6H_2O$ in ethyl alcohol (30 ml). In a few minutes a precipitate was formed which was filtered off and washed with ethanol. The product was purified by recrystallization from CH_2Cl_2/C_2H_5OH to give (yield 85%) orange–red crystals of I, m.p. 283 °C dec. *Anal.* Calcd. for $C_{27}H_{26}P_2Cl_2Ni$: C, 59.83%; H, 4.83%; P, 11.43%; Cl, 13.10%. Found: C, 59.84%; H, 4.97%; P, 9.54%; Cl, 13.08%. M. wt: calcd. 542; found 554. IR: ν(Ni–Cl) = 320, 360 cm^{-1}. ^1H-NMR: 1.5–2.8 τ (complex m., 20H, C_6H_5); 7.4–8.1 τ (complex m., 3H, CH + CH_2); 9.1 τ (d.d., 3H, CH_3; J_{HH} = 6.4 Hz J_{PH} = 13.3 Hz).

$NiCl_2[Ph_2PCH(CH_3)CH(CH_3)PPh_2]$, II

This complex was prepared as I. The crude product was recrystallized from CH_2Cl_2/C_2H_5OH. The yield of pure orange–red microcrystalline powder was 80%, m.p. >320 °C.

Anal. Calc. for $C_{28}H_{28}P_2Cl_2Ni$: C, 60.48%; H, 5.08%; P, 11.14%; Cl, 12.75%. Found: C, 60,82%; H, 5.20%; P, 9.66%; Cl, 12.46%. IR: ν(Ni–Cl) = 318, 362 cm^{-1}. ^1H-NMR: 1.6–2.7 τ (complex m., 20H, C_6H_5); 7.9 τ (m., 2H, CH); 9.2 τ (m., 6H, CH_3).

$NiCl_2[Ph_2PCH(Ph)CH_2PPh_2]$, III

This complex was prepared as I and a yield of 85% of orange–red crystals was obtained; m.p. >320 °C.

Anal. Calc. for $C_{32}H_{28}P_2Cl_2Ni$: C, 63.62%; H, 4.67%; P, 10.25%; Cl, 11.74%. Found: C, 62.94%; H, 4.82%; P, 8.36%; Cl, 12.07%. M.wt.: calc. 604; found 594. IR: ν(Ni–Cl) = 335, 355 cm^{-1}. ^1H-NMR: 1.4–3.5 τ (complex m., 25H, C_6H_5); 6.4 τ (complex m., 1H, CH); 7.6 τ (complex m., 2H, CH_2).

$PdCl_2[Ph_2PCH(CH_3)CH_2PPh_2]$, IV

A solution of 1.1 (2.6 mmol) of (R)-prophos in CH_2Cl_2 was added to a solution of 1.0 g (2.6 mmol) of $PdCl_2(C_6H_5CN)_2$. The reaction mixture was stirred for 1 hr and then by addition of ethanol a pale–yellow compound was precipitated which was separated by filtration. The crude product was purified by recrystallization from CH_2Cl_2/CH_3OH (yield 70%, m.p. >320 °C.

Anal. Calc. for $C_{27}H_{26}P_2Cl_2Pd$: C, 54.99%; H, 4.44%; P, 10.50%; Cl, 12.10%. Found: C, 54.71%; H, 4.31%; P, 9.83%; Cl, 12.54%. M.wt.: calc. 589; found 604. IR: ν(Pd–Cl) = 285 sh, 305 cm^{-1}. ^1H-NMR: 2.0–2.7 τ (complex m., 20H, C_6H_5); 7.2–7.9 τ (complex m., 3H, CH + CH_2); 9.1 τ (d.d., 3H, CH_3; J_{HH} = 6.4 Hz, J_{PH} = 13.7 Hz).

$PdCl_2[Ph_2PCH(CH_3)CH(CH_3)PPh_2]$, V

This complex was prepared as IV. The purification of the crude was carried out by recrystallization from CH_2Cl_2/CH_3OH (yield 70%), m.p. 265 °C dec.

Anal. Calc. for $C_{28}H_{28}P_2Cl_2Pd$: C, 55.70%; H. 4.67%; P, 10.26%; Cl, 11.74%. Found: C, 55.52%; H, 5.00%; P, 9.99%; Cl, 12.80%. IR: ν(Pd–Cl) = 290, 325 cm^{-1}. ^1H-NMR: 1.9–2.9 τ (complex m., 20H, C_6H_5); 7.7 τ (m., 2H, CH); 9.0 τ (d.d., 6H, CH_3; J_{HH} = 6.8 Hz J_{PH} = 13.3 Hz).

$PdCl_2[Ph_2PCH(Ph)CH_2PPh_2]$, *VI*

As the complex IV, this was prepared from 2.6 mmol of (R)phephos and 2.6 mmol of $PdCl_2(C_6H_5CN)_2$ in 15 ml of CH_2Cl_2. Recrystallization from CH_2Cl_2/CH_3OH gave a pale–yellow crystalline compound in 75% yield, which crystallize with 0.75 CH_2Cl_2, m.p. >320 °C.

Anal. Calc. for $C_{32}H_{28}P_2Cl_2Pd{\cdot}0.75CH_2Cl_2$: C, 55.03%; H, 4.16%; P, 8.67%; Cl, 17.36%. Found: C, 55.30%; H, 4.22; P, 8.19%; Cl, 16.97%. M. wt.: calc. (unsolvated complex) 651; found 605. I.R.: ν(Pd–Cl) = 285, 305 cm^{-1}. ^{1}H-NMR: 1.5–3.4 τ (complex m., 25H, C_6H_5); 5.8–7.9 τ (complex m., 3H, CH + CH_2).

$PtCl_2[Ph_2PCH(CH_3)CH_2PPh_2]$, *VII*

A solution of 2.12 mmol of (R)prophos in dichloromethane was added to a solution of 1 g (2.12 mmol) of $PtCl_2(C_6H_5CN)_2$ in 10 ml of CH_2Cl_2 at room temperature. The reaction mixture was stirred for 1 hr and after addition of 20 ml of CH_3OH a microcrystalline white precipitate was formed which was separated by filtration and recrystallized from CH_2Cl_2/CH_3OH. (70% yield), m.p. >320 °C.

Anal. Calc. for $C_{27}H_{26}P_2Cl_2Pt$: C, 47.80%; H, 3.86%; P, 9.13%; Cl, 10.46%. Found: C, 46.99%; H, 3.89%; P, 7.30%; Cl, 11.53%. M.wt.: calc. 678; found 644. I.R.: ν(Pt–Cl) = 290, 305 cm^{-1}. ^{1}H-NMR: 2.0–2.9 τ (complex m., 20H, C_6H_5); 7.0–8.3 τ (complex m., 3H, CH + CH_2); 9.1 τ (d.d., 3H, CH_3; J_{HH} = 6.4 Hz, J_{PH} = 14.2 Hz).

$PtCl_2[Ph_2PCH(CH_3)CH(CH_3)PPh_2]$, *VIII*

This complex was prepared as VII. The crude product was recrystallized from CH_2Cl_2/CH_3OH. The yield of pure white crystals of VIII was 65%, m.p. >320 °C.

Anal. Calc. for $C_{28}H_{28}P_2Cl_2Pt$: C, 48.56%; H, 4.07%; P, 8.94%; Cl, 10.24%. Found: C, 48.02%; H, 4.08%; P, 7.74%; Cl, 10.71%. I.R.: ν(Pt–Cl) = 290, 320 cm^{-1}. ^{1}H-NMR: 1.9–2.9 τ (complex m., 20 H, C_6H_5); 7.7 τ (complex m., 2H, CH); 9.0 τ (complex m., 6H, CH_3).

$PtCl_2[Ph_2PCH(Ph)CH_2PPh_2]$, *IX*

This complex was prepared as VII and a yield of 70% of IX, as white crystals, was obtained; m.p. >320 °C.

Anal. Calc. for $C_{32}H_{28}P_2Cl_2Pt$: C, 51.90%; H, 3.81%; P, 8.37%; Cl, 9.57%. Found: C, 51.10%; H, 3.90%; P, 7.60%; Cl, 9.52%. M. wt.: calc. 740; found 714. I.R.: ν(Pt–Cl) = 285, 318 cm^{-1}. ^{1}H-NMR = 1.7–3.6 τ (complex m., 25 H, C_6H_5); 5.9–7.7 τ (complex m., 3H, CH + CH_2).

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