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CHIRAL POLY(PYRAZOLYL)BORATE LIGANDS AND COMPLEXES

III *. CHIRAL POLY(PYRAZOLYL)BORATE ISONITRILE COMPLEXES OF MOLYBDENUM AND TUNGSTEN

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Summary

The syntheses of enantiomeric and diastereoisomeric $Bpz_4M^*(CO)(NO)(C{\equiv}N{-}R)$ complexes ($M = Mo, W$; $R = CH_2CH_3, CH_2Ph, C^*H(CH_3)(C_6H_5)$) are reported. When $R = CH_2CH_3$ or $CH_2C_6H_5$ the presence of the diastereotopic methylene hydrogens does not allow the detection of the neighbouring chiral center, because they are magnetically equivalent. The diastereoisomeric complexes show different ^1H NMR signals, but cannot be resolved by liquid chromatography or by crystallization.

Introduction

Optically active organometallic compounds in which the transition metal is the center of chirality have been known since 1969, when the first manganese compounds of this type were reported [2]. Since then a great number of chiral transition metal complexes, mostly with the cyclopentadienyl ligand have been synthesized and studied [3]. A family of compounds that form a number of complexes analogous to the cyclopentadienyl types are the poly(pyrazolyl)borates, $[RB(pz)_3]^-$ were R is a noncoordinating substituent and pz is a 1-pyrazolyl group [4]. One of the outstanding characteristics of these complexes is their high stability [5]. This work presents the synthesis of a number of transition metal complexes containing four different

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* For part II see Ref. 1.

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ligands, $pzB(pz)_3M(CO)(NO)$(isonitrile), in which the incorporation of the tetrakis(1-pyrazolyl)borate brings about an increase of the thermal stabilities in relation to their cyclopentadienyl counterparts. Also ^1H NMR studies of these complexes have shown the presence of diastereoisomers when the isonitrile is optically active.

Experimental

All operations were carried out under nitrogen with anhydrous solvents. Microanalyses were performed by the Microanalytical Laboratory Pascher, Bonn (Germany). IR spectra were recorded with a Perkin–Elmer 283 infrared spectrometer. The ^1H NMR spectra were obtained with a Varian XL 100 spectrometer. The isonitrile ligands were prepared by standard literature methods [6]. The complexes $Bpz_4M^*(CO)(NO)(L)$ ($M = Mo$, W; L = α-phenyl ethyl isonitrile, benzyl isonitrile, ethyl isonitrile) were synthetised by reacting the dicarbonyl species $Bpz_4M(CO)_2(NO)$ [7] with the appropriate isonitrile.

Preparation of $Bpz_4Mo^*(CO)(NO)(CNC^*HCH_3C_6H_5)$

In a typical experiment $Bpz_4M(CO)_2(NO)$ (1.8 g, 4 mmol) was dissolved in 15 ml of benzene at 80°C and $CNC^*HCH_3C_6H_5$ (0.67 g, 6 mmol) dissolved in 15 ml benzene was slowly added. The solution was refluxed for 15 h during which time the originally yellow solution became dark red. The solvent was evaporated to dryness under vacuum, and the residue was dissolved in a minimum amount of a dichloromethane/benzene mixture. Column chromatography using benzene as eluant gave a red band which, after removal of the solvent, was extracted with dichloromethane. Red crystals of the title compound were crystallized from dichloromethane/hexane.

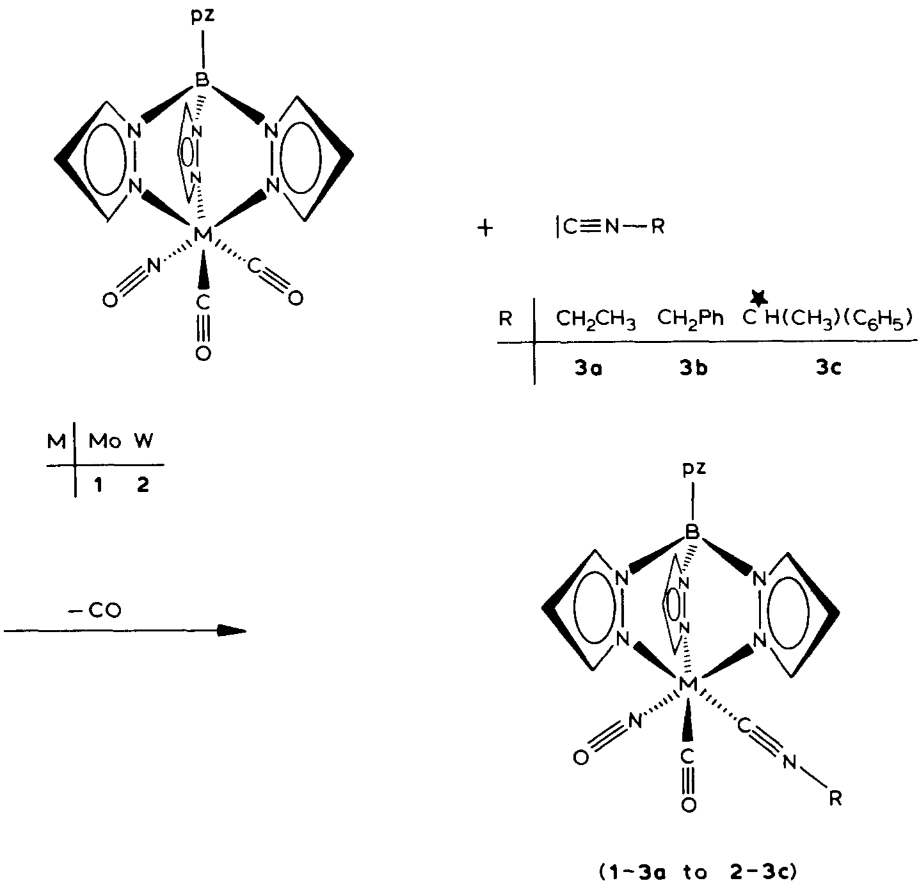
Similar procedures were used with different isonitrile ligands, although longer reaction times (ca. 30 h) were required in the preparation of the tungsten derivatives.

Results and discussion

We recently reported the synthesis of the first unsymmetric dihydrobis(pyrazolyl)borates [8] and of the first optically active poly(pyrazolyl)borate complexes [1]. In the preparation of the latter we used optically pure amino-phosphines as chiral ligands. Only one of several diastereoisomeric poly(pyrazolyl)borate aminophosphine complexes could be resolved completely. In this work we prepared enantiomeric and diastereoisomeric poly(pyrazolyl)borate complexes using isonitriles as ligands according to Scheme 1.

The isonitriles **3a**, **3b**, **3c** readily replaced a CO group of compounds **1** and **2** and the monosubstituted products **1-3a** to **2-3c** were formed in high yields. The compounds were fully characterized by their analytical and spectroscopic data. Table 1 summarizes the analytical data. On attempting to obtain the melting points for these complexes it was observed that they underwent decomposition at temperatures ranging between 140 and 160°C for the molybdenum and between 165 and 200°C for the tungsten derivatives. Table 2 shows the IR data for the isonitrile complexes.

In all complexes four different ligands are coordinated to the metal therefore making it a center of chirality; pairs of enantiomers are formed in the case of the isonitriles **3a** and **3b**. For the preparation of complexes **1-3c** and **2-3c** optically pure



SCHEME 1

S-isonitrile **3c** was used. In each case a pair of diastereoisomers was formed, the components of which differ only in the metal configuration. Whereas the corresponding diastereoisomers of the cyclopentadienyl analogues can be separated by a secuence of 20 recrystallizations [9], all our attempts to separate the diastereoisomers of **1-3c** and **2-3c** failed.

The ^{1}H NMR spectra of all complexes (Table 3) clearly show that the poly(pyrazolyl)borate ligand is fixed in a definite position and does not rotate freely in the complexes. For the complexes **1-3a** through **1-3c** and for **2-3b** four triplets arising from the 4-H pyrazolyl signals (ratio 1/1/1/1) are observed; in complexes **2-3a** and **2-3c** those triplets are overlapping. Free rotation would require two 4-H signals for coordinated and uncoordinated pyrazolyl rings (ratio 3/1). Only the signals of the 4-protons of the pyrazolyl rings can be observed, the signals of the 3,5-protons coincide with the phenyl signals.

The use of ^{1}H NMR spectroscopy for the detection of chiral transition metal atoms in enatiomeric organometallic complexes is well documented [10]. This technique is based on the magnetic nonequivalence of diastereotopic groups [11]

TABLE 1

ANALYTICAL DATA FOR ISONITRILE COMPLEXES

Complex	Analysis (Found (calcd.) (%))				
	C	H	N	Mo	W
$Bpz_4Mo(CO)(NO)(CNCHCH_3C_6H_5)$	46.67	3.81	24.79	16.75	-
	(46.75)	(3.74)	(24.78)	(16.97)	
$Bpz_4W(CO)(NO)(CNCHCH_3C_6H_5)$	40.33	3.35	21.40	-	27.57
	(40.46)	(3.24)	(21.45)		(28.15)
$Bpz_4Mo(CO)(NO)(CNCH_2C_6H_5)$	45.58	3.46	25.81	16.93	-
	(45.84)	(3.48)	(25.40)	(17.44)	
$Bpz_4W(CO)(NO)(CNCH_2C_6H_5)$	39.42	2.80	21.96	-	28.57
	(39.53)	(3 00)	(21.95)		(28.81)
$Bpz_4Mo(CO)(NO)(CNCH_2CH_3)$	33.30	2.78	-	-	-
	(33.36)	(2.98)			
$Bpz_4W(CO)(NO)(CNCH_2CH_3)$	39.13	3.54	-	-	-
	(39.38)	(3.51)	-	-	-

TABLE 2

INFRARED SPECTRA OF ISONITRILE COMPLEXES

Complex	Stretching frecuencies [a]		
	ν(CO) (cm^{-1})	ν(NO) (cm^{-1})	ν(CN) (cm^{-1})
$Bpz_4Mo(CO)(NO)(CNCHCH_3C_6H_5)$	1910vs	1620vs	2125vs
$Bpz_4W(CO)(NO)(CNCHCH_3C_6H_5)$	1885vs	1605vs	2120vs
$Bpz_4Mo(CO)(NO)(CNCH_2C_6H_5)$	1895vs	1620vs	2150vs
$Bpz_4W(CO)(NO)(CNCH_2C_6H_5)$	1890vs	1600vs	2130vs
$Bpz_4Mo(CO)(NO)(CNCH_2CH_3)$	1900vs	1615vs	2150vs
$Bpz_4W(CO)(NO)(CNCH_2CH_3)$	1880vs	1600vs	2140vs
$Bpz_4Mo(CO)_2(NO)$	1925vs	1665vs	-
	2020vs	-	-
$Bpz_4W(CO)_2(NO)$	1905vs	1645vs	-
	2000vs	-	-

[a] Infrared spectra obtained in solid state (KBr disc); vs = very strong.

TABLE 3

^{1}H NMR SPECTRA [a,b] (δ values (ppm), coupling constants (Hz) in parentheses)

	C_6H_5, 3,5-H-pz	4-H-pz		CH-CH_3	CN-CH_2	CH-CH_3
1-3a	7.4-8.1m	6.28t (2.0),	5.75t (2.0)		2.66q (7.2)	0.54t (7.2)
		5.76t (2.0),	5.68t (2.1)			
2-3a	7.4-8.1m	6.28t (2.1),	5.5-5.9m		2.98q (7.0)	0.62t (7.0)
1-3b	7.0-8.1m	6.28t (2.0),	5.83t (2.0)		4.00s	-
		5.75t (2.1),	5.62t (2.1)			
2-3b	7.1-8.1	6.26t (2.0),	5.75t (2.0)		4.22s	
		5.69t (2.0),	5.54t (2.1)			
1-3c	7.1-8.0m	6.63t (2.0),	5.82t (2.0)	4.31q (7.1)	-	1.15d (7.1)
		5.75t (2.0),	5.63t (2.1)	4.36q (7.1)	-	1.13d (7.1)
2-3c	7.1-8.1m	5.70-5.80m,	5.56t (2.0)	4.46m	-	1.2d (7.1)
						1.24d (7.1)

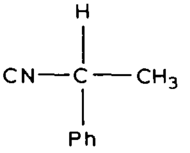
[a] Integrals in agreement with proposed structures. [b] C_6D_6 (i-TMS).

present in a coordinated ligand. The diastereotopic groups do not necessarily have to be vicinal to the chiral metal.

Thus, the ^{1}H NMR spectrum of $C_5H_5Fe(CO)(COCH_2C_6H_5)P(C_6H_5)_3$, where the diastereotopic methylene protons are separated from the center of asymmetry on the iron atom by a CO group, shows a well resolved AB system for the two nonequivalent methylene protons [12]. The complexes $Bpz_4M(CO)(NO)(L)$ **1-3a**, **2-3a**, **1-3b** and **2-3b** contain the isonitriles $CN(CH_2)R$ ($R = CH_3$ and C_6H_5 respectively), bound to an asymmetric transition metal atom; the methylene groups of the isonitriles are therefore diastereotopic. In spite of this fact the ^{1}H NMR spectra (Table 3) show only sharp quartets in the case of **1-3a**, **2-3a** and sharp singlets in the case of **1-3b**, **2-3b**; thus the two protons are magnetically equivalent. This could be due to a rapid racemization of the complexes or a casual equivalence of the methylene protons.

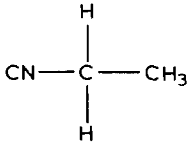
The isonitrile part of the ^{1}H NMR spectrum of **1-3c** and **2-3c** shows two doublets and two quartets. This splitting of the methyl and methine signals clearly indicates the presence of two diastereoisomers in solution and if racemization occurs, it must be slow on the NMR timescale.

The chiral isonitrile **3c** can be thought of as a superposition of the isonitriles **3a** and **3b**:



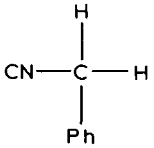
$$\begin{array}{c} H \\ | \\ CN-C-CH_3 \\ | \\ Ph \end{array}$$

(3c)



$$\begin{array}{c} H \\ | \\ CN-C-CH_3 \\ | \\ H \end{array}$$

(3a)



$$\begin{array}{c} H \\ | \\ CN-C-H \\ | \\ Ph \end{array}$$

(3b)

Because of this, the racemization rate for **1/2-3a/3b** should be similar to that of **1/2-3c**, thus the first indicated reason for the equivalence of the methylene protons seems unlikely.

In the case of dimethylphenylphosphine complexes it has been observed that the separation of the signals for the two diastereotopic methyl groups on the phosphorus atom in the ^{1}H NMR spectra depends on the nature of the other ligands bound to the metal. With $C_5H_5Fe^{\star}(CO)(COCH_3)P(CH_3)_2C_6H_5$ [12] for instance, the separation is 0.36 and only 0.04 ppm in the case of $C_5H_5Mo^{\star}(CO)(NO)P(CH_3)_2C_6H_5$ [13]. This can be explained in terms of the carbonyl and nitrosyl ligands having both linear structures, causing greater similarity in the ^{1}H NMR spectra.

In our case the third ligand is a terminal isonitrile, that is also known to form linear $M-C{\equiv}N-R$ structures [14]. Therefore one reason for the magnetic equivalence of the methylene protons could be the presence of three such linear metal–ligand structures.

However the linear isonitrile ligand seems to have, in general little influence on the NMR spectra of chiral complexes. The ^{1}H NMR signals for the different diastereoisomers of $C_5H_5Fe^{\star}(CO)(I)(CNC^{\star}H(CH_3)(C_6H_5))$ [15] are not separated at all and the C_5H_5 signals for the diastereomers of $C_5H_5Co^{\star}(C_3F_7)(SCN)(CNC^{\star}H(CH_3)(C_6H_5))$ [16] are only 0.02 ppm apart. For the complex $C_5H_5Fe^{\star}(CO)(PPh_3)(CH_2C^{\star}H(CH_3)(C_6H_5))$ [17] which is quite similar to the former isonitrile complex, but has the nonlinear $Fe^{\star}CH_2C^{\star}H(CH_3)(C_6H_5)$ structure, the separations are 0.23 for the C_5H_5 and 0.10 ppm for the methyl signals.

The diastereoisomers of the aminophosphine complexes $RB(3,5\text{-}X_2pz)_3Mo^{\star}(CO)(NO)PPh_2R^{\star}$ [1], that differ from **1-3c** and **2-3** by the nonlinear optically active ligand, are much better resolved in the ^1H NMR spectra. All of this indicates, that the reason for the low influence of the isonitrile ligands lies in the particular structure of the linear $M-C{\equiv}N-R$ unit. Cotton [14] found a distance of 4.65 Å between the molybdenum and the *sp*^{3} carbon in $Cp_2Mo_2(CO)_3CNCH_3$; this large distance combined with the linearity of the $M-C{\equiv}N-C{\lessdot}$ group gives rise to a small cone angle and to little interaction of the isonitrile with the rest of the complex.

Our findings show that, even with the more spacefilling polypyrazolylborate (cone angle of $HBpz_3Mo$ 180° compared to C_5H_5Mo 100° [1]), coordinated isonitriles are not satisfactory as NMR probes for the detection of chirality in metal complexes.

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