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Ruthenium hydride complexes of chiral and achiral diphosphazane ligands and asymmetric transfer hydrogenation reactions ☆

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Dedicated to our colleague M. Raja (Late), whose sudden demise had snatched away from our midst a promising young researcher.

Abstract

The half-sandwhich ruthenium chloro complexes bearing chelated diphosphazane ligands, $[(\eta^5\text{-Cp})RuCl\{\kappa^2\text{-P,P-}(RO)_2PN(Me)\text{-}P(OR)_2\}]$ [R = $C_6H_3Me_2$-2,6] (**1**) and $[(\eta^5\text{-Cp}^*)RuCl\{\kappa^2\text{-P,P-}X_2PN(R)PYY'\}]$ [R = Me, X = Y = Y′ = OC_6H_5 (**2**); R = $CHMe_2$, $X_2 = C_{20}H_{12}O_2$, Y = Y′ = OC_6H_5 (**3**) or $OC_6H_4{}^tBu$-4 (**4**)] have been prepared by the reaction of $CpRu(PPh_3)_2Cl$ with $(RO)_2PN(Me)\text{-}P(OR)_2$ [R = $C_6H_3Me_2$-2,6 (**L**^{1})] or by the reaction of $[Cp^*RuCl_2]_n$ with $X_2PN(R)PYY'$ in the presence of zinc dust. Among the four diastereomers (two enantiomeric pairs) possible for the "chiral at metal" complexes **3** and **4**, only two diastereomers (one enantiomeric pair) are formed in these reactions. The complexes **1**, **2**, **4** and $[(\eta^5\text{-Cp})RuCl\{\kappa^2\text{-P,P-Ph}_2PN((S)\text{-}^*CHMePh)PPhY\}]$ [Y = Ph (**5**) or $N_2C_3HMe_2$-3,5 ($S_CS_PR_{Ru}$)-(**6**)] react with NaOMe to give the corresponding hydride complexes $[(\eta^5\text{-Cp})RuH\{\kappa^2\text{-P,P-}(RO)_2PN(Me)\text{-}P(OR)_2\}]$ (**7**), $[(\eta^5\text{-Cp}^*)RuH\{\kappa^2\text{-P,P′-}X_2PN(R)PY_2\}]$ [R = Me, X = Y = OC_6H_5 (**8**); R = $CHMe_2$, $X_2 = C_{20}H_{12}O_2$, Y = $OC_6H_4{}^tBu$-4 (**9**)] and $[(\eta^5\text{-Cp})RuH\{\kappa^2\text{-P,P-Ph}_2PN((S)\text{-}^*CHMePh)PPhY\}]$[Y = Ph (**10**) or $N_2C_3HMe_2$-3,5 ($S_CS_PR_{Ru}$)-(**11a**) and ($S_CS_PS_{Ru}$)-(**11b**)]. *Only one enantiomeric pair* of the hydride **9** is obtained from the chloro precursor **4** that bears sterically bulky substituents at the phosphorus centers. On the other hand, the optically pure trichiral complex **6** that bears sterically less bulky substituents at the phosphorus gives a mixture of *two diastereomers* (**11a** and **11b**). Protonation of complex **7** using different acids (HX) gives a mixture of $[(\eta^5\text{-Cp})Ru(\eta^2\text{-H}_2)\{\kappa^2\text{-P,P-}(RO)_2PN(Me)P(OR)_2\}]X$ (**12a**) and $[(\eta^5\text{-Cp})Ru(H)_2\{\kappa^2\text{-P,P-}(RO)_2PN(Me)P(OR)_2\}]X$ (**12b**) of which **12a** is the major product independent of the acid used; the dihydrogen nature of **12a** is established by T_1 measurements and also by synthesizing the deuteride analogue **7-D** followed by protonation to obtain the **D–H** isotopomer. Preliminary investigations on asymmetric transfer hydrogenation of 2-acetonaphthone in the presence of a series of chiral diphosphazane ligands show that diphosphazanes in which the phosphorus centers are strong π-acceptor in character and bear sterically bulky substituents impart moderate levels of enantioselectivity. Attempts to identify the hydride intermediate involved in the asymmetric transfer hydrogenation by a model reaction suggests that a complex of the type, $[Ru(H)(Cl)\{\kappa^2\text{-P,P-}X_2PN(R)PY_2\}(solvent)_2]$ could be the active species in this transformation.

Keywords: Diphosphazanes; Half-sandwich complexes; Ruthenium; Hydride complexes; Asymmetric transfer hydrogenation; Catalysis

1. Introduction

The characterization and isolation of coordinatively and electronically unsaturated, highly reactive and therefore short-lived transition metal complexes is an area of considerable interest owing to their importance as key intermediates in various homogeneous catalytic processes such as hydrogenation, hydrosilylation, hydroformylation and

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transfer-hydrogenation reactions [1,2]. Among the various catalytic transformations, ruthenium catalyzed asymmetric transfer hydrogenation has evoked considerable interest [2]. Experimental and theoretical studies reveal that the reaction proceeds *via* the formation of a catalytically active metal–hydride species [3–5]. Several research groups have been working on the design of novel ligands for the ruthenium catalyzed transfer hydrogenation of ketones and the chiral variations thereof to achieve high levels of enantioselectivity. A range of transition metal complexes bearing homo- and hetero-donor P–P [6], N–N [6a,7], P–N [8], N–O [9] ligands, terdentate ligands [10] and mixed homo-donor ligands [11] have been reported and their efficiency in transfer hydrogenation investigated. Since the active catalyst or pre-catalyst involves a ruthenium hydride species, the continuing interest could be attributed to the quest to characterize and isolate the hydride intermediates involved in these reactions by fine-tuning the steric and electronic properties of the ancillary ligands. The catalytic species is usually generated *in situ* in the reaction medium from a stable Ru(II) species such as $[RuCl_2(PPh_3)_3]$ or $[RuCl_2(DMSO)_4]$ and the chiral auxiliary.

Recently we reported the synthesis of cyclopentadienyl ruthenium complexes of chiral and achiral diphosphazane ligands [12a]. In continuation of our interest [12a–d] in the organometallic chemistry of diphosphazane ligands [13], we report herein the ruthenium(II) hydride complexes of chiral and achiral diphosphazanes and preliminary investigations on ruthenium catalyzed asymmetric transfer hydrogenation of 2-acetonaphthone in the presence of chiral diphosphazanes.

2. Experimental

2.1. General

All reactions and manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk and vacuum-line techniques. The solvents were purified by standard procedures and distilled under nitrogen prior to use. The NMR spectra (^1H and $^{31}P\{^1H\}$) were recorded in $CDCl_3$ at 298 K using Bruker ACF-200, Bruker AMX-400 or Bruker Avance-400 spectrometers. Elemental analyses were carried out using a Perkin–Elmer 2400 CHN analyser. Melting points were recorded in a Buchi B-540 melting point apparatus and were uncorrected.

The diphosphazane ligands $X_2PN(R)PY_2$ [R = Me, X = Y = OC_6H_5 (**L**^{2}) [14a]; R = $CHMe_2$, $X_2 = C_{20}H_{12}O_2$, Y = OC_6H_5 (**L**^{3}) or $OC_6H_4{}^tBu$-4 (**L**^{4}) [12b]; X = Y = Ph, R = (*S*)-*CHMePh(**L**^{5}) [14b] or $CHMe_2$ (**L**^{6}) [14c]; R = Me, $X_2 = Y_2$ = (*R*) or (*S*)-$C_{20}H_{12}O_2$ (**L**^{7}) [14d] and R = $CHMe_2$, X_2 = (*R*) or (*S*)-$C_{20}H_{12}O_2$, Y = C_6H_5 (**L**^{8}) [14e]; (S_CR_P)-Ph_2PN((*S*)-*CHMePh)P(Ph)($N_2C_3HMe_2$-3,5) (**L**^{9}) [14b], the complexes $[(\eta^5\text{-Cp})RuCl\{\kappa^2\text{-P,P-}X_2PN((S)\text{-}^*CHMePh)PYY'\}]$ [X = Y = Ph, Y′ = Ph (**5**) or $N_2C_3HMe_2$-3,5 ($S_CS_PR_{Ru}$)-(**6**)] [12a] and the starting materials $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$ [15a] (Cp = cyclopentadienyl), $[RuCl_2(PPh_3)_3]$ [15b] and $[RuCl_2(COD)]_n$ [15c] were prepared according to literature methods. $MeN(PCl_2)_2$ was prepared according to Nixon's procedure [16]. $[Cp^*RuCl_2]_n$ (Cp^* = pentamethyl cyclopentadienyl), CF_3SO_3H, $HBF_4 \cdot Et_2O$, CD_3OD, 2,2′-bipyridine, CF_3SO_3Ag, $P(OPh)_3$ (Aldrich), 2,6-dimethyl phenol (Merck) and $P(OMe)_3$ (local source) were used as received.

Table 1
Yields, melting points and CHN analysis for the compounds synthesized in the present study

Compound	Yield	MP	Elemental analysis[a]		
			C (%)	H (%)	N (%)
L^1	61	152 (d)	69.6 (68.8)	7.2 (6.8)	3.2 (2.4)
1	25	182 (d)	58.4 (58.7)	5.9 (5.7)	2.4 (1.8)
2	30	178 (d)	57.1 (57.2)	5.2 (5.2)	2.1 (1.9)
3	30	180 (d)	62.8 (62.7)	5.0 (5.1)	1.8 (1.6)
4	35	182 (d)	65.5 (65.6)	6.3 (6.3)	1.4 (1.3)
7	45	175 (d)	61.2 (61.4)	6.0 (6.1)	2.1 (1.9)
10	70	–	67.8 (67.7)	5.3 (5.4)	2.2 (2.1)
14	60	130 (d)	68.6 (68.8)	5.2 (5.3)	2.4 (2.5)
18	<10%	190 (d)	57.0 (57.1)	5.2 (5.2)	4.5 (4.7)
19	80	180 (d)	59.6 (59.9)	4.9 (5.0)	1.7 (2.1)
20	80	184 (d)	64.2 (64.3)	4.3 (4.4)	1.5 (1.8)

[a] Calculated values are in parentheses.

The yields, melting points and elemental analyses for the compounds synthesized in the present study are listed in Table 1. The spectroscopic data for the compounds and the results of HPLC studies are presented in Tables 2–4.

2.2. Synthesis of $(RO)_2PN(Me)P(OR)_2$ [R = $C_6H_3Me_2$-2,6] (**L**^{1}) [17]

A benzene (60 cm^3) solution of $Cl_2PN(Me)PCl_2$ (2.33 g, 0.01 mol) was added dropwise to a benzene (60 cm^3) solution of 2,6-dimethylphenol (4.88 g, 0.04 mol) and triethylamine (8.4 cm^3, 0.06 mol) at 0 °C over a period of 15 min. The reaction mixture was stirred at 25 °C for 24 h and heated under reflux for 8 h. The precipitate of $Et_3N \cdot HCl$ was filtered and solvent evaporated from the filtrate in *vacuo* to obtain a light yellow oily residue which was purified by column chromatography using benzene/petrol (1:1 v/v). Evaporation of the eluant yielded the title compound as a colorless oil. The oil was dissolved in dichloromethane–petrol and the solution cooled to 0 °C to obtain a colorless solid. Traces of unreacted phenol adhering to the solid could be removed by triturating the product with petrol. Single crystals of the compound suitable for X-ray diffraction were obtained by slow evaporation of a toluene solution of the compound.

2.3. Synthesis of $[(\eta^5\text{-Cp})RuCl\{\kappa^2\text{-P,P-}(RO)_2PN(Me)P(OR)_2\}]$ [R = $C_6H_3Me_2$-2,6] (**1**)

A 100 cm^3 double necked flask was charged with a mixture of $(\eta^5\text{-Cp})Ru(PPh_3)_2Cl$ (0.200 g, 0.203 mmol) and the ligand **L**^{1} (0.117 g, 0.203 mmol) under nitrogen atmosphere. The mixture was dissolved in benzene (50 cm^3) and the solu-