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Optically active complexes of transition metals (Rh^I, Ru^{II}, Co^{II} and Ni^{II}) with 2-aminocarbonylpyrrolidine ligands. Selective catalysts for hydrogenation of prochiral olefins

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Abstract

The synthesis and characterization of optically active complexes containing organic amides [–C(O)NHR] of the type [RhCl(COD)L], [$RhCl(CO)_2L$], [$RhCl(PPh_3)_2L$], [$RuCl_2(COD)L$], [$RuCl_2(PPh_3)_2L$], [Co(acac)L]X and [Ni(acac)L]X, where L = (*S*)-2-*t*-butylaminocarbonylpyrrolidine or (*S*)-2-(3-triethoxysilyl)propylaminocarbonylpyrrolidine are reported. Their cationic species were prepared in the presence of a non-coordinating counterion (X = PF_6^- or ClO_4^-). The amino acid derivative is bi-dentate with *N,N*-coordination. The metal complexes with ligands containing the triethoxysilyl group, were anchored to silica and modified USY-zeolite. These complexes have been characterized by spectroscopic and analytical techniques. The complexes anchored to the zeolite, which contains profuse supermicropores, show a higher activity for alkene hydrogenation and produce a remarkable increase of enantioselectivity ($>95\%$) in the hydrogenation of ethyl (*Z*)-α-benzoylaminocinnamate, taken as a model, and they represent a truly heterogeneous counterpart of the homogeneous organometallic catalysts.

Introduction

Transition-metal promoted asymmetric synthesis has a role of outstanding importance in organic chemistry [1]. In enantioselective catalysis with transition-metal compounds, the optical activity in the organic products to be synthesized derives from the ligands used. Although ligands which bind to the metal by P atoms still dominate the field (P–P type) [2], there are promising developments of ligands which bind to the metal atom by N atoms (N–N type) [3], (N–O type) [4], and to a lesser extent also by S or O atoms [5]. A compilation of ligands useful for enantioselective catalysis is given in ref. 2. Amino acids form the biggest pool of compounds and are used more and more frequently as auxiliary argents in

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asymmetric synthesis; as ligands, amino acids are of interest because of their biological importance and the variety of metal coordination modes they can display [6].

Optically active transition metal compounds can be anchored to surface-rich supports [7], so that they do not dissolve during catalysis. Frequently, these immobilized compounds give an optical induction similar to their soluble counterparts. Heterogenized homogeneous catalysts combine the properties of heterogeneous and homogeneous catalysts [8], although a heterogenized homogeneous catalyst may lose its activity and enantioselectivity owing to metal leaching [9].

In this work we report the preparation and characterization of neutral and cationic complexes of transition metals (Rh, Ru, Co, Ni) with *N*-donor chiral ligands derived from the L-proline. These chiral ligands have been functionalized with silane groups capable of being anchored to inorganic supports (silica and modified USY zeolites) with silanols on the surface, or into micro- and meso-pores.

Tests of their catalytic activity for the enantioselective hydrogenation of ethyl (*Z*)-α-benzoylaminocinnamate, selected as a model, have been made, and oxidation and alkylation studies are in progess.

Experimental

Reactions were carried out under oxygen-free dinitrogen by Schlenk-tube techniques. C, H and N analyses were carried out by the Analytical Department of the Institute of Organic Chemistry (C.S.I.C.) with a Heraeus apparatus. Metal contents were determined by atomic absorption in a Unicam (SP9) Philips apparatus. Infrared spectra were recorded with Nicolet XR60 and Perkin Elmer 681 spectrophotometers (range 4000–200 cm^{-1}). ^1H and ^{13}C NMR spectra were recorded on Varian XR300 and Bruker 200 spectrometers; chemical shifts are given in ppm with tetramethylsilane as internal standard. Optical rotation values were measured with a Perkin Elmer 241 MC polarimeter. The precursors $[\{RhCl(COD)\}_2]$ [10], $[\{RhCl(CO)_2\}_2]$ [11], $[RhCl(PPh_3)_3]$ [12], $[\{RuCl_2(COD)\}_n]$ [13*], $[RuCl_2(PPh_3)_3]$ [14] and $[Co(acac)_2]$ [15] were prepared by published methods. $[Ni(acac)_2]$ was a commercial product (Fluka). All solvents were dried and distilled before use, according to standard procedures. The silylating agent $NH_2(CH_2)_3Si(OEt)_3$ was distilled before use. The inorganic supports were: Merck 60 (particle size 63–200 μm) and ultrastable Y zeolite (USY) prepared by steam calcination at 1300 K of partially ammonium exchanged NaY (SK40 Union Carbide), followed by treatment with a 1 *N* citric acid solution at 333 K for 30 minutes for "cleaning" material of extraframework species. After this, the zeolite was washed, and dried at 403 K. The main characteristics of the resultant zeolite are: unit cell size: 24.40 Å, bulk SiO_2/Al_2O_3: 4.2, crystallinity: 95%.

1. Preparation of the ligands

(S)-1-Benzyloxycarbonyl-2-t-butylaminocarbonylpyrrolidine (2a). A solution of (L)-1-carbobenzoxyproline, (**1**), (3.7 g, 0.013 mol) and triethylamine (1.51 g, 0.013 mol) in tetrahydrofuran was cooled in an ice-bath. Ethyl chloroformate (1.64 g, 0.013 mol) was added dropwise with vigorous stirring and the pasty reaction

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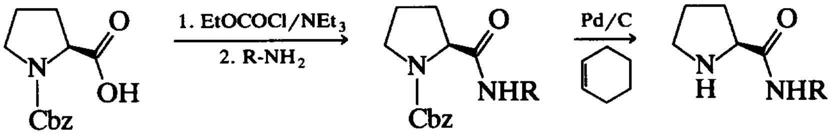
* Reference number with asterisk indicates a note in the list of references.



1 **2a, b** **3a, b**

(**a**: R = $C(CH_3)_3$; **b**: R = $(CH_2)_3Si(OCH_2CH_3)_3$)

Scheme 1.

mixture stirred for an additional 30 min. (temp. 5–10°C), obtaining *in situ* the mixed anhydride. A solution of *t*-butylamine (0.95 g, 0.013 mol) was added dropwise to this mixture during 15 min, while the temperature was kept below 10°C. After 1 h stirring, the mixture was filtered and the solid was thoroughly washed with ethyl acetate. The filtrate and wash liquids were evaporated at reduced pressure, the residue was redissolved in ethyl acetate and successively washed with water, an aqueous sodium hydrogen carbonate solution, and brine. The organic layer was dried over sodium sulphate and evaporated *in vacuo* to give 3.74 g of **2a**. Yield: 82%; m.p.: 81 C (from cyclohexane-ethylacetate); $[\alpha]^{25}_{D} = +40.5$ (EtOH, 1). Anal. Found: C, 66.91; H, 7.80; N, 9.12. $C_{17}H_{24}N_2O_3$ calc.: C, 67.10; H, 7.89; N, 9.21%. IR (cm^{-1}); $\nu(C{=}O)_{amide}$ 1660(s); $\nu(C{=}O)_{Cbz}$ 1704(s); $\nu(NH)$ 3340(m). ^1H-NMR ($CDCl_3$): $\delta = 7.35$ (arom., 5H); 5.20 (CH_2-O, 2H); 3.91 (CH-CONH, 1H); 3.1 (CH_2-N, 2H); 2.2 (CH_2-CH-CONH, 2H); 1.9 (CH_2-CH_2-N, 2H); 1.3 (CH_3, 9H). ^{13}C-NMR ($CDCl_3$): $\delta = 170.78$ (CONH); 155.51 (OCO); 136.51 (C1-phenyl); 128.35 (C2, C6-phenyl); 127.92 (C4-phenyl); 127.76 (C3, C5-phenyl); 67.06 (CH_2O); 61.19 (H*C*-CONH); 50.81 (*C*-CH_3); 47.09 (CH_2-N); 28.89 (*C*H_2-CH-CONH); 28.50 (CH_3); 24.0 (*C*H_2-CH_2N).

(S)-1-Benzyloxycarbonyl-2-(3-triethoxysilyl)propylaminocarbonylpyrrolidine (**2b**). To an ice-cooled solution (0°C) of the mixed anhydride, obtained as above, (5 g, 0.020 mol), 3-aminopropyltriethoxysilane (3.47 g, 0.015 mol) was added dropwise during 15 min. The work-up was the same as previously described, but precautions, such as washing the product rapidly, have to be taken, in order to avoid the hydrolysis of the ethoxysilane groups. Moreover, the temperature should not exceed 35°C during evaporation if cross-linking of the silane is to be avoided. Yield: 80%; pale yellow oil; $[\alpha]^{25}_{D} = -133$ (C_6H_6, 3.1). Anal. Found: C, 58.20; H, 8.29; N, 6.31. $C_{22}H_{36}N_2O_6Si$ calc.: C, 58.41; H, 7.96; N, 6.19%. IR (cm^{-1}): $\nu(C{=}O)_{amide}$ 1665(s); $\nu(C{=}O)_{Cbz}$ 1710(s); $\nu(NH)$ 3330 (m). ^1H-NMR ($CDCl_3$): $\delta = 7.25$ (arom., 5H); 5.06 (CH_2O-Ph, 2H); 4.22 (CH-CONH, 1H); 3.81 (CH_2-OSi, 6H); 3.41 (CH_2-NHCO, 2H); 3.09 (CH_2-N, 2H); 2.2-2.0 (CH_2-CHCONH, 2H); 1.88 (CH_2-CH_2-N, 2H); 1.47 (CH_2-CH_2-Si, 2H); 1.13 (CH_3, 9H); 0.5 (CH_2-Si, 2H).

(S)-2-t-butylaminocarbonylpyrrolidine (**3a**). A mixture of **2a** (5 g, 0.016 mol), cyclohexene (2 g, 0.024 mol) and 0.1 g of commercial Pd/C (10%) in 30 ml of ethanol was heated under reflux for 15–30 min in an argon atmosphere, cooled and filtered. The catalyst was washed with ethanol, and filtrate and wash liquids were evaporated under reduced pressure to give 2.7 g of amide **3a**. Yield: 98%. White crystalline solid. m.p.: 92–93 C (cyclohexane–toluene). Anal. Found: C, 63.78; H, 10.42; N, 16.65. $C_9H_{18}N_2O$ calc.: C, 63.90; H, 10.60; N, 16.57%. IR

(cm^{-1}): ν(C=O) 1660 (s); ν(NH) 3340, 3270 (m). ^{1}H-NMR (CDCl$_3$): $\delta = 7.7$ (NH, NHCO, 2H); 3.84–3.79 (CH-CONH, 1H); 3.3–3.2 (CH$_2$N, 2H); 2.36–2.02 ($C\mathit{H}_2$-CHCONH, 2H); 1.97–1.84 ($C\mathit{H}_2$-CH$_2$-NH, 2H); 1.55 (CH$_3$, 9H). ^{13}C-NMR (CDCl$_3$): $\delta = 173.79$ (CONH); 60.97 (CH-CONH); 49.80 (CH-CH$_3$); 46.88 (CH$_2$-NH); 30.41 (CH$_2$-CHCONH); 28.48 (CH$_3$); 25.79 (CH$_2$-CH$_2$NH).

(S)-2-(3-triethoxysilyl)propylaminocarbonylpyrrolidine (3b). Obtained as described for **3a**; starting from a solution (6 g, 0.013 mol) of 2b in ethanol, 3.6 g of **3b** was obtained. Yield: 84%; $[\alpha]_D^{25} = -88.7$ (C$_6$H$_6$, 1.1). IR (cm^{-1}): ν(C=O) 1665 (s); ν(NH) 3330, 3280 (m). ^{1}H-NMR (CDCl$_3$): $\delta = 4.15$ (CH-CONH, 1H); 3.80 (CH$_2$OSi, 6H); 3.2 (CH$_2$-NHCO, 2H); 2.95 (CH$_2$-NH, 2H); 2.1–1.7 ($C\mathit{H}_2$-CH$_2$Si, $C\mathit{H}_2$-CH$_2$NH, CH$_2$-CHCONH, 6H); 1.2 (CH$_3$, 9H); 0.6 (CH$_2$Si, 2H).

2. *Preparation of Me-complexes with chiral amides as ligands (M=Rh, Ru, Co, Ni)*

(i) Rhodium complexes

To a solution of a precursor rhodium(I) complex, [{Rh(COD)Cl}$_2$], [{Rh(CO)$_2$Cl}$_2$] or [RhCl(PPh$_3$)$_3$] (0.4 mmol) in dry CH$_2$Cl$_2$, was added a solution of the amide **3a** or **3b** in CH$_2$Cl$_2$ (0.6 mmol), and the reaction mixture was stirred for 3 h at room temperature, in an inert atmosphere. Reduction to dryness under reduced pressure gives an oily product, which after washing several times with diethyl ether, leaves the yellow-orange neutral compound **4n–9n** (Table 1a) with the chlorine atom is coordinated to the metal. The corresponding cationic complexes **4c–9c** (Table 1b) have been obtained by a similar procedure adding an equimolecular amount of NH$_4$PF$_6$ to the starting reaction mixture.

Characterization of the different complexes has been carried out by elemental analysis of C, H, N, and Rh and IR, ^{1}H and ^{13}C-NMR spectroscopies. The experimental data are given in Tables 1a, 1b, 2a, 2b.

Table 1a

Physical properties of neutral rhodium complexes

Compound	Analysis (Found (calc.) (%))				$[\alpha]_D^{25}$	Colour	Yield
	C	H	N	Rh			(%)
4n L$_1$, L$_2$ = COD R = C(CH$_3$)	48.7 (49.1)	7.0 (7.2)	6.6 (6.7)	24.4 (24.8)	−22.8 (EtOH, 1)	yellow	73
5n L$_1$, L$_2$ = CO, CO R = C(CH$_3$)$_3$	36.9 (36.3)	5.1 (5.0)	8.0 (7.7)	27.9 (28.3)	−8.5 (EtOH, 1)	orange	68
6n L$_1$, L$_2$ = PPh$_3$ R = C(CH$_3$)$_3$	64.6 (64.9)	5.9 (5.8)	3.6 (3.4)	12.0 (12.4)	10.6 (CH$_2$Cl$_2$, 1)	yellow	80
7n L$_1$, L$_2$ = COD R = (CH$_2$)$_3$Si(OEt)$_3$	46.7 (46.8)	7.0 (7.4)	4.9 (5.0)	18.7 (18.3)	−12.5 (CH$_2$Cl$_2$, 1)	yellow	70
8n L$_1$, L$_2$ = CO, CO R = (CH$_2$)$_3$Si(OEt)$_3$	36.9 (37.5)	5.4 (5.8)	5.1 (5.4)	20.5 (20.1)	−13.8 (CH$_2$Cl$_2$, 1)	orange	65
9n L$_1$, L$_2$ = PPh$_3$ R = (CH$_2$)$_3$Si(OEt)$_3$	60.9 (61.2)	6.4 (6.2)	3.0 (2.9)	9.2 (9.5)	9.6 (CH$_2$Cl$_2$, 1)	orange	82

Table 1b

Physical properties of cationic rhodium complexes

Compound	Analysis (Found (calc.) (%))				$[\alpha]_D^{25}$	Colour	Yield
	C	H	N	Rh			(%)
4c L_1, L_2 = COD R = $C(CH_3)_3$	38.5 (38.9)	5.8 (5.7)	5.5 (5.3)	19.2 (19.6)	−14.0 (EtOH, 1)	yellow	92
6c L_1, L_2 = PPh_3 R = $C(CH_3)_3$	57.1 (57.4)	5.5 (5.1)	3.4 (3.0)	10.8 (10.9)	+7.4 (EtOH, 1)	orange	80
7c L_1, L_2 = COD R = $(CH_2)_3Si(OEt)_3$	39.6 (39.2)	6.6 (6.2)	4.5 (4.2)	15.1 (15.3)	−9.2 (CH_2Cl_2, 1)	orange	78
9c L_1, L_2 = PPh_3 R = $(CH_2)_3Si(OEt)_3$	54.9 (55.1)	5.8 (5.5)	2.7 (2.6)	9.5 (9.4)	+10.1 (CH_2Cl_2, 1)	yellow	79

(ii) Ruthenium complexes

(S)-2-t-Butylaminocarbonylpyrrolidine)dichloro(cyclooctadien)ruthenium(II) (10n). By a procedure similar to that for the preparation of the rhodium

Table 2a

Spectroscopic data of neutral rhodium complexes

Compound	IR (cm^{-1})	^1H NMR (δ, ppm)
4n	ν(NH), 3476, 3200(m) ν(C=O), 1660(s) ν(RhCl), 360(m, br)	6.0(NH, 1H); 4.2(CH=, 4H); 4.0(CH-CONH, 1H); 3.7(NH, 1H); 3.2(CH_2N, 2H); 2.3(CH_2-CH=, 4H); 2.0–1.9(CH_2-CHCON, 2H); 1.8(CH_2-CH=, CH_2-CH_2N, 6H); 1.5(CH_3, 9H)
5n	ν(NH), 3470, 3250(m) ν(CO), 2070, 2000(s) ν(C=O), 1660, 1610(s) ν(RhCl), 350(m, br)	5.2(NH, 1H); 4.8(NH, 1H); 4.0(CH-CONH, 1H); 3.1(CH_2N, 2H); 1.95–1.85 (CH_2-CHCONH, 2H); 1.7(CH_2-CH_2N, 2H); 1.5(CH_3, 9H)
6n	ν(NH), 3460, 3200(m) ν(C=O), 1660, 1600 ν(RhCl), 360(m)	7.4(arom., 30H); 3.95(CH-CONH, 1H); 3.0 (CH_2N, 2H); 1.80(CH_2-CHCONH, 2H); 1.65 (CH_2-CH_2N, 2H); 1.5(CH_3, 9H)
7n	ν(NH), 3480, 3200(m) ν(C=O), 1660, 1600 ν(RhCl), 355	5.1–4.9(NH, 2H); 4.15(CH=, 4H); 4.0(CH-CONH, 1H); 3.7(CH_2-NHCO, 2H); 3.05(CH_2N, 2H); 2.35(CH_2-CH=, 4H); 2.1–1.4(CH_2-CH=, CH_2-CH_2Si, CH_2CHCONH, CH_2-CH_2N, 10H); 1.05(CH_3, 9H); 0.5(CH_2Si, 2H)
8n	ν(NH), 3465, 3300 (m) ν(CO), 2080, 2000(s) ν(C=O), 1670, 1620(s) ν(RhCl), 350(m, br)	5.1–4.3(NH, 2H); 4.0(CH-CONH, 1H); 3.7 (CH_2O, 6H); 3.35(CH_2-NHCO, 2H); 3.0 (CH_2N, 2H); 2.1–1.4(CH_2-CH_2Si, CH_2-CHCONH, C$H_2$$CH_2N$, 6H); 1.15($CH_3$, 9H); 0.55($CH_2Si$, 2H)
9n	ν(NH), 3460, 3190(m) ν(C=O), 1660, 1595(s) ν(RhCl), 360(m, br)	7.4(arom., 30H); 4.0(CH-CONH, 1H); 3.7(CH_2O, 6H; 3.4(CH_2-NHCO, 2H); 3.0(CH_2N, 2H); 2.0–1.4(CH_2-CH_2Si, CH_2-CHCONH, CH_2-CH_2N, 6H); 1.05(CH_3, 9H); 0.55(CH_2Si, 2H)

Table 2b

Spectroscopic data of cationic rhodium complexes

Compound	IR (cm^{-1})	^1H NMR (δ, ppm)
4c	ν(NH), 3450, 3190(m) ν(C=O), 1665, 1606(s) ν(PF), 800(s)	6.9–6.3(NH, 2H); 4.25(CH=, 4H); 4.0(C*H*-CONH, 1H); 3.0–2.8(CH_2N, 2H); 2.6–2.3(C*H*$_2$-CH=, 4H); 2.1–1.7(C*H*$_2$-CH_2N, C*H*$_2$-CH =, C*H*$_2$-CHCONH, 8H); 1.41(CH_3, 9H)
6c	ν(NH), 3455, 3200(m) ν(C=O), 1660, 1600(s) ν(PF), 800(s)	7.3(arom., 30H); 4.0(C*H*-CONH, 1H); 3.1(CH_2N, 2H); 1.92(C*H*$_2$-CH_2N, 2H); 1.88(C*H*$_2$-CHCONH, 2H); 1.66(CH_3, 9H)
7c	ν(NH), 3460, 3200(m) ν(C=O), 1660, 1600(s) ν(PF), 805(s)	6.5–5.9(NH, 2H); 4.3(CH=, 4H); 4.05(C*H*-CONH, 1H); 3.53(CH_2O, 6H); 3.4–3.1(CH_2N, CH_2-CHNHCO, 4H); 2.33(C*H*$_2$-CH=, 2H); 2.1–1.6(CH_2-CHCONH, C*H*$_2$-CH_2N, C*H*$_2$-CH_2Si, C*H*$_2$-CH=, 8H); 1.05(CH_3, 9H); 0.52(CH_2Si, 2H)
9c	ν(NH), 3380, 3030(m) ν(C=O), 1660, 1605(s) ν(PF), 810(s)	7.3(arom., 30H); 4.36(C*H*-CONH, 1H); 3.7(CH_2O, 6H); 3.4(C*H*$_2$-NHCO, 2H); 3.1(CH_2N, 2H); 2.1–1.4(C*H*$_2$-CHCONH, C*H*$_2$-CH_2N, C*H*$_2$-CH_2Si, 6H); 1.05(CH_3, 9H); 0.58(CH_2Si, 2H)

complexes; from amide **3a** (140 mg, 0.82 mmol) and [{$RuCl_2$(COD)}$_n$] (150 mg, 0.54 mmol) in 25 ml of methylene chloride under reflux, 100 mg of **10a** was obtained. Yield: 70%. Light-brown solid, m.p. = 140 C (dec.); $[\alpha]_D^{25} = +4.8$ (CH_2Cl_2, 1). Anal. Found: C, 45.01; H, 6.72; N, 5.99. $C_{17}H_{30}Cl_2N_2ORu$ calc.: C, 45.33; H, 6.67; N, 6.22%. IR (cm^{-1}); ν(NH) 3480, 3200 (m); ν(C=O) 1660, 1600 (s); ν(RuCl) 380 (m, br). ^1H-NMR ($CDCl_3$): $\delta = 6.0$, 5.6 (NH, 2H); 4.5 (HC=, 4H); 4.2 (CH–CONH, 1H); 3.0 (CH_2–N, 2H); 2.6 (CH_2–C=, 4H); 2.2–1.8 (CH_2–C=, C*H*$_2$–CH_2–N, C*H*$_2$–CHCONH, 8H); 1.5 (CH_3, 9H).

(S)-2-t-Butylaminocarbonylpyrrolidine)chloro-bis(triphenylphosphine)ruthenium (II) hexafluorophosphate (11c). A solution of **3a** (106 mg, 0.62 mmol) in CH_2Cl_2 and an equimolecular amount of NH_4PF_6 were added to a solution of [$RuCl_2(PPh_3)_3$] (400 mg, 0.62 mmol) in CH_2Cl_2 under reflux (20 ml); and the reaction mixture was stirred for 3 h. The solvent was evaporated, and the brown viscous oil was washed several times with diethyl ether; the residue was dried *in vacuo* and gave 250 mg of complex **11c**. Yield: 76%. Brown solid, m.p. = 162–166 C (dec.). $[\alpha]_D^{25} = +2.7$ (CH_2Cl_2, 1). Anal. Found: C, 55.65; H, 5.03; N, 2.93. $C_{45}H_{48}ClF_6N_2OP_3Ru$ calc.: C, 55.40; H, 4.92; N, 2.87%. IR (cm^{-1}): ν(NH) 3460, 3150 (m); ν(C=O) 1655, 1610 (s); ν(RuCl) 370 (m, br). ^1H-NMR ($CDCl_3$): $\delta = 7.7$–7.3 (C_6H_5, 30H); 6.7, 6.2 (NH); 4.2 (CH–CONH, 1H); 3.4 (CH_2N, 2H); 2.2–2.1 (C*H*$_2$–CHCONH, 2H); 1.9–1.7 (C*H*$_2$–CH_2N, 2H); 1.6 (CH_3, 9H).

(iii) Cobalt complexes (12c, 13c)

A solution of **3a** or **3b** (20 mmol) and 20 mmol of $LiClO_4$ (in CH_2Cl_2) was added to a solution of Co(acac)$_2$ (514 mg, 20 mmol) in CH_2Cl_2 (in benzene for **3b**) and the reaction mixture was slightly warmed for 24 h. The precipitate was filtered and washed with CH_2Cl_2 and ethyl ether and the resultant pink solid (**12c**, **13c**) was dried *in vacuo*.

(S)-2-t-Butylaminocarbonylpyrrolidine)-pentan-2,4-dionato)cobalt(II) perchlorate (12c). Yield: 95%. Pink solid; m.p. = 154–160 C (dec.); $[\alpha]_D^{25} = -23.6$ (MeOH, 1). Anal. Found: C, 38.95; H, 5.91; N, 6.20; Co, 13.31. $C_{14}H_{25}ClCoN_2O_7$ calc.: C, 39.30; H, 5.85; N, 6.55; Co, 13.80%. IR (cm^{-1}); ν(NH) 3430, 3200 (m); ν(C=O) 1655, 1605 (s).

(S)-2-(3-Triethoxysilyl)propylaminocarbonylpyrrolidine)(pentan-2,4-dionato)-cobalt(II) perchlorate (13c). Yield 90%. Pink dark solid, m.p. = 148–152 C (dec.). $[\alpha]_D^{25} = -15.8$ (EtOH, 1.2). Anal. Found: C, 39.56; H, 6.69; N, 4.36; Co, 9.67. $C_{19}H_{37}ClCoN_2O_{10}Si$ calc.: C, 39.62; H, 6.43; N, 4.86; Co, 10.25%. IR (cm^{-1}): ν(NH) 3480, 3370 (m); ν(C=O) 1660, 1610 (s).

(iv) Nickel complexes (14c, 15c)

To a solution of $[Ni(acac)_2]$ (450 mg, 17.5 mmol) in dry MeOH were added (297 mg, 17.5 mmol) of ligand **3a** or **3b** (in MeOH) and (186 mg, 17.5 mmol) of $LiClO_4$ or NH_4PF_6. The reaction mixture was stirred for 2 days. The solution was filtered and the solvent was evaporated; the blue solid was washed several times with diethyl ether and dried *in vacuo*.

(S)-2-t-Butylaminocarbonylpyrrolidine)-(pentan-2,4-dionato)nickel(II)perchlorate (14c). Yield 95%. Blue solid, m.p. > 230 C (dec.). $[\alpha]_D^{25} = -22.7$ (MeOH, 1). Anal. Found: C, 39.7a; H, 6.01; N, 6.34; Ni, 13.99. $C_{14}H_{25}ClN_2NiO_7$ calc.: C, 39.32; H, 5.85; N, 6.55; Ni 13.74%. IR (cm^{-1}): ν(NH) 3300 (s); ν(C=O) 1660, 1630 (s). UV-Vis: $\lambda_{max} = 294.5$ nm ($\epsilon = 9400$).

Table 3

Analytical data for the supported complexes

Compound	L_1, L_2	Metal/% anchor.	Analysis (Found (calc.)(%))			
			C	H	N	Metal
Sil-7n	COD	Rh/95	7.95	1.70	0.86	1.63
			(8.24)	(2.00)	(0.94)	(1.71)
Sil-8n	CO, CO	Rh/98	4.26	1.31	0.45	2.02
			(5.03)	(1.60)	(0.63)	(2.14)
Sil-7c	COD	Rh/89	4.81	1.79	0.60	0.91
			(4.68)	(1.01)	(0.50)	(1.10)
Zeol-7n	COD	Rh/80	4.28	1.12	0.30	0.90
			(4.86)	(1.36)	(0.35)	(1.30)
Zeol-7c	COD	Rh/82	4.34	1.02	0.91	1.16
			(4.79)	(1.30)	(1.11)	(1.50)
Sil-13c	Acac	Co/95	4.65	1.32	1.01	1.07
			(5.01)	(1.54)	(0.98)	(1.01)
Sil-15c	Acac	Ni/98	3.01	1.43	0.87	0.97
			(2.59)	(1.36)	(0.48)	(1.01)
Zeol-13c	Acac	Co/85	5.03	1.43	0.87	0.72
			(4.89)	(1.50)	(0.75)	(1.00)
Zeol-15c	Acac	Ni/88	4.02	1.54	0.50	0.99
			(3.78)	(1.37)	(0.50)	(1.04)

Table 4

Data of catalytic hydrogenation of ethyl-α-benzoylaminocinnamate with Rh^I, Ru^{II}, Ni^{II}, Co^{II}

Catalyst	Turnover (mmol/mmolM·h)	Time (h) [a]	ee(%)
4c	10.4	10	85.6
Sil-**4c**	7.7	16	92.2
Zeol-**4c**	10.4	12	99.0
10n	6.55	52	70.3
Zeol-**10n**	11.8	30	92.0
11c	22.4	30	76.3
Zeol-**11c**	22.1	20	91.3
13c	2.83	52	59.5
Zeol-**13c**	2.90	48	73.5
15c	5.98	48	69.1
Zeol-**15c**	11.1	32	85.5

[a] Conversion total measured by HPLC.

(S)-2-(3-triethoxysilyl)propylaminocarbonylpyrrolidine)-(pentan-2,4-dionato) nickel(II) perchlorate (15c). Yield 90%. Blue light. m.p. > 200 C. $[\alpha]_D^{25} = -40.7$ (MeOH, 1). Anal. Found: C, 39.30; H, 6.27; N, 4.57; Ni, 10.19. $C_{19}H_{37}ClN_2NiO_{10}Si$ calc.: C, 39.63; H, 6.43; N, 4.86; Ni, 10.20%. IR (cm^{-1}): ν(NH) 3300 (s); ν(C=O) 1660 (s); ν(SiOC) 1100 (m). UV-Vis: $\lambda_{max} = 293.8$ nm ($\epsilon = 8900$).

3. *Anchoring of transition metal complexes*

General procedure

A metal complex (**7**, **8**, **13**, **15**), described previously, (0.15 mmol) in dry CH_2Cl_2 (10 ml) was added to a suspension of the inorganic support (silica, or USY-zeolite) (1 g) in dry toluene (50 ml) and the mixture was stirred for 24 h at room temperature. The solid was then filtered off, extracted in a Soxhlet apparatus with CH_2Cl_2/ether for 7 h to remove non-supported complex and dried *in vacuo*. Analytical data for the supported complexes are shown in Table 3.

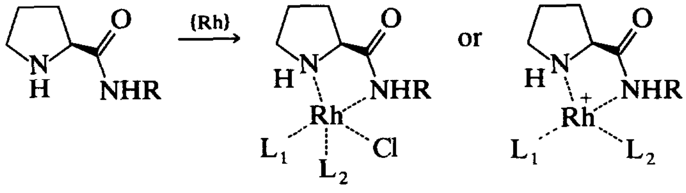
4. *Catalytic experiments*

Ethyl (*Z*)-α-benzoylaminocinnamate, selected as a model compound, was hydrogenated in a batch reactor (Autoclave Engineers) of 100 ml capacity, at 338 K and 5 atm of dihydrogen pressure. The molar ratios of catalyst/substrate were 1:100, 1:1000, and 1:10,000. The olefins were added to a solution or suspension of the catalyst in a mixture of toluene/ethanol (1/2, 50 ml) or methyl isobutyl ketone. After the hydrogenation, the catalyst, when supported, was separated by filtration and used again. The reaction products were analyzed by HPLC. Total conversion for the different catalysts was achieved in 5–48 h (Table 4).

Results and discussion

1. *Rhodium complexes*

The compounds derived from (L)-proline, **3a** and **3b**, react at room temperature in dicloromethane solution with Rh^I complexes [{RhCl(COD)}$_2$] and



3a, b **4n–9n** **4c–9c**

$R = C(CH_3)_3$ or $(CH_2)_3Si(OCH_2CH_3)_3$

$L_1, L_2 = 1,5\text{-}C_8H_{12}(COD)$, CO, CO; or PPh_3, PPh_3

Scheme 2.

[{$RhCl(CO)_2$}$_2$] by cleavage of chlorine bridges and with [$RhCl(PPh_3)_3$] by ligand displacement, to give mononuclear neutral complexes (Table 1a), where the chiral ligand is an *N*,*N*-donor (**4n–9n**) (Scheme 2). The low molar conductivities of the samples in acetone ($12–18.10^{-4}$ ohm^{-1} m^2 mol^{-1}) support the formulations as neutral species.

Cationic square planar complexes (**4c–9c**), were obtained by displacement of chlorine from the coordination sphere, by carrying out the reaction in the presence of an equimolecular amount of a non-coordinating anion, such as PF_6^-, or by treatment of the corresponding neutral complexes in dichloromethane with NH_4PF_6 for several hours. The second method gives poor yields and requires a longer purification process. The complexes are stable in air and moisture for a long time, and precautions have to be taken only in the case of animopropyltriethoxysilane derivatives, to avoid hydrolysis and polymerization.

Since no suitable crystals could be obtained, the structures of the complexes were established by IR and NMR spectroscopy, and elemental analysis, (see Table 1a).

The ^1H- and ^{13}C-NMR data for the rhodium complexes are listed in Table 2a. The spectroscopic data and the elemental analysis are in agreement with the proposed structures. Thus, the IR spectra of the rhodium complexes **4n–9n** (Table 2a) ν(N–H) at 3480–3200 cm^{-1} at higher frequencies than in the free bases which indicates Rh–N coordination. The $\nu(C{=}O)_{amide}$ at 1660 and 1600 cm^{-1}, close to the values of the free bases, excludes linkage of the ligand through the C=O group (Rh–O bond), and confirms the *N*,*N*-attachment. In neutral complexes there appears a band at 350–360 cm^{-1} corresponding to ν(RhCl). Cationic complexes show an additional band at 800 cm^{-1} due to ν(PF).

Those complexes with CO ligands (compounds **5n** and **8n**) show two intense bands at 2080–2000 cm^{-1}, assigned as two *cis*-dicarbonyl vibrations. Bands corresponding to phosphine, COD or $-C(CH_3)_3$ appear in their expected places.

The ^1H and ^{13}C NMR spectra (Tables 2a and 2b) show the signals corresponding to ring protons and carbons slightly downfield shifted and the C=O resonance is upfield shifted with respect to the free base. The ^1H and ^{13}C-NMR signals of the atoms close to the metal are remarkably broadened due to the metal, and to conformational no-rigidity on the NMR time-scale. On the other hand, the cyclooctadiene, carbonyl and triphenylphosphine ligands give rise to resonances in

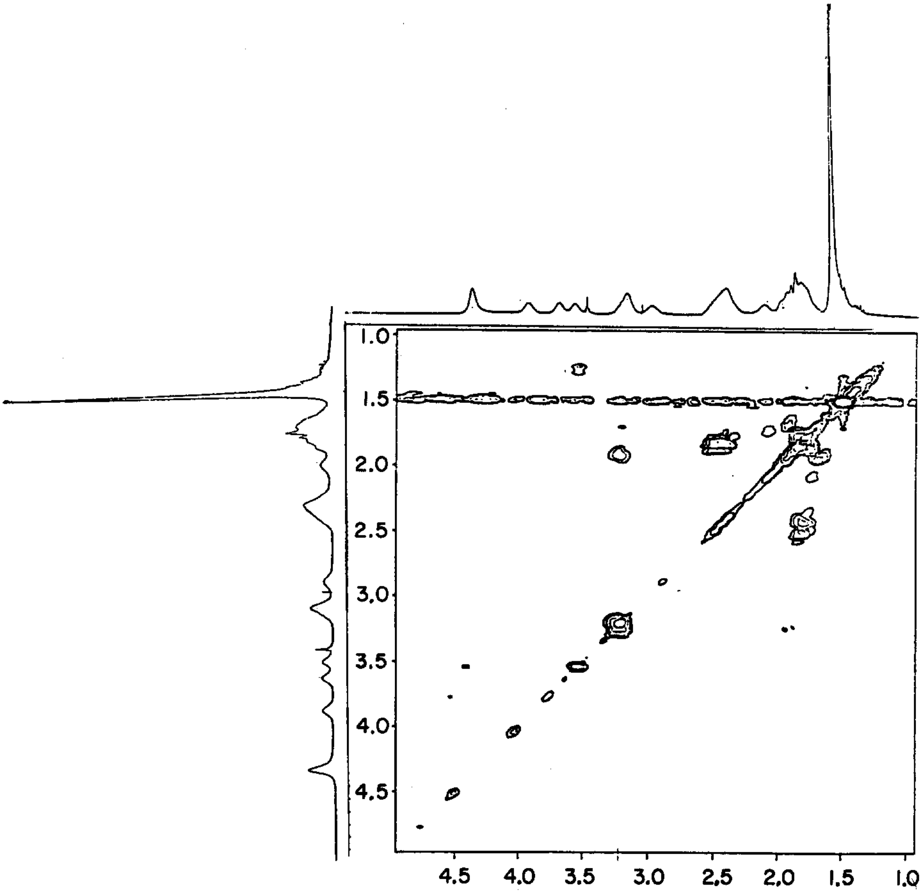


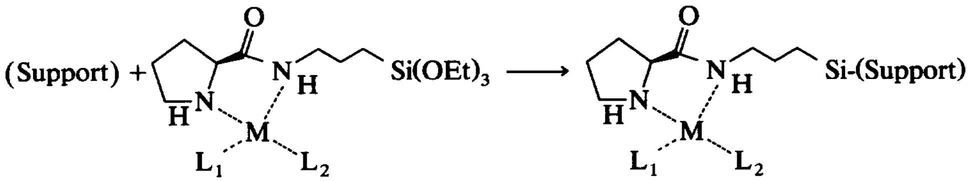
Fig. 1. COSY of compound **4c**.

the expected positions. A heteronuclear COSY experiment of the **4n** complex ([RhCl(COD)(**3a**)]) (Fig. 1) is consistent with the proposed structure and the assignment of the signals.

2. Ruthenium complexes

Cycloocta-1,5-diene reacts with ethanolic ruthenium(III) chlorides to form the polymeric highly insoluble brown complex [$\{RuCl_2(diene)\}_n$]. This product is a useful synthetic precursor to a ruthenium(II) complex, for the halogen bridges are cleaved by amide (**2a**, **3a**) at 50°C to give monomeric [$RuCl_2$(L)(COD)] (**10n**) for which two isomeric structures are possible. We propose the *trans*-chloro-structure [18].

The characteristics and behaviour of the Ru complexes (**10n**, **11c**) are similar to those of rhodium ones. They are stable in air and moisture and the analytical and spectroscopic data (IR and NMR) agree with the proposed structures. The molar conductivities (14 and 98.10^{-4} ohm^{-1} m^2 mol^{-1}) support the formulation as neutral and cationic compounds, respectively. The formulation as a five-coordinative 16-electron cation (**11c**) (as confirmed by C, H, N, and ruthenium elemental



7n, 7c, 8n, 13c, 15c

Sil–**7n, 7c, 8n, 13c, 15c**
Zeol–**7n, 7c, 8n, 13c, 15c**

L_1, L_2 = COD; CO, CO; acac

Scheme 3.

analysis) rather than a saturated species is because of the steric bulk of the triphenylphosphine ligands.

3. Cobalt and nickel complexes

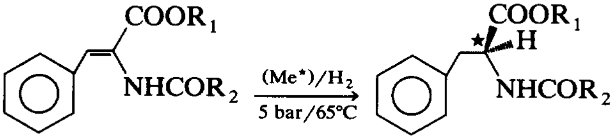
The Co and Ni complexes (**12c**, **13c**, **14c**, **15c**) are stable in air. They are insoluble in organic solvents, except in MeOH with ClO_4^- as counterion. Their IR spectra show ν(NH) at 3400–3300 cm^{-1} and ν(CO) at 1650 cm^{-1}, as in the corresponding Rh and Ru complexes. The analytical data are in agreement with the proposed stoichiometries. The NMR spectra of the complex **12c** ($X = PF_6$) correspond to the proposed structure with signals ascribed to prolinamide and acetylacetonate. The IR spectrum has a band at 850 cm^{-1} due to ν(PF).

4. Supported complexes on inorganic matrices

The preparation of supported complexes generally started with the triethoxysilylpropyl complexes (**7n**, **7c**, **8n**, **13c**, **15c**) by controlled hydrolysis of Si–OEt bonds and reaction of the free silanols (Si–OH) on the surface of an inorganic matrix (silica and USY-zeolite), very stable, covalently bonded complexes resulting (Scheme 3).

The sequence of reactions we have followed for preparing the catalysts has been: ligand → organometallic compound → anchored complex. This presents certain advantages with respect to the alternative route: ligand → functionalized support → anchored complex. For example, the ligand-to-metal ratio may be rigorously controlled, the structure of the organometallic compound can be determined by conventional methods, and, once the complex is formed, it can easily be immobilized on the support. The control and analysis steps are not always possible when the ligand has been previously attached to the support. The structure of the metal species is maintained when it is attached to the surface, as confirmed by analytical and spectroscopic data, it is unlikely that the nature of the complex is substantially altered under the relatively mild conditions of the anchoring reaction. The supported complexes were characterized by elemental analysis of C, H, N, and Rh (Table 3). The loading of metal is always ca. 1%. IR spectroscopy confirms that the soluble complex has not been altered by anchoring, because the frequencies of ν(CO) and ν(RhCl) do not change.

Such complexes can be used as supported catalysts, combining the advantages of the homogeneous catalysts with the easy handling of the heterogeneous catalysts



16 **17**

Scheme 4.

[16]. A great deal of work has been performed with organic polymers as macromolecular supports, whereas inorganic macromolecules, such as silica and zeolites, have been utilized less although they have physical properties which offer considerable advantages as supports for large scale applications of heterogeneous catalysts [17]. Organic polymers do not have a rigid structure, so their conformation, and hence the shape and size of the chains, is strongly influenced by the solvent, temperature and pressure. This may limit their use in large scale apparatus where long catalyst beds and large pressure drops are encountered. The inorganic matrices, silica and zeolite, are mechanically rigid and remain unaffected by the most severe solvent and temperature conditions.

Catalytic experiments

To date, some chiral Rh complexes have been described and successfully used in the hydrogenation of simple olefins [19] and in the asymmetric hydrogenation of the dehydroaminoacid derivatives [20].

The Rh, Ru, Co, and Ni complexes **4c**, Sil–**7c**, Zeol–**7c**, **10n**, Zeol–**10n**, **11c**, Zeol–**11c**, **13c**, Zeol–**13c**, **15c**, Zeol–**15c** (1 : 100 to 1 : 10,000 catalyst/substrate ratio) were tested for hydrogenation of ethyl-α-benzoylaminocinnamate **16** (Scheme 4) mainly at 65 C under 5 atm of dihydrogen, in different solvents, yielding the corresponding substituted phenylalanine derivative **17** with quantitative conversion and high enantioselectivity. The products have minor dependence on temperature (40–80 C) and on small changes of dihydrogen pressure (3–12 atm).

With the same molar amount of catalyst, the neutral and cationic Rh complexes supported on silica (Sil–7c) show an increase in the induction period (sigmoid kinetic profiles) with respect to the homogeneous catalyst (4c) (Fig. 2). In contrast, when any catalyst was supported on USY-zeolite, no induction period was observed, and its activity was higher than when it was unsupported. This is probably a consequence of the concentration effect of the zeolite and the interaction of the catalyst with the electrostatic fields present in the zeolite, which assist the formation of the catalytic active species.

Moreover, the enantioselectivity is higher on the zeolite-supported complexes than on either the silica-supported or unsupported complexes (Table 4). These facts suggest the important role of the steric constraints of the support, especially in the zeolite case where the reaction must take place in the confined spaces of supermicropores (20–60 Å), when the metal complexes are anchored.

The zeolite-supported catalysts were reused several times without any loss in activity or metal-content, as measured by atomic absorption. The increase obtained in the enantioselectivity indicates that this type of catalyst is a truly heterogeneous

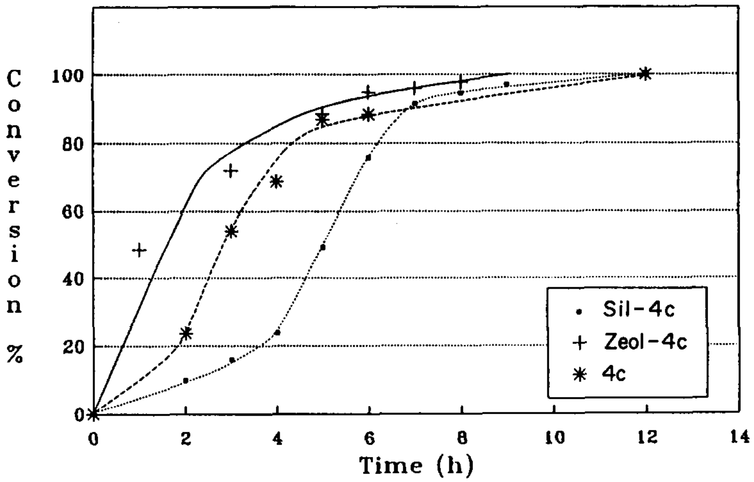


Fig. 2. Hydrogenation of ethyl (*Z*)-α-benzoylaminocinnamate with different catalysts of rhodium.

counterpart of homogeneous transition metal complex catalysts for hydrogenation of prochiral olefins.

Studies of oxidation processes of olefins with molecular oxygen catalyzed by Co complexes, and alkylation reactions catalyzed by Ni complexes, are in progress.

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References and notes

1 (a) I. Ojima, N. Clos and C. Bastos, Tetrahedron, 45 (1989) 6901; (b) S.L. Blystone, Chem. Rev., 89 (1989) 1663; (c) G. Consiglio and R.M. Waymouth, Chem. Rev., 89 (1989) 257; (d) R. Noyori, Chem. Soc. Rev., 18 (1989) 187; (e) H. Brunner, Synthesis, (1988) 645; (f) H.B. Kagan, Bull. Soc. Chim. Fr., (1988) 846.

2 H.B. Kagan, in J.D. Morrison (Eds.), Asymmetric Synthesis, Vol. 5, Academic Press, Orlando, Florida, 1985, p. 1.

3 (a) J. Ehlers, W.A. König, S. Lutz, G. Wenz and H. tom Dieck, Angew. Chem., Int. Ed. Engl., 27 (1988) 1556; (b) H. Brunner, R. Becker and G. Riepl. Organometallics, 3 (1984) 1354; (c) H. Brunner and M. Fisch, J. Organomet. Chem., 335 (1987) 1.

4 (a) T. Hayashi, M. Konishi, M. Fukushima, K. Kanekiva, T. Hioki and M. Kumada, J. Org. Chem., 48 (1983) 2195; (b) B.K. Vriesema and R.M. Kellog, Tetrahedron Lett., 27 (1986) 2049.

5 M.G. Finn and K.B. Sharpless, in J.D. Morrison (Ed.), Asymmetric Synthesis, Vol. 5, Academic Press, Orlando, Florida, 1985, p. 247; (b) H.B. Kagan, Phosphorus and Sulfur, 27 (1986) 127.

6 S.M. Laurie, in G. Wilkinson, R.R. Gillard and J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, Vol. 2, Pergamon, Oxford, 1987, p. 739.

7 (a) N. Takashi, J. Am. Chem. Soc., 100 (1978) 264; (b) T. Masuda and J.K. Stille, J. Am. Chem. Soc., 100 (1978) 268; (c) N. Ishizuka, M. Togashi, M. Inoue and S. Enomoto, Chem. Pharm. Bull., 35 (1987) 1686; (d) M. Inoue, K. Ohta, N. Ishizuka and S. Enomoto, Chem. Pharm. Bull., 31 (1983) 3371; (e) M. Mazzei, W. Marconi and M. Riocci, J. Mol. Catal., 9 (1980) 381; U. Nagel, Angew. Chem., Int. Ed. Engl., 23 (1984) 435.

8 (a) F.R. Hartley, in Supported metal complexes, D. Reidel, Netherlands, 1985, p. 308; (b) R.V. Paris, D. Habidi and V. Mohanmadi, J. Organomet. Chem., 369 (1989) 17; (c) H. Brunner, E. Bieldmeier and J. Wiehl, J. Organomet. Chem., 384 (1990) 223; (d) K. Achiwa, Chem. Lett., (1978) 905.
9 U. Nagel and E. Kinzel, J. Chem. Soc., Chem. Commun., (1986) 1089.
10 J. Chatt and L. Venanzi, J. Chem. Soc., (1957) 4715.
11 L.G. Lipson, M.L. Maddox and D. Herbert, Inorg. Synth., 8 (1966) 211.
12 J.A. Osborn, F.H. Jardine, J.F. Young and G. Wilkinson, J. Chem. Soc. (A), (1966) 1711.
13 $[\{RuCl(COD)\}_n]$ was obtained from $RuCl_3 \cdot nH_2O$ in dichloromethane under reflux in the presence of COD for 3 days, following the standard procedure.
14 R. Holm, Inorg. Synth., 12 (1970) 238.
15 J.B. Ellern and R.O. Ragsdale, Inorg. Synth., 11 (1978) 82.
16 (a) E.W. Abel and M.A. Bennett, J. Chem. Soc., (1959) 3178; (b) M.A. Eisen and G. Wilkinson, Chem. Ind. (London), (1950) 1516.
17 J.H. Lunsford, Rev. Inorg. Chem., 9 (1987) 1.
18 M.A. Bennett, M.I. Bruce and T.W. Matheson, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol 4, Pergamon Press, Oxford, 1982, p. 691.
19 A. Corma, M. Iglesias, C. del Pino and F. Sánchez, J. Mol. Catal., 70 (1991) 369.
20 A. Corma, M. Iglesias, C. del Pino and F. Sánchez, J. Chem. Soc., Chem. Commun., (1991) 1253.