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Journal of Organometallic Chemistry 608 (2000) 89–95

Journal of Organometallic Chemistry

Quincoridine-based aminophosphite ligands and their Rh(I) and Pd(II) complexes

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Received 28 February 2000; received in revised form 10 May 2000

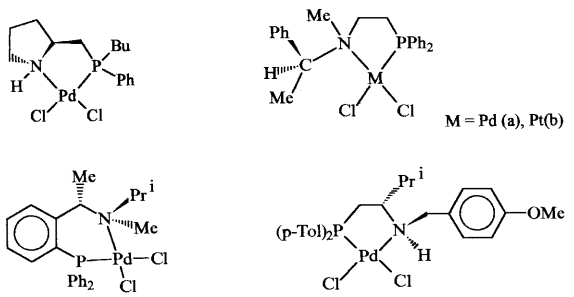
Abstract

New chiral P,N-bidentate ligands containing a quincoridine fragment with a configuration-stable N-donating center were obtained. Coordination of the ligands to Rh(I) and Pd(II) atoms was carried out. Chlorocarbonyl rhodium and dichloride palladium complexes were found to be *cis*-chelates with P,N-bidentate ligands. © 2000 Published by Elsevier Science S.A.

Keywords: Aminophosphites; P,N-ligands; Chirality; Quincoridine derivatives; Rhodium complexes; Palladium complexes

1. Introduction

Chiral phosphorus-containing ligands that incorporate an additional nitrogen donor center acquire a progressively growing importance in the development of asymmetric catalysis and coordination chemistry. Being structurally dissymmetric, P,N-bidentate ligands are also characterized by marked electronic non-symmetry. It is possible to vary widely both the steric and electronic parameters of the two donor centers and the structure of the bridge between them. Such ligands can provide good results in a number of enantioselective transition metal-catalyzed reactions: allylic substitution [1,2], hydroboration [3,4], cross-coupling [5,6], hydrosilylation [7,8] and others [9,10]. One of the possible ways to enhance the efficiency of P,N-ligands is to increase the π-acceptor character of the phosphorus donor center by using a phosphite (amidophosphite) fragment in the ligand structure [11–21]. Another principally important parameter is the stereochemical characteristics of the donor centers. In particular, growing interest in enantioselective catalysts with ligands that contain chiral donor atoms is currently observed (see [22] and Refs. cited therein). However, only a few complexes with a fixed N*-stereocenter configuration, thanks to N-metal bonding, are described thus far [22–25]:



Unfortunately, they undergo a fast epimerization [24] or fast exchange between several metalacycle conformations [22,25]. These processes essentially decrease their potency as stereoselectors. A possible way out of the situation is to use compounds bearing a permanent asymmetric nitrogen atom at the head of a bridge, where the pyramidal inversion is not sterically allowed. Synthesis and complexation of a series of cinchona alkaloid-based phosphorus derivatives [26–28] can serve as an example of this approach. However, these ligands are tridentate as they have two nitrogen centers

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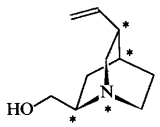
0022-328X/00/$ - see front matter © 2000 Published by Elsevier Science S.A.
PII: S0022-328X(00)00373-9

(quinoline and quinuclidine ones) in addition to a phosphorus atom. As a rule, two nitrogen atoms compete with one another for the coordination to a metal, thus leading to non-selective complexation [28].

In the present paper, we describe the synthesis and complexation of aminophosphites **2a**–**c** with Rh(I) and Pd(II). Ligands **2a**–**c** are derived from the unique aminoalcohol quincoridine (QCD) that contains four asymmetric atoms (a nitrogen one among them). The skeleton of QCD is identical to the framework of quinidine. Thus, new aminophosphites **2a**–**c** are the first P,N-bidentate ligands bearing a configuration-stable N*-stereogenic center when in a free state.



QCD

2. Experimental

2.1. General comments

All reactions were carried out under a dry argon atmosphere. All the solvents were distilled and carefully dehydrated before use.

IR spectra were recorded on a Specord M80 or Nicolet 750 instrument. ^{31}P- and ^{13}C-NMR spectra were recorded on a Bruker AMX-400 or a Bruker WP-200-SY instrument (162.0 and 81.0 MHz for ^{31}P; 100.6 and 50.3 MHz for ^{13}C). ^{1}H-NMR spectra were recorded on a Bruker WM-250 instrument (250.1 MHz). The complete assignment of all resonances in ^{1}H- and ^{13}C-NMR spectra was achieved using homonuclear decoupling or DEPT technique, respectively. Chemical shifts (ppm) are given relative to Me_4Si (^{1}H- and ^{13}C-NMR) and 85% H_3PO_4 (^{31}P-NMR). Mass spectra were recorded on a Kratos MS 890 spectrometer (EI), on a MSVKh time-of-flight spectrometer with ionization by californium-252 fission fragments (plasma desorption technique) and a Vision 2000 time-of-flight spectrometer with matrix assisted laser desorption ionization (MALDI) using UV laser (337 nm). Sedimentation analyses were performed on a MOM-3180 analytical ultracentrifuge according to published techniques [29–31]. Elemental analyses were performed at the Laboratory of Microanalysis (Institute of Organoelement Compounds, Moscow). Optical rotation was measured on a Perkin–Elmer 141 polarimeter.

Quincoridine was aseotropically dried with benzene and distilled before use. Aminophosphites **1a**–**c** [31–33], $[Rh(CO)_2Cl]_2$ [34] and $[PdCl_2(COD)]$ [35] were synthesized as published.

2.2. Preparation of ligands

2.2.1. {[(2′R,4′S,5′R)-5′-Vinylquinuclidyl]-2′-methoxy}-1,3,2-dioxaphospholane (2a)

An equimolar mixture of quincoridine (1.000 g, 0.006 mol) and (*N*,*N*-diethyl)amido-1,3,2-dioxaphospholane (**1a**) (0.978 g) was stirred at 140°C for 1 h. Then the mixture was stirred in a vacuum (2 mmHg) at 110°C for 1 h in order to remove $HNEt_2$ and distilled at 1 mmHg (bath temperature 190–200°C) to give **2a** as a colourless liquid (1.080 g, 70% yield). $[\alpha]_D^{27} = 119.46$ ($c = 2.94$, $CHCl_3$). EIMS (70 eV) m/z (%): 257 [4, M^+], 150 (49), 136 (100), 108 (50), 107 (17), 91 (100). Anal. Calc. for $C_{12}H_{20}NO_3P$: C, 56.01; H, 7.84; P, 12.05. Found: C, 55.56; H, 7.61, P, 12.30%.

2.2.2. {[(2′R,4′S,5′R)-5′-Vinylquinuclidyl]-2′-methyl}-diisopropylphosphite (2b)

An equimolar mixture of $(i\text{-PrO})_2PNEt_2$ (**1b**) (1.989 g, 0.009 mol) and quincoridine (1.500 g) in toluene (10 ml) was stirred under reflux for 3 h. Then 2/3 of the solvent was evaporated, the residue was filtered, dried in vacuum (2 mmHg) at 100°C for 0.5 h, and distilled at 0.8 mmHg to give a colourless liquid (2.268 g, 80% yield). B.p. 115–117°C (0.8 mmHg). $n_D^{20} = 1.4781$. $[\alpha]_D^{27} = 92.00$ ($c = 2.66$, $CHCl_3$). EIMS (70 eV) m/z (%): 315 [5, M^+], 256 (3), 230 (14), 150 (48), 148 (89), 136 (76), 108 (66), 58 (100). Anal. Calc. for $C_{16}H_{30}NO_3P$: C, 60.91; H, 9.59; P, 9.83. Found: C, 60.71; H, 9.46; P, 10.06%.

2.2.3. {[(2′R,4′S,5′R)-5′-Vinylquinuclidyl]-2′-methyl}-dibornylphosphite (2c)

An equimolar mixture of quincoridine (1.000 g, 0.006 mol) and $(BornylO)_2PNEt_2$ (**1c**) (2.454 g) was stirred at 120°C for 1.5 h. Then the mixture was stirred in vacuum (2 mmHg) at 110°C for 1 h in order to remove $HNEt_2$. White paraffin-like substance (2.777 g, 92% yield). EIMS (70 eV) m/z (%): 503 [1, M^+], 350 (12), 231 (100), 150 (54), 137 (67), 136 (77). Anal. Calc. for $C_{30}H_{50}NO_3P$: C, 71.52; H, 10.01; P, 6.15. Found: C, 71.65; H, 10.34; P, 6.47%.

2.3. Preparation of complexes

2.3.1. ({[(2′R,4′S,5′R)-5′-Vinylquinuclidyl]-2′-methoxy}-1,3,2-dioxaphospholane-P,N) chlorocarbonyl rhodium(I) (3a)

A solution of ligand **1a** (0.093 g, 3.6×10^{-4} mol) in CH_2Cl_2 (5 ml) was added dropwise to a stirred solution of $[Rh(CO)_2Cl]_2$ (0.070 g, 1.8×10^{-4} mol) in the same solvent (15 ml) at 20°C. The reaction mixture was stirred at 20°C for 0.5 h. The excess of the solvent was then removed in vacuum (40 mmHg) and 10 ml of hexane was added to the residue. The precipitate obtained was separated by centrifugation, washed with

hexane (10 ml) and dried in vacuum (1.5 mmHg). Yellow solid. Yield 0.131 g (86%). M.p. 156–158°C (dec.). Anal. Calc. for $C_{13}H_{20}NO_4ClRhP$: C, 36.88; H, 4.77; N, 3.31; P, 7.32. Found: C, 37.00; H, 4.42; N, 3.41; P, 7.08%.

2.3.2. ({[(2′R,4′S,5′R)-5′-Vinylquinuclidyl]-2′-methyl}-diisopropylphosphite-P,N) chlorocarbonyl rhodium(I) (3b)

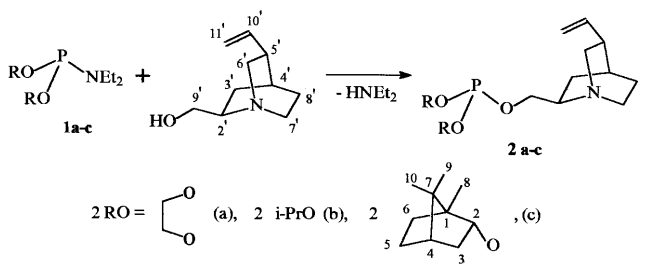
The procedure described above for **3a** was followed using 0.113 g (3.6×10^{-4} mol) of compound **2b** and 0.070 g (1.8×10^{-4} mol) of $[Rh(CO)_2Cl]_2$. Yellow solid. Yield 0.163 g (94%). M.p. 117–119°C (dec.). Anal. Calc. for $C_{17}H_{30}NO_4ClRhP$: C, 42.41; H, 6.28; N, 2.91; P, 6.44. Found: C, 42.66; H, 6.37; N, 3.08; P, 6.48%.

2.3.3. ({[(2′R,4′S,5′R)-5′-Vinylquinuclidyl]-2′-methyl}-dibornylphosphite-P,N) chlorocarbonyl rhodium(I) (3c)

The procedure described above for **3a** was followed using 0.181 g (3.6×10^{-4} mol) of compound **2c** and 0.070 g (1.8×10^{-4} mol) of $[Rh(CO)_2Cl]_2$. Yellow solid. Yield 0.222 g (92%). M.p. 179–201°C (dec.). Anal. Calc. for $C_{31}H_{50}NO_4ClRhP$: C, 55.59; H, 7.53; N, 2.09; P, 4.63. Found: C, 55.83; H, 7.38; N, 1.89; P, 4.30%.

2.3.4. Cis-dichloro({[(2′R,4′S,5′R)-5′-Vinylquinuclidyl]-2′-methyl}-diisopropylphosphite-P,N) palladium(II) (4b)

A solution of compound **2b** (0.120 g, 3.8×10^{-4} mol) in CH_2Cl_2 (5 ml) was added dropwise to a stirred solution of $[PdCl_2(COD)]$ (0.108 g, 3.8×10^{-4} mol) in the same solvent (15 ml) at 20°C. The reaction mixture was stirred at 20°C for 30 min. The excess of the solvent was then removed in vacuum (40 mmHg) and 10 ml of diethyl ether was added to the residue. The precipitate obtained was separated by centrifugation, washed with ether (2×10 ml), and dried in vacuum (1.5 mmHg). Yellow solid. Yield 0.166 g (89%). M.p. 121–123°C (dec.). Anal. Calc. for $C_{16}H_{30}NO_3Cl_2PdP$: C, 39.10; H, 6.16; N, 2.85; P, 6.31. Found: C, 39.26; H, 6.10; N, 3.17; P, 6.15%.



Scheme 1. Ligands **2a**–**c** react with $[Rh(CO)_2Cl]_2$ in $CHCl_2$ to form complexes **3a**–**c**.

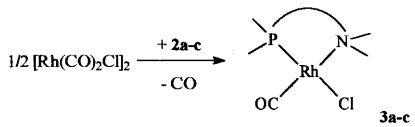
2.3.5. Cis-dichloro({[(2′R,4′S,5′R)-5′-vinylquinuclidyl]-2′-methyl}-dibornylphosphite-P,N) palladium(II) (4c)

The procedure described above for **4b** was followed, using 0.176 g (3.5×10^{-4} mol) of compound **2c** and 0.100 g (3.5×10^{-4} mol) of $[PdCl_2(COD)]$. Yellow solid. Yield 0.217 g (91%). M.p. 204–206°C (dec.). Anal. Calc. for $C_{30}H_{50}NO_3Cl_2PdP$: C, 53.00; H, 7.42; N, 2.06; P, 4.56. Found: C, 52.81; H, 7.50; N, 2.20; P, 4.72%.

3. Results and discussion

New P,N-bidentate ligands **2a**–**c** were obtained by a one-step phosphorylation of quincoridine using aminophosphites **1a**–**c** (Scheme 1). Their ^{1}H-, ^{13}C-, ^{31}P-NMR and mass spectral data are summarized in Tables 1–3 (^{13}C-NMR spectrum of **2b** is shown in Fig. 1). Analogously to the ligand based on *N*,*N*-dimethylaminoethanol [31], the ^{13}C-NMR spectra of **2b**,**c** show non-equivalence of carbon atoms of isopropyl and bornyl fragments of **2b**,**c**.

Ligands **2a**–**c** react with $[Rh(CO)_2Cl]_2$ in CH_2Cl_2 to form complexes **3a**–**c**:



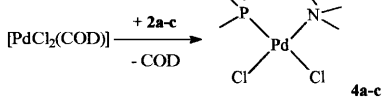
^{13}C- and ^{31}P-NMR data prove a P,N-bidentate coordination of the ligands with rhodium atom (Tables 2 and 3, ^{13}C-NMR spectrum of **3b** is shown in Fig. 2). Thus, the ^1J(P,Rh) and ^1J(C,Rh) values are characteristic of square-planar chelate Rh(I) complexes with *cis*-coordinated P,N-ligands [36]. Essential downfield coordination shifts $\Delta\delta_C$ for the carbon atoms neighboring phosphorus or nitrogen atoms should also be marked (Table 2). Absorption bands ν(CO) (2008–2032 cm^{-1}) and ν(Rh–Cl) (284–306 cm^{-1}) in the IR spectra of **3a**–**c** (Table 4) are in good agreement with the supposed structure of these compounds. The similarity of IR spectroscopy data for **3a**–**c** in $CHCl_3$ solution and in the solid state demonstrates the complexes do not undergo reorganization during dissolution.

The plasma desorption and MALDI mass spectra of complexes **3a**–**c** contain both molecular ion peaks and peaks of products of reorganization (association), but the results of sedimentation analysis in DMF (Table 5) prove the chelate mononuclear structure of the complexes. In addition, based on the coefficient of diffusion, it was found that molecules **3a**–**c** can be inscribed into a sphere of 9.9–12.0 Å in diameter. This is in good agreement with the computer simulation data (MM2 force field method).

Table 1
^{1}H-NMR data for compounds **2a**,**b**, **3a**,**b** in $CDCl_3$, δ_H (J (Hz))

H atom	Compound			
	2a	**3a**	**2b**	**3b**
2′	2.71–2.84	3.05 m	2.82 m	2.55 m
3′	1.14 m	1.21 m, 1.65 m	1.28 m	0.55 dddd (13.4, 10.4, 1.8, 1.8)
	1.38 m		1.44 m	0.74 dddd (13.4, 9.2, 4.9, 1.8)
4′	1.64 m	1.82 m	1.68 m	1.16 m
5′	2.13 m	2.45 m	2.18 m	2.05 m
6′	2.56 m	2.52 m	2.65 m	2.21 ddd (13.4, 9.2, 2.4)
	2.71–2.84		2.89 m	4.55 ddd (13.4, 9.2, 1.4)
7′	2.71–2.84	3.05 m, 4.01 m	2.83 m	2.72 dddd (13.4, 9.8, 2.3, 2.0) 4.47 m
8′	1.49 m	1.60–1.75	1.51 m	0.95 m 1.16 m
9′	3.54 m	3.72 ddd (31.5, 13.2, 1.8)	3.72 m	3.10 ddd (30.5, 13.4, 1.8)
	3.70 m			3.78 ddd (13.4, 9.2, 7.3)
10′	5.75 m	5.65 m	5.80 m	5.27 ddd (17.1, 10.4, 6.4)
11′	4.90 m	5.01 ddd (17.1, 1.5, 1.2)	4.92 m	4.69 ddd (17.1, 1.5, 1.2)
	4.94 m	5.06 ddd (10.4, 1.5, 1.2)	4.97 m	4.87 ddd (10.4, 1.5, 1.2)
CH_2	3.88 m	4.01, 4.12–4.32		
	4.09 m			
CH			4.31 m	4.93–4.88
CH_3			1.19 d (6.0)	1.19 d (6.1)
			1.21 d (6.0)	1.24 d (6.1) 1.26 d (6.1)

Complexation of ligands **2a**–**c** with $[PdCl_2(COD)]$ follows the scheme:



4a-c

The reaction with **2a** has been found to proceed unselectively. Thus, the ^{31}P-NMR spectrum shows, besides the main resonance δ_P 97.35 of the chelate product, several minor resonances 50.64 (^2J(P,P) 100.7 Hz), 53.46 (^2J(P,P) 74.0 Hz), 127.72 (^2J(P,P) 100.7 Hz), 130.15 (^2J(P,P) 74.0 Hz), which are characteristic of $PdCl_2L$ complexes with P-monodentate coordinated **2a**. It seems to be connected with internal strains of the chelate metalacycle when a metal-containing *spiro*-structure is formed. In this case, chelate complexes with a central palladium ion are less stable than with a rhodium one. The ^{31}P- (Table 3) and ^{13}C- (Table 2, ^{13}C-NMR spectrum of **4b** is shown in Fig. 3) NMR data prove the formation of mononuclear chelate complexes **4b**,**c** when **2b**,**c** reacts with $[PdCl_2(COD)]$. In particular, the resonances observed in the ^{31}P-NMR spectra are typical for acyclic aminophosphites coordinated to a palladium atom [31,33]. The ^{13}C-NMR spectra demonstrate essential downfield coordination shifts $\Delta\delta_C$ for carbon atoms neighbouring phosphorus and nitrogen atoms, thus indicating the formation of Pd–P and Pd–N bonds in **4b**,**c**. It must be noted that isopropyl and bornyl substituents in **4b**,**c** are non-equivalent, this causes doubling of resonances of the corresponding carbon atoms in the ^{13}C-NMR spectra. The same is observed for rhodium complexes **3a**–**c**. *Cis*-orientation and terminal position of chlorine atoms in the coordination sphere of the palladium atom results from the far field IR spectral data [37]: ν(Pd–Cl) values for **4b**,**c** (in $CHCl_3$ solution) are equal to 286, 340 and 282, 338 cm^{-1}, respectively.

Analogously to **3a**–**c**, the sedimentation analysis data prove the chelate structure of **4c** (see Table 5).

Steric and electronic parameters of ligands are of great importance for coordination chemistry and for metal complex catalysis. As a qualitative estimation of these criteria for a series of compounds, it is necessary to create a spectrochemical sequence and correlate stereochemical properties of the ligands with the results of catalysis. An adequate qualitative characterization of the steric parameter of phosphorus donor centers has been realized by calculating their cone angle using the semi-empirical quantum-mechanical method AM1 [38]. Sterical demands of the phosphorus donor center have been found to increase from **4a** ($\Theta^A = 96°$) through **4b** ($\Theta^A = 127°$) to **4c** ($\Theta^A = 134°$). On the other hand, values of ν(CO) for rhodium complexes **3a**–**c** (Table 4) allow the estimation of the degree of 'electronic non-symmetry' for ligands **2a**–**c**, i.e. the difference between the acceptor abilities of the phosphorus and nitrogen atoms [7,39]. When the nitrogen donor center remains constant, a change in the electronic characteristics of a ligand can be ascribed to the phosphorus-containing fragment entirely. The degree of the ligand 'electronic non-symmetry' should be expected to increase with the growth of the π-acceptor character of the phosphorus center, with the ν(CO) frequency in IR spectra of

chlorocarbonyl rhodium(I) complexes indicating this tendency. Indeed, the 'electronic non-symmetry' increases within the row **2b**–**c**–**a**, i.e. the dioxaphospholane phosphorus center possesses the greatest, and the diisopropyl phosphorus center possesses the least π-acceptor character among **2a**–**c**.

Table 2
^{13}C-NMR data for solutions of compounds **2a**–**c**, **3a**–**c**, **4b**,**c** in $CDCl_3$, δ_C (J(C,P) (Hz))

Carbon atom	Compound							
	2a	**3a**	**2b**	**3b**	**4b**	**2c**	**3c**	**4c**
2′	55.69	61.90	55.81	61.51	61.18	55.92	61.86	61.64
	(3.8)	(8.4)	(4.3)	(6.1)	(4.4)	(5.6)	(5.6)	(4.4)
3′	23.76	25.14	24.35	24.97	25.13	24.59	24.84	25.48
4′	27.17	26.53	27.42	26.53	26.77	27.48	26.46	26.04
5′	39.36	38.59	39.81	38.51	39.29	39.77	38.44	39.34
6′	47.19	48.37	47.58	48.30	51.92	47.80	48.33	52.13
7′	48.59	50.70	48.99	50.98	55.00	49.06	50.88	55.20
8′	26.23	25.69	26.64	25.76	26.37	26.58	26.55	26.63
9′	63.74	65.62	61.58	64.82	64.09	62.21	64.85	64.59
	(9.0)	(5.5)		(4.9)	(4.8)	(2.8)	(4.0)	(4.6)
10′	139.94	137.25	140.40	137.54	136.51	140.28	137.43	136.70
11′	114.03	115.88	114.15	115.79	115.87	114.34	115.68	116.24
CH_2	63.42	64.28						
	(10.0)	(7.0)						
	63.59	64.65						
	(10.4)	(7.0)						
*C*H			66.25	70.26	73.91			
			(16.6)	(4.9)	(4.9)			
			66.41	70.59	74.16			
			(16.4)	(<2.0)	(<2.0)			
CH_3			24.25	23.69	23.07			
			24.27	(5.4)	(7.3)			
			24.31	23.81	23.22			
			24.35	(4.6)	(4.5)			
				23.89	23.36			
				(2.4)	(3.0)			
				23.92	23.53			
				(3.2)	(4.1)			
1						49.39	49.40	49.70
							(4.9)	(5.0)
							49.57	49.83
							(8.1)	(7.7)
2						77.78	81.85	85.32
						(12.3)		(3.8)
						78.16	82.01	85.84
						(13.6)	(8.6)	(8.3)
3						37.84	37.14	36.61
							37.45	37.29
4						44.81	44.68	44.50
							44.77	44.71
5						28.01	27.80	27.75
							27.86	27.82
6						26.43	25.64	26.33
							26.37	26.42
7						47.36	47.22	47.24
							47.30	47.48
8						18.64	18.57	18.64
							18.82	18.81
9						19.85	19.62	19.60
							19.71	19.67
10						13.28	13.20	13.26
							13.28	13.48
CO		184.60 ($^1J_{C,Rh}$ 68.7, $^2J_{C,P}$ 24.8)		185.60 ($^1J_{C,Rh}$ 70.0, $^2J_{C,P}$ 20.5)			185.34 ($^1J_{C,Rh}$ 70.3, $^2J_{C,P}$ 20.7)	

Table 3
^{31}P-NMR data for solutions of compounds **3a–c**, **4a–c** in $CDCl_3$

Compound	δ_P (^1J(P,Rh) (Hz))
2a	134.47
3a	139.23 (281.1)
2b	138.61
3b	126.78 (261.5)
4b	75.67
2c	140.53
3c	129.50 (269.1)
4c	75.51

Table 5
Sedimentation analysis data for complexes **3a–c** in DMF

Compound	Molecular weight		Diameter of molecule [a] (Å)	
	Obtained	Calculated	Obtained	Calculated by MM2 method
3a	555	424	9.9	10.8
3b	485	481	10.6	12.0
3c	656	669	12.8	13.6
4c	726	680	12.0	14.2

[a] 'Diameter of molecule' means the diameter of the sphere in which a molecule of the discussed compound can be inscribed.

Thus, reaction of ligands **2b**,**c** with $[Rh(CO)_2Cl]_2$ and $[PdCl_2(COD)]$ gives stable chelate complexes with *cis*-coordination of two donor centers of the ligands. Interaction of **2a** with $[Rh(CO)_2Cl]_2$ proceeds analogously, while the reaction with $[PdCl_2(COD)]$ leads to a mixture of products. That is why **2b**,**c** can be expected to be more effective in the asymmetric induction in a catalytic processes.

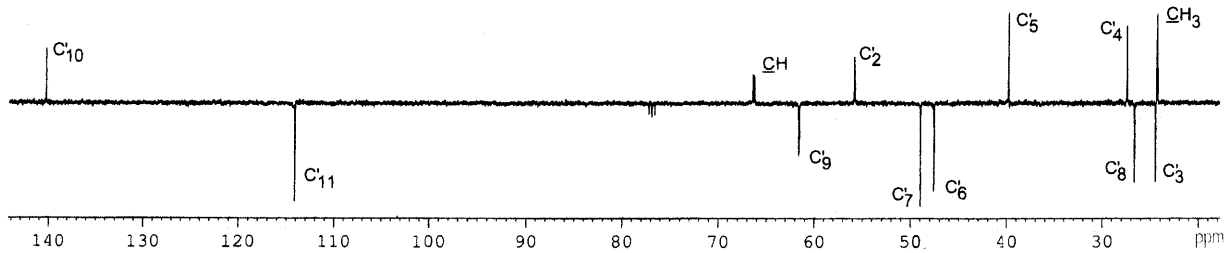


Fig. 1. ^{13}C-NMR spectrum of a solution of **2b** in $CDCl_3$.

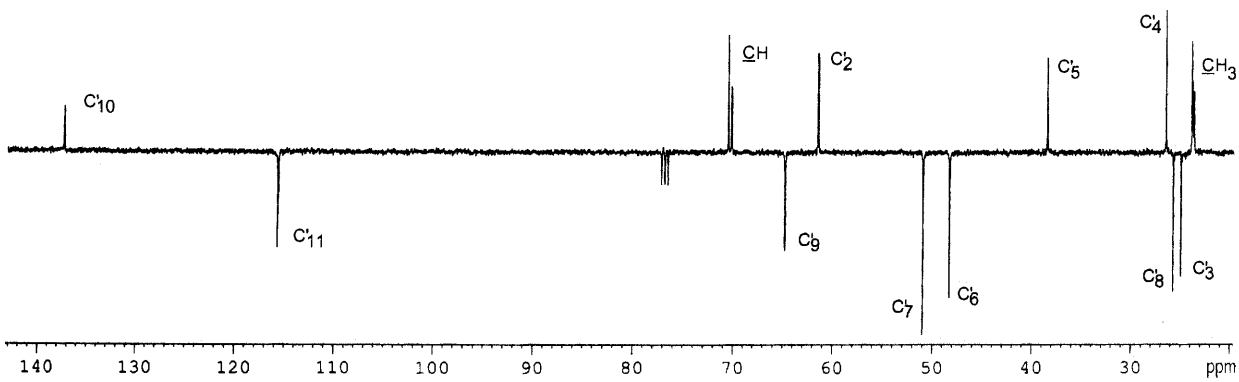


Fig. 2. ^{13}C-NMR spectrum of a solution of **3b** in $CDCl_3$.

Table 4
IR data for compounds **3a–c**

Compound	ν(Rh–Cl) (cm^{-1}) (Nujol)	ν(CO) (cm^{-1}) (press. KBr)	ν(Rh–Cl) (cm^{-1}) ($CDCl_3$)	ν(CO) (cm^{-1}) ($CDCl_3$)
3a	304	2012	306	2032
3b	289	2008	284	2020
3c	295	2010	288	2026

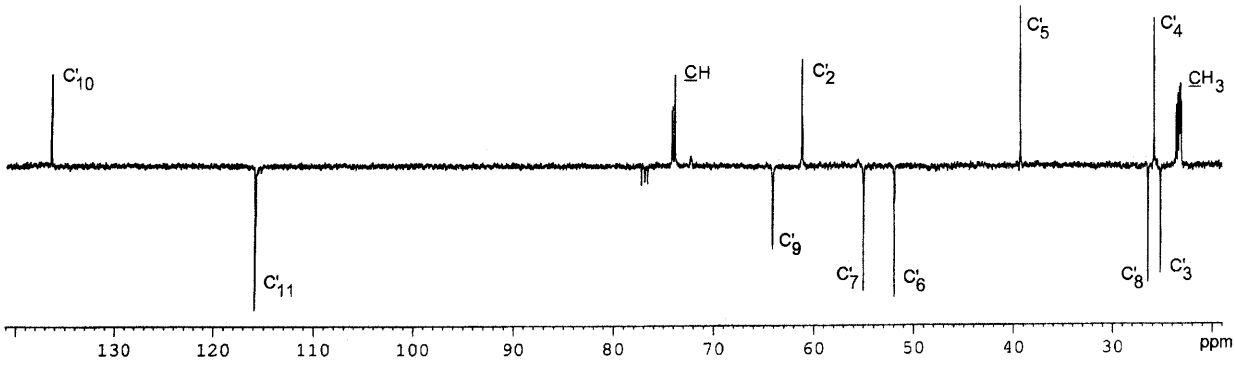


Fig. 3. ^{13}C-NMR spectrum of a solution of **4b** in $CDCl_3$.

Acknowledgements

The authors gratefully acknowledge receiving quincoridine from Buchler GmbH (Germany) and wish to thank G.V. Tcherkaev, B.V. Lokshin (Institute of Organoelement Compounds, Moscow) for their assistance in characterizing the products. This work has been partially supported by The Scientific Training Center of Biomedical Chemistry (Grant No. K0599, the Federal Target Program 'Integration') and the Russian Foundation for Basic Research (Grant No. 96-15-97328).

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